Chemorheological response of elastomers at elevated temperatures: Experiments and simulations

John A. Shaw\textsuperscript{a,}\textsuperscript{*}, Alan S. Jones\textsuperscript{b}, Alan S. Wineman\textsuperscript{c}

\textsuperscript{a}Department of Aerospace Engineering, The University of Michigan, 1320 Beal Ave, Ann Arbor, MI 48109-2140, USA
\textsuperscript{b}Department of Theoretical and Applied Mechanics, The University of Illinois at Urbana-Champaign, IL, USA
\textsuperscript{c}Department of Mechanical Engineering, The University of Michigan, MI, USA

Received 25 January 2005; received in revised form 30 June 2005; accepted 7 July 2005

Abstract

An experimental study and a method for simulating the constitutive response of elastomers at temperatures in the chemorheological range (90–150 °C for natural rubber) are presented. A comprehensive set of uniaxial experiments for a variety of prescribed temperature histories is performed on natural rubber specimens that exhibit finite elasticity, entropic stiffening with temperature, viscoelasticity, scission, and oxygen diffusion/reaction effects. The simulation approach is based on a multi-network framework for finite elasticity, isothermal incompressibility, thermal expansion, and temperature-induced degradation. The model extends previous work to account for kinetics of scission for arbitrary time-varying temperature histories and incorporates the effects of viscoelastic relaxation and diffusion-limited oxidative scission. The model is calibrated to experiments performed on a commercially-available filled natural rubber material, and numerical simulations are compared favorably to experiments for a variety of temperature histories.

© 2005 Elsevier Ltd. All rights reserved.

Keywords: Chemorheological degradation; Elastomer; Natural rubber; Scission; Elevated temperature
1. Introduction

Elastomeric materials are in ubiquitous use in the automotive, aerospace and energy industries. They are widely used in pumps to seal interfaces and in bushings, engine mounts and tires to dampen dynamically transmitted forces. Elastomers encounter severe thermal, chemical and mechanical stress conditions that can cause degradation resulting in altered performance and failure. In addition, elastomeric seals are used in many applications where they are relatively inaccessible and replacement is expensive. A 50 year service life for seals is now a clearly stated objective for the energy industry (Hertz, 1997). In addition, the life expectation for elastomeric components in vehicles has changed dramatically over the past few years (Pett, 1997). Previously, many rubber components were viewed as items to be replaced one or more times during the vehicle’s life. Now, elastomeric components are expected to last the life of the vehicle, which is currently defined as 10 years/150,000 miles for passenger and light trucks. The failure of an elastomeric component can be accelerated by high temperatures and can lead to catastrophic consequences. Excessive temperature in elastomeric components can be caused by the ambient environment or by intrinsic heating due to internal dissipation during cyclic loading (which is exacerbated by the low thermal conductivity of rubber). For example, the recent tread separation problem in Firestone tires has been attributed, in part, to elastomer degradation due to excessive heating (National Highway Traffic Safety Administration, 2001). As another example, Schapery and Cantey (1966) studied self-heating in solid rocket propellant due to viscoelastic effects during cyclic loading and some interesting dynamical instabilities that can result. Thus, there is a clear need for constitutive models suitable for use in numerical simulations to predict the degradation and useful lifetime of elastomeric components subjected to thermo-mechanical loading.

The engineering analysis and design of elastomeric components can be performed in a simulation-based environment using the mathematical models of nonlinear thermo-elasticity or thermo-viscoelasticity. These models have been used to study many physical factors that affect the performance and/or durability of an elastomeric component, including large deformations, generation of high internal temperatures due to the conversion of mechanical energy to heat, and poor heat transfer within the component. However, they do not account for the degradation of elastomers, i.e., changes in microstructure and the consequent changes in material properties. Furthermore, few examples of the application of these mathematical models have appeared in the open literature.

The general theory of nonlinear thermoelasticity within the framework of continuum mechanics has been available for many years. A number of authors (Chadwick, 1974; Chadwick and Creasy, 1984; Ogden, 1987, 1992) have worked on the development of a continuum model to incorporate observed thermomechanical response of elastomers. A corresponding general theory of nonlinear thermo-viscoelastic solids was presented in Coleman (1964), and the development of constitutive theories has been discussed in Crochet and Naghdi (1978). However, these theories only provide a general framework and have not been applied to a
specific material. Morman (1994, 1995) proposed a constitutive theory for rubber-like thermo-viscoelasticity, adapted from the general theory, that attempted to incorporate observed thermo-mechanical response, much as was done in the case of rubber elasticity. However, the constitutive theories for nonlinear thermo-elasticity or thermo-viscoelasticity do not account for microstructural changes of the macromolecular network.

Microstructural changes, such as scission of macromolecular networks and crosslinking, occur when the temperature becomes sufficiently high. Scission is the severing of macromolecular chains and crosslinks, and crosslinking occurs as severed junctions recoil and reattach and/or as excess curing reagents are reacted. Tobolsky (Tobolsky et al., 1944) presented the first experiments on natural rubber strips that exhibited scission at elevated temperatures. This work led to the conclusion that the rubber had undergone chemically based changes in its molecular structure. In these experiments a natural rubber strip at one temperature, say 20°C, was subjected to a fixed uniaxial stretch and then held at a higher fixed temperature in the range 100–150°C for a specified time interval. The stress was observed to relax with time, and if held long enough, the stress asymptotically decayed to zero. At the end of the time interval, the specimen was unloaded and returned to its original temperature. The specimen was observed to have different mechanical properties as well as permanent stretch. Experiments were carried out for different applied stretch ratios, temperatures and time intervals. He concluded that the decrease in stress was due to scission of macromolecular chains. The rate of stress relaxation was shown to be relatively independent of the stretch ratio, at least for stretches up to about 3. The permanent stretch was attributed to a new network that formed when the macromolecules crosslinked in the stretched state. That is, two macromolecular networks exist, each with its own unstressed reference configuration. Accordingly, Tobolsky proposed a two network model that accounted for the reduction in modulus and permanent set, and he considered these effects to be significant for temperatures greater than a chemorheological temperature, near \( T_c = 100°C \) for natural rubber.

Scission of macromolecular networks occurs at elevated temperature due to (1) excessive thermal activation of chemical bonds (anaerobic) and/or (2) oxidative scission, an autocatalytic sequence of chemical reactions that involve oxygen and free radical generation/recombination within the elastomer (see Tobolsky, 1960). Murakami et al. (1983) performed stress decay experiments on elastomers in uniaxial extension at 140°C and different oxygen concentrations, showing that oxidative scission was the dominant mode of degradation. Further complications arise when either the rubber component is somewhat thick or when the temperature is sufficiently high. This leads to so-called diffusion-limited oxidation, which occurs whenever the rate of oxygen consumption in the scission reaction within the elastomer is initially greater than the rate at which it can be resupplied by diffusion through the elastomer from the surrounding atmosphere. In fact, Gent (2001) recommended that at temperatures above 110°C the specimen thickness should be less than 0.25 mm in order to avoid diffusion-limited oxidation. This effect was studied by several authors (see van Amerongen, 1964; Cunliffe and Davis, 1982; Gillen and Clough, 1992; Wise et al., 1997). Gillen et al. (1996) presented experimental results showing that diffusion-limited...
oxidation leads to material properties that vary spatially within a specimen. Nasdala et al. (2002) performed a numerical simulation using a diffusion-reaction equation for the oxygen concentration and a constitutive equation for viscoelasticity in which the material parameters are functions of the oxygen concentration. They were able to simulate the experimental results of Murakami et al. and Gillen et al. However, Nasdala’s model did not connect the results to the mechanical consequences of scission/crosslinking, such as permanent set and induced anisotropy. There has been little other work to date in the mechanical engineering literature.

While the current paper is focussed on temperature-induced scission, it should be noted that scission and crosslinking may also be deformation-induced. Wineman and Rajagopal (1990) and Rajagopal and Wineman (1992) first introduced a model for deformation-induced scission that occurs at large stretch ratios, typically greater than 4. Subsequently, there has been some work on models for temperature-induced scission effects. Based on the previous work of Tobolsky, Septanika and Ernst (1998a, b), and later in independent work, Wineman et al. (2002, 2003) presented constitutive equations that account for microstructural changes at elevated temperatures. Both approaches have similar mathematical structures, consider only the elastic response of elastomers and relate scission directly to the temperature.

The aim of the current paper, therefore, is to present experiments on commercially available, carbon-black filled, natural rubber material under extreme temperature environments and to demonstrate a constitutive model that is capable of predicting the thermomechanical response to a variety of temperature histories. While the theoretical treatment developed in this paper is intended to account for general deformation histories, the experiments presented include only simple deformation histories in order to focus attention on scission kinetics for arbitrarily complex temperature histories. More complex deformation histories, for which crosslinking and healing play a significant role, will be the subject of future work. This paper is organized as follows. Section 2 presents the experimental setup and procedure used as well as selected experiments that illustrate the thermomechanical phenomena of interest. Section 3 presents a theoretical multi-network constitutive framework including thermoelasticity, scission, and crosslinking. Section 4 presents the constitutive model for uniaxial extension that includes nonlinear viscoelasticity, a proposed form for scission kinetics, and an efficient numerical implementation. The model is calibrated to experiments and then simulations are compared to experiments at different temperatures. Section 5 presents a model and numerical method to study the effect of oxygen depletion arising from diffusion-limited oxidative scission. Simulations are compared to experiments on specimens subject to simple and complex temperature histories and conclusions are drawn in Section 6 regarding the role of oxygen diffusion/reaction on scission kinetics.

2. Experimental setup and selected results

This section describes the material and experimental procedure and presents a few experiments that illustrate the material behavior of interest. Further experimental
results will be presented in Sections 4 and 5 with corresponding numerical simulations.

2.1. Specimen materials and experimental procedure

Experiments are conducted on commercial-grade, carbon-black filled, natural rubber that is representative of elastomers typically used in automotive bushings. Sheets of rubber (152 × 152 × 2 mm) were provided by Tenneco Automotive Corp. The precise formulation of the rubber is proprietary, but some physical properties are provided by Tenneco as shown in Table 1. Uniaxial specimens (50.8 × 12.7 mm) are cut from the sheets, and the free gage length is approximately 32 mm when installed in the grips of an EnduraTec ER32, 12.5 kN servo-pneumatic testing machine. Custom-built low thermal mass (aluminum) grips are used that consist of clamped parallel plates. The axial load on the specimen is measured using a Lebow 444 kN load cell. A custom-built temperature-controlled air chamber surrounds the specimen within the testing machine. It is constructed of thin inner and outer steel shells and low density silicate insulation. The chamber is capable of reaching 250 °C and holding a prescribed temperature to within ±0.1 °C. The load cell is located outside the temperature chamber and is cooled by an exterior fan to avoid any temperature-induced artifacts in the force measurement. Three exposed-junction K-type thermocouples are used to monitor temperatures at the top, middle, and bottom along the specimen length during the experiments.

In order to maximize the flexibility of the testing system, control of the testing machine and temperature chamber as well as data acquisition are performed on a Macintosh desktop computer running custom-written software in a LabView environment. The maximum data acquisition rate is 50 records/s, but this is rarely necessary. The rate of data acquisition is usually based on measured changes in variables compared to user-selected threshold values to reduce the amount of data taken during long experiments. In this way, data is kept only when there is action in an incoming signal, resulting in nonuniform time increments between data records.

The axial stretch ratio of the specimen is measured by a non-contacting laser extensometer (Electronic Instrument Research, model LE-05) that interrogates the relative locations of a pair of small retro-reflective tags attached to the specimen. The laser extensometer uses parallel beam scanning of a collimated 670 nm laser. The parallel beam allows the tags to be measured through the glass window of the

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Properties of carbon-black filled natural rubber samples</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (kg/m³)</td>
<td>1070</td>
</tr>
<tr>
<td>Bulk modulus (MPa)</td>
<td>3510</td>
</tr>
<tr>
<td>Coefficient of linear thermal expansion (K⁻¹)</td>
<td>$2.09 \times 10^{-6}$</td>
</tr>
<tr>
<td>Thermal diffusivity (m²/s)</td>
<td>$1.36 \times 10^{-7}$</td>
</tr>
<tr>
<td>Thermal conductivity (W/mK)</td>
<td>0.211</td>
</tr>
<tr>
<td>Specific heat (J/kg K)</td>
<td>1560</td>
</tr>
</tbody>
</table>
temperature chamber without any parallax effects (see Fig. 1). It projects an effective 127 mm planar laser sheet and measures the distance between the tags to within 1 μm resolution at rates up to 100 scans/s. The laser extensometer measurement is used as a control signal for the testing machine in order to facilitate local stretch control of the specimen. Due to stroke limitations of the testing machine, ASTM D-638 “dog-bone” specimens could not be used for the stretch ratios of interest. Instead, parallel-sided (prismatic) strip specimens are used. A finite element analysis study was performed that showed the axial extent (referential length) of non-uniform deformation near the grips to be only about 6.5 mm (Jones, 2003), accounting for lateral clamping of the grips and an axial stretch ratio of 2. In all experiments, the tags are placed at least 9.4 mm away from the grips to ensure that a uniform uniaxial region exists between them.

2.2. Selected experimental results

Fig. 2 shows the room temperature uniaxial mechanical responses of natural rubber specimens at three levels of degradation. The responses are shown in engineering stress (axial force, $F$, divided by reference cross-sectional area, $A_0$), stretch ($\lambda = L/L_0$, current length/reference length) space, where the stretch is measured by the laser extensometer. The stretch is controlled at the rather slow rate
Fig. 2. Uniaxial engineering stress vs. stretch of natural rubber at three levels of degradation: (a) room temperature response of virgin material (curve I), then stress relaxation for 2h at 125 °C and \( \lambda = 1.5 \), followed by room temperature response (curve II); (b) stress relaxation for 26.2h at 125 °C and \( \lambda = 1.5 \), followed by room temperature response (curve III).

Fig. 2a shows the stress-stretch response of the virgin, as-received material in curve (I). The specimen was then elongated to a stretch ratio of 1.5 and held for 2h at 125 °C, during which time the stress relaxed to 31% of its original value. The specimen was then unloaded and the temperature returned to room temperature. The specimen had a permanent stretch of 1.31. Another room temperature mechanical test was then performed as shown by curve (II), and the material had a reduced modulus compared to the virgin material. Fig. 2b shows an experiment on a second specimen that was stretched to \( \lambda = 1.5 \) and held for 26.2h at 125 °C, during which time the stress relaxed to 2.5% of its original value, before being unloaded and returned to room temperature. In this case the permanent stretch was 1.45. A subsequent room temperature mechanical test was performed as shown by curve (III), where the specimen fractured near the grip during unloading.

The dashed lines in the figure show the initial elastic moduli for the room temperature responses: (I) 3.37 MPa, (II) 2.14 MPa, (III) 1.18 MPa. Thus, increasing the duration of stress relaxation at high temperature causes both a significant reduction in apparent modulus and an increase in permanent set.

Fig. 3 shows a stress relaxation experiment performed over 11h. The dashed and dotted lines show the prescribed stretch (\( \dot{\lambda} \)) and temperature (\( T \)) histories, respectively, with associated scales shown on the right-axis of the figure. The solid line shows the engineering stress response. At time \( t = 0 \) the stretch was quickly ramped to \( \dot{\lambda} = 2 \) and then held fixed for the duration of the experiment. For approximately 3h the temperature remained at room temperature, but was then ramped to 125 °C and held fixed for the remainder of the experiment. The stress response during the initial 3h shows a viscoelastic (or physical) stress relaxation from 2.25 to 1.82 MPa. Although not shown, other experiments show that unloading at this point results in a slight residual stretch that recovers over time. In other words, this portion of the stress relaxation response, although time dependent due to viscous effects, does not result in a noticeable permanent set, and one can consider the
reference state of the material to remain unchanged. During the temperature ramp up to 125°C in Fig. 3 the stress is observed to rise initially, due to the well-known entropic stiffening effect in rubber, but then reaches a maximum of 1.97 MPa and then decreases rapidly once the temperature is sufficiently high that scission effects dominate. This latter part, called chemical stress relaxation, asymptotically approaches a stress free state and is associated with significant permanent deformation of the material upon complete unloading. Thus, one challenge in the modeling of rubber materials over this temperature range is to distinguish between stress relaxation effects that are viscoelastic from those which are chemical in nature.

Since the temperatures of interest are well above the glass transition temperature for natural rubber (typically $T_g = -70^\circ C$), viscoelastic stress relaxation is relatively insensitive to temperature. On the other hand, chemical stress relaxation is quite sensitive to temperatures in this range. Fig. 4 shows several relaxation experiments,
each performed on a virgin specimen at a constant stretch ($\lambda = 2$) at a selected chemorheological temperature between 95 and 150°C. In each curve, the force response is normalized by the initial maximum force, $F_0(T)$, at that temperature. This series of experiments shows that the rate of scission is significantly increased by increasing the temperature.

3. General theory

In this section, the theory of finite thermoelasticity is reviewed and is then combined with the multinetwork framework for scission/crosslinking.

3.1. Finite thermoelasticity

Consider a rubbery material in a stress free reference configuration at an absolute temperature $T_0$. If $x$ is the position at current time $t$ of a material particle located at $X$ in the reference configuration, the deformation gradient at time $t$ is $F(t) = \partial x(t)/\partial X$. The relative volume change is $J(t) = \det(F(t))$. The left Cauchy–Green tensor is $B = F(t)F(t)^T$, and its invariants are selected as $I_1 = \text{tr}(B)$, $I_2 = \text{tr}(B^{-1})$, and $J$.

Our temperature range of interest is room temperature (22°C) to 150°C, and as will be quantified later in Section 4, thermal expansion effects are noticeable. Due to isotropy, the stress free thermal expansion of a cube is an equi-triaxial extension with thermal stretch $\lambda_T$ on each side, producing a relative volume change

$$J = \lambda_T(T)^3.$$  \hspace{1cm} (3.1)

This can be regarded as a constraint if mechanical incompressibility is assumed at fixed temperature.

Chadwick (1974) discussed a constitutive theory for the finite thermoelastic response of typical rubber materials that was derived from thermodynamic considerations. He introduced a specific form for the free energy and with it showed very good agreement between calculated and measured results for a variety of thermomechanical experiments. The theory accounts for entropic stiffening with temperature under fixed deformation and for volume changes due to thermal expansion. He also addressed the limiting case of materials that are mechanically incompressible at a fixed temperature but have thermally induced volume changes according to Eq. (3.1). In this case, the Cauchy stress at time $t$ is given by

$$\sigma = \frac{T}{T_0} \left[ J^{-1} \frac{\partial W}{\partial F} F^T - qI \right],$$  \hspace{1cm} (3.2)

where $T$ is the current absolute temperature, $T_0$ is a reference temperature, $W = W(I_1, I_2, J)$ is a normalized (isothermal) strain energy density function, $I$ is the identity tensor, and $q$ is an arbitrary scalar arising from the isothermal incompressibility constraint. It is presumed that Eq. (3.2) is valid for a range of
deformations and temperatures in which the material response can be regarded as isotropic and nonlinearly elastic.

We note that Eq. (3.2) is based on conventional entropic elasticity, and more sophisticated models that account for internal energy contributions could also be used, as discussed by Chadwick and Creasy (1984). We chose the simpler model (3.2) for convenience, and it was used successfully to simulate the experiments on the specimen material used in this study.

Chadwick (1974) and Dunwoody (2000) discussed a form of $W$ of a generalized Mooney–Rivlin type,

$$W(I_1, I_2, J) = c_1(J^{-2/3} I_1 - 3) + c_2(J^{2/3} I_2 - 3),$$  \hspace{1cm} (3.3)

where $c_1$ and $c_2$ are material constants. This is a special case of the more general form:

$$W = \tilde{W}(J^{n_1} I_1, J^{n_2} I_2),$$  \hspace{1cm} (3.4)

where the exponents $n_1$ and $n_2$ are constants. Eqs. (3.2) and (3.4) lead to

$$\sigma = 2 \frac{T}{T_0} [\tilde{w}_1 J^{n_1-1} B - \tilde{w}_2 J^{n_2-1} B^{-1} - q I],$$  \hspace{1cm} (3.5)

where $\tilde{w}_1$ and $\tilde{w}_2$ denote derivatives with respect to the first and second arguments of $\tilde{W}$, respectively. In component form with respect to the principal stretch directions, Eq. (3.5) becomes

$$\sigma_i = 2 \frac{T}{T_0} [\tilde{w}_1 J^{n_1-1} \lambda_i^2 - \tilde{w}_2 J^{n_2-1} \lambda_i^{-2} - q], \hspace{1cm} i = 1, 2, 3,$$

where $\lambda_i$ are the principal stretch ratios. Substituting the constraint, Eq. (3.1), this reduces to

$$\sigma_i = 2 \frac{T}{T_0} \left[ \tilde{w}_1 J^{n_1-1/3} \left( \frac{\lambda_i}{\lambda_T} \right)^2 - \tilde{w}_2 J^{n_2-5/3} \left( \frac{\lambda_i}{\lambda_T} \right)^{-2} - q \right], \hspace{1cm} i = 1, 2, 3,$$  \hspace{1cm} (3.7)

which suggests the natural interpretation that stress arises only due to $\lambda_i/\lambda_T$, the mechanical stretch ratio relative to the thermally expanded state. The apparent elastic moduli are temperature dependent through the temperature ratio $T/T_0$ and through the relation $J = \lambda_T(T)^3$.

Returning to the special case of a generalized Mooney–Rivlin material ($c_x = 2\tilde{w}_x$, temperature-independent constants for $x = 1, 2$) and choosing the exponents as $n_1 = 1/3$ and $n_2 = 5/3$, Eq. (3.7) reduces to

$$\sigma_i = \frac{T}{T_0} \left[ c_1 \left( \frac{\lambda_i}{\lambda_T} \right)^2 - c_2 \left( \frac{\lambda_i}{\lambda_T} \right)^{-2} - q \right], \hspace{1cm} i = 1, 2, 3.$$  \hspace{1cm} (3.8)

Specializing to the case of uniaxial extension with stress free lateral boundaries allows $q$ to be determined, leading to the uniaxial stress equation:

$$\sigma = \frac{T}{T_0} \left[ \left( \frac{\lambda}{\lambda_T} \right)^2 - \left( \frac{\lambda}{\lambda_T} \right)^{-1} \right] \left[ c_1 + c_2 \left( \frac{\lambda}{\lambda_T} \right)^{-1} \right].$$  \hspace{1cm} (3.9)
The engineering stress of a prismatic specimen is then
\[ \sigma_E = \frac{F}{A_0} = \frac{\lambda^3}{L} \sigma, \]  
(3.10)
where \( F \) is the axial force and \( A_0 \) is the cross-sectional area in the reference configuration.

3.2. Multinetwork framework

Using uniaxial experiments at constant temperature and constant stretch, Tobolsky (1960) introduced a two-network model that accounts for scission of the original network and formation of a new network with a different reference configuration. This idea was later generalized for continuous formation of networks and arbitrary deformation histories in Wineman et al. (2002), Wineman and Min (2003) and Wineman et al. (2003). The underlying assumption is that the Cauchy stress, \( \sigma \), consists of the superposition of two contributions, the stress supported by the original (possible degraded) network, \( \sigma^{(1)} \), and the stress supported by all new networks, \( \sigma^{(2)} \),
\[ \sigma(t) = \sigma^{(1)}(t) + \sigma^{(2)}(t). \]  
(3.11)
From here on, superscripts \( (1) \) and \( (2) \) denote quantities associated with the original network and new networks, respectively. The networks are viewed as interpenetrating and independent (non-interacting), each of which responds as a nonlinear elastic material. We presume that at time \( t = 0 \) the initial temperature is below the chemorheological range \( (T_0 < T_{cr}) \) and identify the microstructural network as entirely network \( (1) \). The strain energy density function for the first network is similar to Eq. (3.4), i.e., \( \tilde{W}^{(1)}(J_1^{1/3}I_1, J_5^{5/3}I_5) \). The stress in network (1) before the onset of scission is given by Eq. (3.5), where now \( \tilde{W} \) and \( \tilde{w}_z \) are replaced by \( \tilde{W}^{(1)} \) and \( \tilde{w}_z^{(1)} \), respectively. For subsequent temperatures in the chemorheological range \( (T > T_{cr}) \) scission of this initial network occurs continuously in time. Let \( b^{(1)}(t) \) denote the volume fraction of original network that remains at time \( t \). In general, it could depend on deformation, temperature history, and time, i.e., \( b^{(1)}(t) = b^{(1)}(B, T(s)[0, t]). \) This function, initially unity \( (b^{(1)}(0) = 1) \), is a monotonically decreasing function of \( t \) when \( T > T_{cr} \) and is constant when \( T < T_{cr} \). Tobolsky’s experiments indicated that \( b^{(1)}(t) \) did not depend on the uniaxial stretch ratio \( (\lambda) \) provided that the stretch was less than about 3. This was supported by the results of Scanlan and Watson (1958) and has been independently confirmed by us in stress relaxation experiments conducted at 115 °C for several stretch ratios between 1.37 and 2 (Jones, 2003). Accordingly, we adopt the simplifying assumption that \( b^{(1)} \) is independent of deformation, i.e., \( b^{(1)}(t) = b^{(1)}(T(s)[0, t]). \) The stress in the first network is then
\[ \sigma^{(1)}(t) = b^{(1)}(t) \frac{T(t)}{T_0} [\tilde{w}_1^{(1)} J(t)^{-2/3} B(t) - \tilde{w}_2^{(1)} J(t)^{2/3} B(t)^{-1} - \dot{q}^{(1)}(t) I]. \]  
(3.12)
The remaining discussion in this subsection is related to the contribution of newly formed networks. Although only simple stretch histories will be considered in the remainder of this paper, for which the stress in new networks can be neglected, we continue the theoretical development here for continuity of the discussion and to show the complete multinetwork framework. Experiments and simulations addressing the contributions of new networks will be the subject of forthcoming work.

Now consider an intermediate time, \( \hat{t} \in [0, t] \), and the corresponding deformed configuration of the original material which is related to its reference configuration by \( F(\hat{t}) \). A new network may be formed during the interval from \( \hat{t} \) to \( \hat{t} + d\hat{t} \) whose reference configuration is the deformed configuration of the original material at \( \hat{t} \). As suggested by Tobolsky et al. (1944) this is assumed to be an unstressed configuration for the newly formed network. Under subsequent deformation, the configurations of the newly formed network coincide with that 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 a later time \( t \) the material formed at time \( \hat{t} \) has the relative deformation gradient \( F(t, \hat{t}) = F(t)F(\hat{t})^{-1} = \partial x/\partial \hat{x} \), where \( \hat{x} \) is the position of the particle at time \( \hat{t} \) and \( x \) is the position at time \( t \). The corresponding relative volume ratio is \( J(t, \hat{t}) = \det(F(t, \hat{t})) \). As for the first network, the new network is assumed to respond as an isotropic nonlinear elastic material that exhibits thermal expansion but is mechanically incompressible. Let the relative left Cauchy–Green tensor \( \hat{B}(t, \hat{t}) = F(t, \hat{t})F(t, \hat{t})^{T} \) be introduced for deformations of this new network, and let the invariants be \( \hat{I}_{1} = \text{tr}(\hat{B}) \), \( \hat{I}_{2} = \text{tr}(\hat{B}^{-1}) \), and \( \hat{J} \). Its strain energy density function is then \( \tilde{W}^{(2)}(J^{1/3} \hat{I}_{1}, J^{5/3} \hat{I}_{2}) \).

During the time interval between the creation time \( \hat{t} \) of the new network and the current time \( t \), the temperature may have changed from \( T(\hat{t}) \) to \( T(t) \). Suppose a free thermal expansion occurs during this time, isotropy of the new network will result in an equi-triaxial extension with thermal stretch ratio \( \lambda_{T}(T(t), T(\hat{t})) \). Under subsequent deformations of this network the relative volume change must satisfy the constraint \( \hat{J}(t, \hat{t}) = [\lambda_{T}(T(t), T(\hat{t}))]^{3} \). The Cauchy stress \( \sigma^{(2)}(t, \hat{t}) \) at time \( t \) in the network formed at time \( \hat{t} \) is then given by

\[
\sigma^{(2)}(t, \hat{t}) = 2 \frac{T(t)}{T_{0}} \left[ \tilde{W}^{(2)}(J(t, \hat{t})^{-2/3} \hat{B}(t, \hat{t}) - \tilde{w}_{2}^{(2)} \hat{J}(t, \hat{t})^{2/3} \hat{B}(t, \hat{t})^{-1} - q^{(2)}(t, \hat{t}) I \right].
\]

(3.13)

Note that \( \tilde{w}_{1}^{(2)} \) and \( \tilde{w}_{2}^{(2)} \) associated with the function \( \tilde{W}^{(2)} \) need not be the same as those for the original network. Eq. (3.13) can be written with respect to the principal directions in a manner analogous to Eq. (3.7):

\[
\sigma_{i}^{(2)}(t, \hat{t}) = 2 \frac{T(t)}{T_{0}} \left[ \tilde{w}_{1}^{(2)} \left( \frac{\lambda_{T}(t)/\lambda_{T}(\hat{t})}{\lambda_{T}(T(t), T(\hat{t}))} \right)^{2} - \tilde{w}_{2}^{(2)} \left( \frac{\lambda_{T}(t)/\lambda_{T}(\hat{t})}{\lambda_{T}(T(t), T(\hat{t}))} \right)^{2} - q^{(2)}(t, \hat{t}) \right],
\]

\( i = 1, 2, 3. \)
Let $a(\hat{t})$ be a scalar-valued function that represents the rate at which the volume fraction of new network is formed at time $\hat{t}$. Thus, $a(\hat{t}) > 0$ and $a(\hat{t}) \, d\hat{t}$ is the amount of newly formed material during the time interval from $\hat{t}$ to $\hat{t} + d\hat{t}$. Let $b^{(2)}(t, \hat{t})$ denote the volume fraction of network formed at time $\hat{t}$ that remains at time $t$. The properties of $b^{(2)}$ are similar to $b^{(1)}$ in that $b^{(2)}(\hat{t}, \hat{t}) = 1$ and $b^{(2)}(\hat{t}, \hat{t})$ decreases with $t$ for fixed $\hat{t}$ when $T > T_{cr}$. It is also assumed that $b^{(2)}$ is independent of the deformation of the new network and depends on the temperature history and time, i.e., $b^{(2)}(t, \hat{t}) = b^{(2)}(T(s)|_{\hat{t}}, t)$. The amount of network created at time $\hat{t}$ that remains at time $t$ is therefore $a(\hat{t}) b^{(2)}(t, \hat{t}) \, d\hat{t}$.

The total current stress in the macromolecular system is then the superposition of stress in the remaining portion of the original network and the stress in the newly formed networks,

$$\sigma(t) = -p(t) I + 2b^{(1)}(t) \frac{T(t)}{T_0} [\tilde{w}_1^{(1)} J(t)^{-2/3} B(t) - \tilde{w}_2^{(1)} J(t)^{2/3} B(t)^{-1}],$$

$$+ 2 \frac{T(t)}{T_0} \int_0^t a(\hat{t}) b^{(2)}(t, \hat{t})[\tilde{w}_1^{(2)} \dot{J}(t, \hat{t})^{-2/3} \dot{B}(t, \hat{t}) - \tilde{w}_2^{(2)} \dot{J}(t, \hat{t})^{2/3} \dot{B}(t, \hat{t})^{-1}] \, d\hat{t},$$

(3.15)

where the indeterminate scalars $q^{(1)}$ and $q^{(2)}$ from the individual contributions of each network have been lumped together into the indeterminate scalar $p$.

4. A specific chemorheological constitutive model

In this section, the general framework of Eq. (3.15) is used to develop a specific constitutive model that can be used to predict material response for a wide range of extreme thermomechanical loading conditions. It is calibrated to uniaxial experiments based on the generalized Mooney–Rivlin model, although in principle any of a number of popular hyperelastic models, such as the Ogden model (Ogden, 1972), Arruda–Boyce model (Arruda and Boyce, 1993), or Gent model (Gent, 1996), could easily have been used instead. For the remainder of the paper we focus our attention on scission kinetics and the response of the original macromolecular network associated with $\sigma^{(1)}$. The experiments presented all involve constant stretch histories, for which the reponse of any new networks can be neglected and $\sigma^{(2)}$ is approximately zero.1 As mentioned previously, more complex deformation histories, for which new networks play a more significant role, will be the subject of future work. In this section a generalized Mooney–Rivlin model is calibrated to experiments, viscoelastic effects are quantified, and a simulation scheme for scission kinetics for arbitrary temperature histories is derived and calibrated against experiments.

---

1The reader may notice that even for a constant stretch any newly formed networks may still contribute to $\sigma^{(2)}$ through its dependence on thermal expansion, but this contribution was confirmed to be quite small in the experiments presented herein.
4.1. Generalized Mooney–Rivlin model

Rewriting Eq. (3.9) for a generalized Mooney–Rivlin material and accounting for scission by $b^{(1)}$, the stress supported in the original network is

$$\sigma^{(1)}(t) = b^{(1)}(T(s)|_{0}, t) \frac{T(t)}{T_0} \sum_{j=1}^{4} \hat{c}_j^{(1)} \left[ \frac{\lambda(t)}{\lambda_{T}(t)} \right]^{m_j},$$

(4.1)

where the Mooney–Rivlin constants and exponents are

$$\begin{bmatrix}
    c_1^{(1)} \\
    c_2^{(1)} \\
    c_3^{(1)} \\
    c_4^{(1)}
\end{bmatrix} = \begin{bmatrix}
    2 \tilde{w}_1^{(1)} \\
    -2 \tilde{w}_1^{(1)} \\
    2 \tilde{w}_2^{(1)} \\
    -2 \tilde{w}_2^{(1)}
\end{bmatrix}, \quad \begin{bmatrix}
    m_1 \\
    m_2 \\
    m_3 \\
    m_4
\end{bmatrix} = \begin{bmatrix}
    2 \\
    -1 \\
    1 \\
    -2
\end{bmatrix}.$$  

(4.2)

The notation $b^{(1)}(T(s)|_{0}, t)$ indicates that $b^{(1)}$ may be a functional of the temperature history for the time interval $s \in [0, t]$. For the experiments to follow the room temperature mechanical behavior of our material is represented by the average values $(\tilde{w}_1^{(1)}, \tilde{w}_2^{(1)}) = (1.078, 0.075)$ MPa. As much as $\pm 15\%$ variability was found in the mechanical response of different specimens, so the simulations to follow each used a set of Mooney–Rivlin constants that are generally chosen to match the initial room temperature stress peak.

The thermal expansion coefficient for natural rubber is approximately $\alpha = 209 \times 10^{-6}/K$, resulting in a thermal stretch ($\lambda_{T} = 1 + \alpha \Delta T$) of approximately 1.027 and a relative volume change of 8.3% over the temperature range 22–150$^\circ C$. While the thermal stretch is relatively small compared to the imposed stretch ratios prescribed in the experiments (usually 1.5–2.0), neglecting it could result in noticeable modeling errors, especially at low stress levels. The relative volume change $J(t) = \lambda_{T}(t)^3$ is also included in the conversion from Cauchy stress to engineering stress according to Eq. (3.10), which is needed to compare simulation results with the force response measured in the experiments.

4.2. Viscoelastic relaxation

Fig. 3 showed a response due to two relaxation processes, viscoelastic relaxation at room temperature followed by chemical stress relaxation due to scission at high temperature. In contrast to chemical stress relaxation, viscoelastic stress relaxation (also called physical relaxation) occurs by the sliding of macromolecular chain entanglements rather than severing of chains/crosslinks. Consequently, deformation is generally recovered upon release of the load after sufficient time. In other words, it does not lead to permanent set of the material. Furthermore, most viscoelastic models assume that in viscoelastic stress relaxation the stress approaches a nonzero value for long time, in contrast to chemical stress relaxation where stress asymptotically approaches zero for sufficiently long time. The view taken here is that viscoelastic stress relaxation takes place independent of scission processes.
Therefore, it is assumed that the viscoelastic response \( \sigma^{(\text{ve})} \) can be captured by a viscoelastic relaxation function, \( G(t) \), according to

\[
\sigma^{(\text{ve})}(t) = \sigma(t) + \int_0^t \sigma(s) \dot{G}(t - s) \, ds,
\]

(4.3)

where \( \sigma(t) \) is the “elastic stress” in the absence of viscous effects and \( \dot{G} \) denotes the derivative with respect to its argument. From here on the superscript (ve) refers to a “viscoelastic”-related quantity. In this way Eq. (4.3) represents a viscoelastic “wrapper” that can be used once the purely thermoelastic, possibly degraded, response is calculated. We call the \( \sigma(t) \) the chemoelastic stress and \( \sigma^{(\text{ve})}(t) \) the chemoviscoelastic stress. Note that in this paper we will only be concerned with the degraded response of the original network for which \( \sigma(t) = \sigma^{(1)}(t) \). The viscoelastic relaxation function \( G(t) \) is normalized such that \( G(0) = 1 \) and we assume it to be independent of temperature, as was discussed in Section 2. This framework is consistent with the quasi-linear viscoelastic framework of Fung (1972), and it was chosen for its simplicity in the current context. It captures the notion that abrupt changes in elastic stress regardless of the mechanism, be it mechanical or thermal, cause a viscous-like response. It can be shown that Eq. (4.3) reduces to a linear viscoelastic model by replacing \( \sigma(s) \) with \( E\varepsilon(s) \) (where \( E \) is the elastic modulus and \( \varepsilon \) is the infinitesimal strain) and swapping the derivatives in the integral kernel in the usual way.

We assume \( G(t) \) to be of the form

\[
G(t) = G_\infty + (1 - G_\infty) \sum_{m=1}^{m_{\text{max}}} \xi_m^{(\text{ve})} \exp \left( \frac{-t}{\tau_m^{(\text{ve})}} \right),
\]

(4.4)

where \( G_\infty \in [0, 1] \) is the ratio of the long time stress to the initial stress \( (\sigma^{(\text{ve})}(\infty)/\sigma^{(\text{ve})}(0)) \), \( m \) is an integer index in the range \( \{1, 2, \ldots, m_{\text{max}}\} \), \( \xi_m^{(\text{ve})} \) are dimensionless coefficients, and \( \tau_m^{(\text{ve})} \) are relaxation time constants. For a constant step history in the stretch at time \( t = 0 \) the room temperature stress response is \( \sigma^{(\text{ve})}(t) = G(t)\sigma^{(1)}(0) \).

Fig. 5a shows the measured room temperature viscoelastic relaxation (solid line) over 40 h at constant stretch, \( \lambda = 2 \). The dotted line in the figure shows a fit of the measured data with Eq. (4.4) where a series of \( \tau_m^{(\text{ve})} \)'s were chosen on a logarithmic scale, \( 4^{(m-1)} \) s \( (m = 1, 2, \ldots, 12) \), and \( G_\infty \) and \( \xi_m^{(\text{ve})} \)'s were determined by a numerical fit of the data. The procedure incorporated the constraints that \( \sum_{m=1}^{12} \xi_m^{(\text{ve})} = 0 \) and that each \( \xi_1^{(\text{ve})} \geq 0 \). The set of \( (\tau_m^{(\text{ve})}, \xi_m^{(\text{ve})}) \) is plotted in Fig. 5b. A close inspection of Fig. 5a reveals that even after 40 h the slope of the force relaxation response is still somewhat negative, and the numerical fit predicts an asymptotic level of \( G_\infty = 0.68 \), which corresponds to a stress level of about 1.35 MPa in Fig. 5a.

\footnote{An equally good fit of the viscoelastic stress relaxation data can be obtained by \( G(t) = 1 - b \ln(1 + t) \) with \( b = 0.01967 \) and \( t \) in seconds, but unfortunately this form leads to an inefficient numerical implementation of the convolution integral in Eq. (4.3). By contrast, the exponential form of Eq. (4.4) allows a recurrence relation to be used in time (as discussed in Appendix A) that significantly reduces the computational cost.}
The simulation procedures of later sections calculate the “chemoelastic” stress at discrete time steps, 
\[ \sigma_n = \sigma(t_n) \] for \( n = 1, \ldots, n_{\text{max}} \), taking the corresponding measured temperatures and deformations \( \{ T_n, \lambda_n \} \) as input data. The subscript \( n \) refers to any quantity evaluated at time \( t_n \). The numerical procedure that is used to convert an arbitrary “chemoelastic” stress history to a corresponding “chemoviscoelastic” stress history, through the use of the viscoelastic relaxation function \( G(t) \) and Eq. (4.3), is derived in Appendix A.

### 4.3. Scission kinetics

Now, we turn our attention to the \( b^{(1)} \) function, which describes scission kinetics. As a first step, scission kinetics under constant temperature, \( T(t) = T_1 \), is considered. If the stretch state is also held fixed throughout the process, any new networks that form do not contribute to the stress \( (\sigma^{(2)} = 0) \), since their reference configuration is assumed to be the current one, and a plot of \( \sigma(t)/\sigma(0) = b^{(1)}(t) \) from such an isothermal relaxation experiment is sufficient to determine the scission relaxation function. Tobolsky (and others) have used the function,

\[
b^{(1)}(t) = e^{-q(t)/n(0)} \tag{4.5}
\]

to describe random main chain scission, in which \( q(t) \) is the molar density of chain scissions and \( n(0) \) is the initial pre-scission network molar density. If the scission rate is constant, \( q(t) = q_0 t \), the stress relaxation is termed Maxwellian, and the history of \( \ln[\sigma(t)/\sigma(0)] \) is predicted to be linear. Typical experimental data of natural rubber shows that Maxwellian decay is reasonable at sufficiently long times, but not for short to intermediate times. This led Tobolsky (1960) and Ono et al. (1978), for example, to describe a nonlinear function for \( q(t) \) in Eq. (4.5) to capture the response.

Here, an alternative view is taken in which a number of first-order chemical relaxation processes \( (p = 1, \ldots, p_{\text{max}}) \) take place simultaneously, each one of which is Maxwellian. Each process, \( p \), has a characteristic time constant, \( \tau^{(sc)}_p \), and involves a portion, \( N_p(t) \), of the total number of networks, \( N(t) = \sum_{p=1}^{p_{\text{max}}} N_p(t) \). The superscript \( (sc) \) refers to a “scission”-related quantity. The set of governing first-order
differential equations describing these processes is
\[
\frac{dN_p(t)}{dt} = -\frac{N_p(t)}{\tau_p^{(sc)}(T_1)}, \quad p = 1, 2, \ldots, p_{\text{max}}. \quad (4.6)
\]

Since the scission relaxation function, \(b^{(1)}(t)\), can also be interpreted as the ratio of remaining networks relative to the initial number, the solution to the above differential equations leads to the Prony series,
\[
b^{(1)}(T_1, t) = \frac{N(t)}{N(0)} = \sum_{p=1}^{p_{\text{max}}} \xi_p^{(sc)} e^{-t/\tau_p^{(sc)}(T_1)}, \quad (4.7)
\]

where the Prony coefficients, \(\xi_p^{(sc)}\), are interpreted as initial "phase fractions" \(\xi_p^{(sc)} = N_p(0)/N(0)\). In practice, Eq. (4.7) works well to fit experimental stress relaxation data. The number of terms \(p_{\text{max}}\) to include depends on the complexity of the chemical makeup of the material and the desired accuracy of the fit. When fitting data, the following constraints must be satisfied:
\[
\sum_{p=1}^{p_{\text{max}}} \xi_p^{(sc)} = 1, \quad \xi_p^{(sc)} \geq 0, \quad p = 1, 2, \ldots, p_{\text{max}}, \quad (4.8a, 4.8b)
\]

The relaxation function has been shown experimentally to be a strong function of temperature through the temperature dependence of each characteristic time \(\tau_p^{(sc)}(T_1)\) (see again Fig. 4). It appears that one needs several stress relaxation experiments, each at a different constant temperature \((T_1)\), to fully calibrate this function. It is found that the temperature dependence of each characteristic time can be represented as
\[
\tau_p^{(sc)} = \frac{h}{kT} \exp \left[ \frac{Q_p}{RT} + \varepsilon \left( \frac{T}{T_\varepsilon} \right)^{-\gamma} \right], \quad p = 1, 2, \ldots, p_{\text{max}}, \quad (4.9)
\]

where \(Q_p\) are activation energies, \(h\) is Planck’s constant, \(k\) is Boltzmann’s constant, and \(R\) is the universal gas constant. The parameters \(\varepsilon, T_\varepsilon,\) and \(\gamma\) are taken as \(\varepsilon = 0.5\), \(T_\varepsilon = 378.15\, \text{K} (=105^\circ\text{C})\), \(\gamma = 20\). This produces a function that is asymptotic \((\varepsilon \to 0)\) to the Eyring relation (Eyring, 1936) at high temperatures but diverges above it as the temperature is decreased below 105 °C.

Fig. 6 shows an experiment at constant \(\lambda = 2\) in which the temperature was held at room temperature for about 4 h and then ramped quickly to 105 °C and held constant. During the room temperature relaxation a large portion of the viscoelastic force relaxation occurs, followed by entropic stiffening during the temperature ramp, followed by chemical stress relaxation at the high temperature. The experiment is used to calibrate the \(b^{(1)}\) scission function, and the fit, including viscoelasticity, entropic stiffening, and scission, is shown by the dotted line. The scission spectrum that was extracted from this fit is shown in Fig. 7. The fit initially included 21 terms in the Prony series for \(b^{(1)}\), corresponding to the selected activation energies shown between 80 and 130 kJ/mol/K. This is equivalent to selecting time constants \(\tau^{(sc)}\) on a
logarithmic scale (similar to the procedure used for the viscoelastic spectrum). It can be observed that the fitting procedure produced many terms with a zero coefficient for \( x^{(sc)} \), leaving 11 nontrivial terms in the spectrum with widely spaced activation energies in the lower half of the range. While the coefficients of a Prony series can be changed somewhat without changing the quality of the fit, we are not able to obtain a good fit of the data with a smoother spectrum. This suggests that no chemical processes exist with activation energies near the zeros of the spectrum. Now that the spectrum has been calibrated it is used for all the remaining simulations throughout this paper.

Now consider the response when the temperature is not held constant. Fig. 8a shows an experiment for step changes in temperature between 140 and 125°C and back again. (The drop in temperature below 100°C momentarily was due to the door of the temperature chamber being opened briefly during the experiment.) The force response decays quickly initially, then slows when the temperature is reduced, and then quickens again when the temperature is raised. Fig. 8b shows how portions of the measured force response compare to the corresponding force responses from Fig. 4 at constant temperatures, 140 and 125°C, respectively. One can see that a shifting of the response from one curve to the next, starting at the degradation level from the previous temperature level as an initial point for the next step, agrees quite well with the constant temperature responses.
It must be emphasized that Eq. (4.7) is valid only for the case of a constant temperature history. Fortunately, the case of time-varying temperature can be easily included by a suitable modification of Eq. (4.6) with the temperature history $T(t)$. As
suggested by the results of Fig. 8, each process is assumed to depend only on the instantaneous temperature according to

$$\frac{dN_p(t)}{dt} = - \frac{N_p(t)}{\tau_p^{(sc)}(T(t))}, \quad p = 1, 2, \ldots, p_{\text{max}}. \quad (4.10)$$

In this case the solution to this set of differential equations is

$$N_p(t) = N_p(0) \exp \left( - \int_0^t \frac{ds}{\tau_p^{(sc)}(T(s))} \right), \quad p = 1, 2, \ldots, p_{\text{max}}, \quad (4.11)$$

which leads to the generalized relaxation function,

$$b^{(1)}(t) = \sum_{p=1}^{p_{\text{max}}} \tau_p^{(sc)} \exp \left( - \int_0^t \frac{ds}{\tau_p^{(sc)}(T(s))} \right), \quad (4.12)$$

that can be calculated for arbitrary temperature histories. Here, the explicit functional notation for $b^{(1)}$ has been dropped with the understanding that it is a functional of the temperature history. The integral in the exponential plays the role of a “pseudotime”. In the commonly used time-temperature superposition approach of viscoelasticity, for example, all the characteristic times are shifted by the same amount with temperature for a so-called “rheologically simple” material. Here, by contrast, it is seen from Eq. (4.9) that each characteristic time has a different shift factor with temperature according to individual activation energies.

The numerical procedure for calculating scission kinetics for arbitrary temperature histories is derived in Appendix B. The procedure takes the measured temperature data at discrete time steps as input and calculates the corresponding $b^{(1)}$ values using the scission spectrum above. An example of the response to a complex temperature history is shown in Fig. 9a. This is an experiment in which the stretch is held constant ($\lambda = 2$) and the temperature is initially held for almost 4 h at room temperature and then oscillated between that and 70 °C for 11 cycles. The measured (solid line) and simulated (dotted line) force response is shown in Fig. 9b. The simulated chemoviscoelastic force response involves the numerical implementation of Eqs. (4.1), (4.3), and (3.10). As can be seen the agreement between simulation and experiment is excellent, capturing the initial viscoelastic relation, entropic stiffening, a small amount of scission (arising from the lowest activation energy of Fig. 7), followed by entropic stiffening/softening cycles as the temperature is oscillated.

5. Diffusion-limited oxidative scission

It has been shown (see, for example, Tobolsky, 1960) that the rate of stress relaxation is significantly slowed when experiments are conducted in low oxygen environments. Furthermore, at extreme temperatures in air the rate of oxygen consumption in the scission reaction may compete with the rate of oxygen diffusion supplied from specimen boundary surfaces. Therefore, specimens of finite thickness may have distinctly nonuniform oxygen concentration distributions, which would
tend to arrest the rate of oxidative scission. Therefore, unless very thin specimens are used (typically <0.25 mm thick, Gent, 2001), oxygen depletion should be considered when predicting scission kinetics. This section begins with an analysis of the linear oxygen diffusion-reaction equation that is solved for time-dependent coefficients. A modification to the previous $b^{(1)}$ function is then proposed, based on the normalized oxygen concentration profile, and several simulations are compared to experiments at temperatures for which oxygen depletion is expected to be significant.

5.1. The oxygen diffusion-reaction boundary value problem

A strip rubber specimen is assumed to have one dimension sufficiently thin compared to the width and length such that the time-dependent oxygen concentration, $C(z, t)$, can be considered to be a function of one spatial coordinate through the thickness, $z$. The mid-thickness plane is located at $z = 0$ and the free lateral surfaces are located at $z = \pm h$. The linear partial differential equation for diffusion and reaction of oxygen is

$$\frac{\partial \psi}{\partial t} = D(t) \frac{\partial^2 \psi}{\partial z^2} - K(t) \psi,$$  (5.1)
where \( \psi \equiv C(z, t)/C_0 \) is the normalized oxygen concentration, \( C_0 \) is the ambient (constant) oxygen concentration, \( D(t) \) is the oxygen diffusivity in the rubber and \( K(t) \) is the reaction rate coefficient (reactivity) leading to the consumption of oxygen in the scission reaction. As discussed in Ono et al. (1978) we recognize that oxidative scission may be largely autocatalytic, so that oxygen is not consumed in a straightforward manner according to linear kinetics (e.g., the \(-K\psi\) term); however, in the absence of more definitive information and in the interest of simplicity we use Eq. (5.1) to get a first-order approximation of the effect of oxygen depletion in moderately thick specimens. The simplifying assumptions leading to Eq. (5.1) and the general solution for the case where \( D \) and \( K \) are constant are provided in Ono et al. (1978). However, both \( D(t) = \tilde{D}(T(t)) \) and \( K(t) = \tilde{K}(T(t)) \) are strongly time-dependent through their dependence on the temperature history, so we proceed here to solve the case with non-constant coefficients.

Assuming that the specimen is initially in chemical equilibrium, immersed in an atmosphere of oxygen concentration \( C_0 \) and the temperature is low \((K \approx 0)\), the respective boundary conditions and initial conditions are

\[
\psi(\pm h, t) = 1, \quad (\text{5.2}) \\
\psi(z, 0) = 1. \quad (\text{5.3})
\]

Using a straightforward separation of variables approach, the transient solution for arbitrary time-dependent coefficients, \( D(t) \) and \( K(t) \), can be shown to be

\[
\psi(z, t) = 1 - 2 \sum_{k=0}^{\infty} \frac{(-1)^k}{\eta_k} c_k(t) d_k(t) \cos(\eta_k z/h),
\]

\[
c_k(t) = \exp \left\{ - \int_0^t \left[ K(s) + \frac{\eta_k^2}{h^2} D(s) \right] ds \right\},
\]

\[
d_k(t) = \int_0^t \frac{K(s)}{c_k(s)} ds,
\]

where \( \eta_k \equiv (k + \frac{1}{2})\pi \). The oxygen concentration history is a functional of the temperature history alone through the temperature dependence of \( D \) and \( K \). We choose Arrhenius relations for the diffusivity and reactivity, following Ono et al. (1978), van Amerongen (1964) and Murakami and Ono (1979), respectively:

\[
D(t) = D_0 \exp \left[ \frac{-Q(D)}{RT(t)} \right],
\]

\[
K(t) = K_0 \exp \left[ \frac{-Q(K)}{RT(t)} \right],
\]

where \( Q(D) = 34.75 \text{ kJ/mol} \) and \( Q(K) = 104.67 \text{ kJ/mol} \) are activation energies, and \( D_0 = 191.9 \text{ mm}^2/\text{s} \) and \( K_0 = 2.302 \times 10^{11} \text{ s} \), and \( R = 8.3157 \text{ J/mol K} \) is the universal gas constant. The steady-state distribution \( (\psi(z, t) \rightarrow \psi_{\infty}(z) \text{ for } T(t) \rightarrow T_{\infty}) \)
after a long time \( (t \to \infty) \) is
\[
\psi_\infty(z) = \frac{\cosh(z/h^*)}{\cosh(h/h^*)},
\]
where \( h^* = \sqrt{\tilde{D}(T_\infty)/\tilde{K}(T_\infty)} \) is a characteristic length scale for the oxygen concentration profile. This provides a convenient parameter to check whether oxygen will become significantly depleted in the interior of the specimen. If \( h \ll h^* \) then \( \psi_\infty(z) \approx 1 \) and oxygen depletion need not be considered. In our case, for example, \( h = 1 \text{ mm} \) which is much less than \( h^* = 38 \text{ mm} \) at room temperature. However, oxygen depletion cannot be neglected at chemorheological temperatures, since \( h^* = 2.2 \text{ mm} \) at 100 °C and \( h^* = 0.6 \text{ mm} \) at 150 °C.

5.2. Scission dependence on oxygen concentrations

Ultimately, the effect of oxygen depletion is to slow the rate of oxidative scission. To a first approximation we assume that each characteristic rate coefficient in the scission process is proportional to the normalized oxygen concentration, \( \psi(z, t) \). We recognize that this neglects any contribution from anaerobic scission, which we suspect might become more significant for temperatures above 150 °C, but is not a significant contribution for the temperature range considered here. The factor, \( \psi(z, t) \), plays a similar role to the temperature-dependent shift function used for rheologically simple viscoelastic materials. We modify the first-order kinetic equations in Eq. (4.10) according to
\[
\frac{dN_{p}(z, t)}{dt} = -\frac{\psi(z, t)}{\tau_{p}(T(t))}N_{p}(z, t), \quad p = 1, 2, \ldots, p_{\text{max}},
\]
thereby leading to a spatially dependent scission function according to the oxygen concentration profile,
\[
b^{(l)}(z, t) = \frac{N(t)}{N(0)} = \sum_{p=1}^{p_{\text{max}}} \xi_{p}(T(t)) \exp \left[ -\int_{0}^{t} \frac{\psi(z, t)}{\tau_{p}(T(s))} \mathrm{d}s \right].
\]
According to Eq. (4.1) a spatially dependent chemoelastic stress \( \sigma^{(l)}(z, t) \) is given by
\[
\sigma^{(l)}(z, t) = b^{(l)}(z, t) \frac{T(t)}{T_0} \sum_{j=1}^{4} c^{(l)}_{j} \left( \frac{\dot{\lambda}(t)}{\dot{\lambda}_{T}(t)} \right)^{m_{j}}.
\]
The chemoviscoelastic stress associated with the original network is then
\[
\sigma^{(\text{ve})}(z, t) = \sigma^{(l)}(z, t) + \int_{0}^{t} \sigma^{(l)}(z, s) \dot{G}(t - s) \mathrm{d}s
\]
and the average engineering stress is
\[
\sigma_{E}(t) = \frac{\dot{\lambda}_{T}(t)^{3}}{\dot{\lambda}(t)} \frac{1}{h} \int_{0}^{h} \sigma^{(\text{ve})}(z, t) \mathrm{d}z,
\]
which can then be compared to the measured force response.
Simulations of the evolution of oxygen concentration profiles, Eq. (5.4), and the consequent force response, through Eqs. (5.8)–(5.11), were performed using Mathematica 5 (2003). The details of the numerical implementation is addressed in Appendix C.

5.3. Experiments and simulations with oxygen depletion

Figs. 10–13 show a series of four experiments and corresponding simulations for nearly piecewise constant temperature histories starting at room temperature and then stepping up to progressively higher chemorheological temperatures.

- Fig. 10a shows the measured temperature history (dotted line, $T$), consisting of room temperature for about 3 h followed by nearly 40 h at 115°C. It also includes the calculated evolution of the normalized mid-thickness oxygen concentration (solid line, $\psi(0, t)$), to investigate the level of oxygen depletion. At 115°C the figure shows that the mid-thickness oxygen concentration is predicted to reach about 80% of the ambient value. Fig. 10b shows the measured force (actually, engineering stress) response (solid line, $F_{\text{data}}$) which decays initially due to room
temperature viscoelastic relaxation, stiffens momentarily due to entropic effects as the temperature is raised, but then decays to near zero stress when the temperature is held at 115°C. The corresponding simulated force response (average chemoviscoelastic stress) that includes the effects of oxygen depletion is overlaid (dotted line, $F_{\text{sim}}$). A third predicted response that neglects any oxygen depletion, as if the specimen was infinitesimally thin, is also overlaid for comparison (dashed line, $F_{\text{thin}}$). The simulation with oxygen depletion agrees quite well with the measured force response; whereas, the one neglecting oxygen depletion overpredicts the rate of scission somewhat.

- A second similar experiment that ends at 125°C is shown in Fig. 11a. In this case, the calculated mid-thickness oxygen concentration reaches about 70% of its initial value. The force response in Fig. 11b is very well simulated by including oxygen depletion and again somewhat overpredicts the rate of scission if oxygen depletion is not included.
- Fig. 12 shows a third experiment that ends at 135°C. In this experiment a temperature overshoot occurred, so the calculated oxygen concentration momentarily dips to only 30%, but then reaches a steady value near 58% once
the temperature steadies out (see Fig. 12a). The simulated force response in Fig. 12b does not agree quite as well as the previous cases, seeming to overpredict the scission rate during the temperature overshoot, but the shape of the response is similar to the measured one. The simulation without oxygen depletion overpredicts the scission rate by a larger amount.

- The fourth experiment and simulations are shown in Fig. 13 which ends at a temperature of 145°C. The calculated steady state oxygen concentration is near 41% in this case. Similar to the previous case the simulated force response overpredicts the rate of scission somewhat, while the simulation without oxygen depletion significantly overpredicts the scission rate.

In summary, the agreement between simulation and data can be characterized as excellent-to-good as experiments progress from low-range to high chemorheological temperatures, respectively. It should be noted that considering the previously noted limitations of the linear oxygen reaction–diffusion equation, Eq. (5.1), and the use of typical (chosen from the literature), rather than measured, values for the oxygen diffusivity ($D$) and reactivity ($K$), the simulations capture the trends seen in the experiments quite well. We suspect that even better fits at the highest temperature...
could be achieved through an optimization of these parameters, but that was not done here.

Figs. 14 and 15 show two experiments and their simulations for more complex temperature histories. Fig. 14a shows several ramp changes in temperature in the mid-chemorheological range and the predicted oxygen concentration evolution that tracks in an inverse manner to the temperature. The agreement between simulation and data in Fig. 14b is excellent with nearly overlaying curves. The simulated force response without oxygen depletion, as before, is somewhat shifted below the other two. Fig. 15a shows several ramp changes in temperature in the high-chemorheological range and the corresponding oxygen concentration evolution. The simulation in Fig. 15b is again in excellent agreement with the data, with the simulation only slightly shifted below the data after the short hold at 150°C. The simulated force response without oxygen depletion is shifted further below the other two. Even for the rather thin (2 mm) specimens used in this study, the effects of oxygen depletion are noticeable in our simulations. The effects of oxygen depletion would play a much more important role for typical elastomeric components that have dimensions of several centimeters or larger. Thus, this study underscores the importance of including the effects of oxygen depletion on scission processes, especially in high-temperature simulations of elastomeric components.
6. Summary and conclusions

Experiments and simulations were presented for the response of commercial-grade, carbon-black filled, natural rubber subject to finite deformation and temperatures in the chemorheological range (90–150°C for natural rubber). The experimental results exhibited the phenomena of viscoelastic relaxation, entropic stiffening, thermal expansion, and oxidative scission with consequent chemical stress relaxation. The constitutive equation presented by Chadwick for entropic hyperelasticity for materials that are mechanically incompressible, but undergo thermal expansion, was used in a multinetwork theoretical framework. This theory was extended to account for complex temperature histories and applied to uniaxial experimental results for natural rubber. The two stress relaxation mechanisms of viscoelasticity (physical relaxation) and scission (chemical relaxation) were numerically calibrated to experiments at constant temperature histories through the use of respective discrete relaxation spectra. An efficient numerical procedure was developed to account for arbitrarily complex temperature histories.

Fig. 14. (a) Prescribed complex temperature history (dotted line) between 110 and 130°C and calculated mid-thickness oxygen concentration history (solid line) (constant $\lambda = 2$). (b) Measured force response (solid line), simulation results with oxygen depletion (dotted line), and simulation results without oxygen depletion (dashed line).
A method for connecting oxygen diffusion and consumption to the scission processes was also developed. At chemorheological temperatures, the consumption of oxygen in the interior of the rubber specimen was predicted to occur initially faster than the resupply of oxygen through diffusion from the boundary surfaces, which led to depletion of oxygen in the interior of the specimen and slowing of the scission rates in the interior. Therefore, at high temperatures the specimens used could no longer be considered sufficiently thin, i.e., a thickness effect was present that tended to slow the rate of chemical stress relaxation. A numerical scheme was presented that calculated the oxygen concentration profiles for arbitrary temperature histories and then accounted for nonuniform scission kinetics in the interior of the specimen. Good agreement was achieved between the simulated and experimental force responses over the entire chemorheological temperature range with especially good results obtained for low to mid-chemorheological temperatures. It was shown that neglecting the depletion of oxygen at high temperatures would overpredict the rate of scission, even for the relatively thin specimens used in this study.

The overall simulation scheme outlined herein, including viscoelastic relaxation, entropic effects, thermal expansion, and diffusion-limited oxidative scission, does an
effective job of predicting the uniaxial response of natural rubber specimens subject to a wide variety of temperature histories.

The primary contribution of this work is the comprehensive simulation method that was experimentally validated for the response of rubber material over a wide range of temperature histories. It included all the above listed coupled phenomena. The good agreement with experimental data provides confidence that all the phenomena of interest can be predicted well. The theoretical framework presented included both: (1) the effects of the initial degraded macromolecular network and (2) the formation of new networks with new reference configurations. So far, however, the simulation scheme demonstrated the response of the initial network only by considering simple constant stretch histories for which new networks do not contribute to the overall stress. Forthcoming work will include such simulations of newly formed networks on the material response to account for arbitrary deformation histories. In particular, the effect of new networks is necessary to account for permanent set. With this accomplished, an effective computational tool should be available for predicting the durability and useful lifetime of elastomeric components subject to elevated temperatures.

7. Acknowledgments

The financial support from the National Science Foundation (Chemical and Thermal Sciences grant CTS-9908925) and Sandia National Laboratory (Award No. 199068) is acknowledged with sincere thanks. Material was supplied by Tenneco Automotive Corporation at no cost, and the cooperation of Guy Smith, Josh Goossens, and John Lane is greatly appreciated. Helpful discussions with Alan Gent (University of Akron), who brought the issue of oxygen depletion to our attention, are also acknowledged.

Appendix A. Numerical implementation of viscoelasticity

This section develops the numerical procedure to calculate the corresponding “chemoviscoelastic” stress history, \(\sigma^{(ve)}_n\), taking the calculated set of discrete chemoelastic stress values, \(\sigma_n\) \((n = 1, \ldots, n_{\text{max}})\), as input to Eq. (4.3). Considering discrete time increments, Eq. (4.3) can be rewritten as

\[
\sigma^{(ve)}_n = \sigma_n - (1 - G_\infty) \sum_{m=1}^{m_{\text{max}}} \frac{\tau_m^{(ve)}}{\tau_m^{(ve)}} I^{(ve)}_{m,n},
\]

where

\[
I^{(ve)}_{m,n} = \int_0^{t_n} \sigma(s) \exp\left(-\frac{t_n - s}{\tau_m^{(ve)}}\right) ds, \quad m = 1, \ldots, m_{\text{max}}.
\]
Rather than recalculate these integrals at every time step, it is possible to update them, since

$$I_{m,n+1}^{(ve)} = I_{m,n}^{(ve)} e^{-\Delta t_n/\tau_m^{(ve)}} + \int_{t_n}^{t_{n+1}} \sigma(s) \exp\left(-\frac{t_{n+1}-s}{\tau_m^{(ve)}}\right) ds, \quad m = 1, \ldots, m_{\text{max}},$$

(A.3)

where the time increment is $\Delta t_n = t_{n+1} - t_n$. This provides an efficient recursion relation to march the solution forward in time, using the starting values $I_{m,0}^{(ve)} = 0$. The second integral term in Eq. (A.3) can be approximated numerically at each time step. While a simple trapezoidal rule is a tempting choice, it requires very small time steps to produce an accurate approximation, since the viscoelastic relaxation is initially driven by small time constants. We find that a better alternative is to assume a linear ramp in chemoelastic stress during the time interval $s \in [t_n, t_{n+1}]$ according to $\sigma(s) = \sigma_n + (s - t_n)(\sigma_{n+1} - \sigma_n)/\Delta t_n$. This can be integrated analytically in the second term of Eq. (A.3), and the updated relation becomes

$$I_{m,n+1}^{(ve)} = I_{m,n}^{(ve)} e^{-\Delta t_n/\tau_m^{(ve)}} + \frac{\tau_m^{(ve)}}{\Delta t_n} [\sigma_{n+1}(\tau_m^{(ve)} e^{-\Delta t_n/\tau_m^{(ve)}} + \Delta t_n - \tau_m^{(ve)}) - \sigma_n((\Delta t_n + \tau_m^{(ve)}) e^{-\Delta t_n/\tau_m^{(ve)}} - \tau_m^{(ve)})], \quad m = 1, \ldots, m_{\text{max}}.$$

(A.4)

Eq. (A.4) allows much larger time increments to be used without sacrificing accuracy of the numerical approximation.

### Appendix B. Numerical implementation of scission kinetics

In this section, a numerical approach is developed to predict the chemoelastic stress response, $\sigma(t)$, to time-varying temperature, $T(t)$, histories. As mentioned before, thermomechanical experiments have been conducted where all quantities were measured and synchronized over a set of discrete times, i.e., data records $\{t_n, T_n, \dot{\lambda}_n, F_n\}$ for $n = \{1, 2, \ldots, n_{\text{max}}\}$. The numerical simulation scheme, therefore, accepts $\{t_n, T_n, \dot{\lambda}_n\}$ as input and calculates corresponding $\sigma_n$ values.

As was done for the viscoelastic history integral in Appendix A, we seek to avoid calculation of the entire history integral in Eq. (4.12) at each time step. Fortunately, a recursive update scheme is possible again, in which integrals evaluated at time $t_n$ can be updated to produce corresponding values at time $t_{n+1}$. The integrals play the role of “internal state variables” which are then updated at each time step according to the kinetic relations inherent in Eq. (4.12).

It will be helpful in the derivation that follows to introduce the definition

$$I_{p,n}^{(sc)} \equiv \exp\left[-\int_0^{t_n} \frac{ds}{\tau_p^{(sc)}(T(s))}\right].$$

(B.1)
As before, a subscript \( n \) denotes any quantity evaluated at time \( t_n \). In this way, the value of the relaxation function at time step \( t_n \) is

\[
b_n^{(1)} = \sum_{p=1}^{p_{\text{max}}} \zeta_p I_{p,n}^{(sc)}.
\]  

(B.2)

The value at time step \( t_{n+1} \) is, similarly,

\[
b_{n+1}^{(1)} = \sum_{p=1}^{p_{\text{max}}} \zeta_p I_{p,n+1}^{(sc)}
\]  

(B.3)

but \( I_{p,n+1}^{(sc)} \) can be decomposed into

\[
I_{p,n+1}^{(sc)} = \exp \left[ - \int_{t_n}^{t_{n+1}} \frac{ds}{\tau_p^{(sc)}(T(s))} \right]
\]  

which produces the recursion relation and initial condition

\[
I_{p,n+1}^{(sc)} = I_{p,n}^{(sc)} D_{p,n+1}, \quad \text{and} \quad I_{p,0}^{(sc)} = 1, \; p = 1, \ldots, p_{\text{max}}.
\]  

(B.5)

The multiplying factor is defined as

\[
D_{p,n+1}^{(sc)} = \exp \left[ - \int_{t_n}^{t_{n+1}} \frac{ds}{\tau_p^{(sc)}(T(s))} \right].
\]  

(B.6)

If the time step \( (t_{n+1} - t_n) \) is sufficiently small this could be approximated by the trapezoidal rule. However, since the experimental data are occasionally taken at widely spaced time steps, a numerical quadrature approximation to the integral is used instead to ensure reasonable accuracy. Now, the chemoelastic stress in the original network is computed from Eq. (4.1) as

\[
\sigma_n^{(1)} = \left( \sum_{p=1}^{p_{\text{max}}} \zeta_p I_{p,n}^{(sc)} \right) \frac{T_n}{T_0} \left( \sum_{j=1}^{4} \frac{\lambda_j}{\lambda_{T_n}} \right)^{m_j}, \; n = 1, \ldots, n_{\text{max}},
\]  

(B.7)

having used Eq. (B.5) to determine the \( I_{p,n}^{(sc)} \) values from the temperature history data.

**Appendix C. Numerical implementation of diffusion-limited oxidative scission**

The simulation of the material response to diffusion-limited oxidative scission is performed in a two step sequence: (1) the evolution of oxygen profiles are calculated based on the temperature history; (2) the mechanical response with spatially dependent scission is then calculated based on procedures adapted from Appendix A and B.
The evolution of oxygen profiles is calculated based on Eq. (5.4) through the truncated series

\[ c(\bar{z}, t) = \frac{1}{C_0} \sum_{k=0}^{k_{\text{max}}} \left( -\frac{\eta_k}{\eta} \right)^k c_k(t) d_k(t) \cos(\eta_k \bar{z}), \]

\[ c_k(t) = \exp \left\{ - \int_0^t \left[ K(s) + \frac{\eta_k^2}{h^2} D(s) \right] ds \right\}, \]

\[ d_k(t) = \int_0^t \frac{K(s)}{c_k(s)} ds, \]  

(C.1)

where the spatial coordinate has been normalized by \( \bar{z} = \frac{z}{h} \). We find that \( k_{\text{max}} = 10 \) produces acceptably converged results. Similar to the approach used in the history integrals of Appendix A and B, a recursive update scheme is used to calculate \( \psi_n(\bar{z}) \) from \( c_{k,n} = c_k(t_n) \) and \( d_{k,n} = d_k(t_n) \) at discrete times:

\[ \psi_n(\bar{z}) = 1 - 2 \sum_{k=0}^{k_{\text{max}}} \left( -\frac{\eta_k}{\eta} \right)^k c_{k,n} d_{k,n} \cos(\eta_k \bar{z}), \]  

(C.2)

where

\[ c_{k,n+1} = c_{k,n} \exp \left\{ - \int_{t_n}^{t_{n+1}} \left[ K(s) + \frac{\eta_k^2}{h^2} D(s) \right] ds \right\}, \]

\[ d_{k,n+1} = d_{k,n} + \int_{t_n}^{t_{n+1}} \frac{K(s)}{c_k(s)} ds, \quad k = 1, \ldots, k_{\text{max}}. \]  

(C.3)

with the initial conditions,

\[ c_{k,0} = 1, \]

\[ d_{k,0} = 0. \]  

(C.4)

If the time step, \( \Delta t_n = t_{n+1} - t_n \), is sufficiently small, Eqs. (C.3) can be approximated by the trapezoidal rule as

\[ c_{k,n+1} = c_{k,n} \exp \left[ - \frac{\Delta t_n}{2} \left( K_n + K_{n+1} + \frac{\eta_k^2}{h^2} (D_n + D_{n+1}) \right) \right], \]

\[ d_{k,n+1} = d_{k,n} + \frac{\Delta t_n}{2} \left[ \frac{K_n}{c_{k,n}} + \frac{K_{n+1}}{c_{k,n+1}} \right]. \]  

(C.5)

If the time step is not sufficiently small it is subdivided, and the trapezoidal rule is applied to the subincrements in sequence. To determine whether or not the current time step is small it is compared to the smallest characteristic time considered in Eq. (C.3). Presuming the temperature is a monotonic ramp in time during the interval, it is sufficient to check the characteristic times at the end points of the
interval. The smallest characteristic time is then
\[
\tau_{\text{min}} = \min \left\{ \frac{1}{K_n + (k_{\text{max}} + \frac{1}{2})(\pi/h)^2 D_n}, \frac{1}{K_{n+1} + (k_{\text{max}} + \frac{1}{2})(\pi/h)^2 D_{n+1}} \right\}.
\]
(C.6)
The time step is subdivided whenever \( \Delta t_n \geq \tau_{\text{min}} \) to assure the accuracy of the oxygen profiles.

Now we turn to the calculation of the resulting spatially dependent chemoelastic stress, Eq. (5.9), which is repeated here as
\[
\sigma^{(1)}(\bar{z}, t) = b^{(1)}(\bar{z}, t) \frac{T(t)}{T_0} \sum_{j=1}^{4} c_j^{(1)} \left[ \frac{\lambda(t)}{\lambda_1(t)} \right]^{m_j}.
\]
(C.7)
Assuming plane sections remain plane and the temperature is spatially uniform, all the dependence on \( \bar{z} \) enters through \( b^{(1)}(\bar{z}, t) \). Denoting the undegraded stress as
\[
\sigma^{(0)}(t) = \frac{T(t)}{T_0} \sum_{j=1}^{4} c_j^{(1)} \left[ \frac{\lambda(t)}{\lambda_1(t)} \right]^{m_j}
\]
gives the decomposition
\[
\sigma^{(1)}(\bar{z}, t) = b^{(1)}(\bar{z}, t)\sigma^{(0)}(t),
\]
(C.8)
which leads to
\[
\sigma^{(v)}(\bar{z}, t) = b^{(1)}(\bar{z}, t)\sigma^{(0)}(t) + \int_0^t b^{(1)}(\bar{z}, s)\sigma^{(0)}(s)\dot{G}(t - s) \, ds.
\]
(C.9)
Now define the average scission function across the specimen thickness as
\[
b^{(1)}(\bar{z}, t) = \int_0^1 b^{(1)}(\bar{z}, t) \, d\bar{z}.
\]
(C.10)
Then the engineering stress in the specimen is
\[
\sigma_E(t) = \frac{\dot{\lambda}_1(t)^3}{\lambda(t)} \left[ b^{(1)}_{\text{ave}}(t)\sigma^{(0)}(t) + \int_0^t b^{(1)}_{\text{ave}}(s)\sigma^{(0)}(s)\dot{G}(t - s) \, ds \right],
\]
(C.11)
which can be compared directly to the measured force history from an experiment. The previously derived numerical procedure (Appendix A) can be used to evaluate the effects of viscoelasticity in Eq. (C.12) once \( b^{(1)}_{\text{ave}}(t) \) is known. This is approximated by Gaussian quadrature as
\[
b^{(1)}_{\text{ave}}(t) \approx \sum_{i=1}^{l_{\text{max}}} w_i b^{(1)}(\bar{z}_i, t),
\]
(C.12)
where \( \{\bar{z}_i, w_i\} \) are the set of Gauss points in the interval \( \bar{z}_i \in [0, 1] \) and the weights, respectively \( (i = 1, \ldots, l_{\text{max}}) \). The oxygen profiles are quite smooth, so satisfactory results can be obtained through the use of only a few Gauss points. The values of the local scission functions \( b^{(1)}_{i,j} = b^{(1)}(\bar{z}_i, t_n) \) are calculated following the procedure of
Appendix B, but now at each Gauss point \((i)\),

\[
I_{i,n}^{(1)} = \sum_{p=1}^{p_{\text{max}}} \varepsilon_p^{(sc)} I_{p,i,n}^{(sc)}
\]

(C.14)

where

\[
I_{p,i,n}^{(sc)} \equiv \exp \left[ - \int_{t_0}^{t_n} \frac{\psi(\bar{z}_i,s)}{\tau_p^{(sc)}(T(s))} \, ds \right].
\]

(C.15)

The history variable \(I_{p,i,n}^{(sc)}\) is similar to the one used in Eq. (B.2), where the index \(p\) denotes one of the scission activation energies and the index \(n\) denotes the discrete time instant, but now the spatial dependence enter through the Gauss point index \(i = 1, \ldots, i_{\text{max}}\). This again leads to a recursion relation and initial condition (for each Gauss point):

\[
I_{p,i,n+1}^{(sc)} = I_{p,i,n}^{(sc)} D_{p,i,n+1}^{(sc)}, \quad \text{and} \quad I_{p,i,0}^{(sc)} = 1, \quad p = 1, \ldots, p_{\text{max}},
\]

(C.16)

where the multiplying factor is defined as

\[
D_{p,i,n+1}^{(sc)} \equiv \exp \left[ - \int_{t_0}^{t_{n+1}} \frac{\psi(\bar{z}_i,s)}{\tau_p^{(sc)}(T(s))} \, ds \right].
\]

(C.17)

The integral in this factor is approximated numerically in time with an adaptive Gaussian quadrature with error estimation based on the Kronrod points (Mathematica 5, 2003).

References


