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ORIGINAL ARTICLE

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Influence of thermally induced chemorheological changes on the torsion of elastomeric circular cylinders

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Abstract When an elastomeric material is deformed and subjected to temperatures above some characteristic value T_{cr} (near 100°C for natural rubber), its macromolecular structure undergoes time and temperature-dependent chemical changes. The process continues until the temperature decreases below T_{cr}. Compared to the virgin material, the new material system has modified properties (reduced stiffness) and permanent set on removal of the applied load.

A new constitutive theory is used to study the influence of the changes of macromolecular structure on the torsion of an initially homogenous elastomeric cylinder. The cylinder is held at its initial length and given a fixed twist while at a temperature below T_{cr}. The twist is then held fixed and the temperature of the outer radial surface is increased above T_{cr} for a period of time and then returned to its original value. Assuming radial heat conduction, each material element undergoes a different chemical change. After enough time has elapsed such that the temperature field is again uniform and at its initial value, the cylinder properties are now inhomogeneous. Expressions for the time variation of the twisting moment and axial force are determined, and related to assumptions about material properties. Assuming the elastomeric networks to act as Mooney-Rivlin materials, expressions are developed for the permanent twist on release of torque, residual stress, and the new torsional stiffness in terms of the kinetics of the chemical changes.

Keywords Elasticity · Elastomer · Constitutive theories

1 Introduction

The temperature in an elastomeric structural component, such as a bushing, seal or tire, can increase due to the environment in which it operates or due to internal dissipation. When the temperature becomes sufficiently high, the structure of the elastomer can change due to a process consisting of the scission of macromolecules and their subsequent crosslinking to form new networks with new stress free configurations. This process is time and temperature-dependent and can result in substantial softening of response and permanent set on removal of applied loads.

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Tobolsky [1] presented results of experiments that provided significant insight into this process. It occurs at elevated temperatures, is faster at higher temperatures, and stops when temperature drops below some level. If the material is loaded during scission and crosslinking and is then unloaded and cooled, it develops a permanent set and has a modified stiffness. Tobolsky also proposed a constitutive equation for uniaxial stretch at constant temperature. An extension of this constitutive equation to arbitrary deformation and temperature histories has been proposed and studied by Wineman and Min [2], Jones [3] and Shaw, Jones and Wineman [4].

When an elastomeric structure is subjected to simultaneous transient mechanical loads and heat conduction, each material element experiences a different temperature and deformation history and, hence, undergoes a different scission and crosslinking process. As a consequence, the structure develops inhomogeneity in its properties, permanent set and residual stresses upon unloading and cooling. The abovementioned constitutive equation has been used to study these phenomena in a sheared elastomeric layer by Wineman and Min [5]. Here, they are studied for torsion of an elastomeric circular cylinder when there is time-dependent and radially dependent scission and crosslinking. Torsion is chosen for study because the assumed form of the deformation is possible for any choice of the material properties in the constitutive equation and for any radial and time dependence of the scission/crosslinking processes within the cylinder. It provides a convenient setting for studying the interaction between deformation and the scission/crosslinking process. Relations are developed that connect results obtained in torsion experiments to deformation and temperature history of the elastomer, its mechanical properties, and the scission and crosslinking processes.

The constitutive equation is outlined in Sect. 2. The problem of torsion in the presence of transient radial heat conduction is formulated in Sect. 3. Section 4 treats the time-dependent response during scission and crosslinking while the cylinder is maintained at a fixed twist. It is shown that the time variation of the twisting moment is proportional to the time variation of the axial force when the material properties satisfy certain conditions, a result amenable to experimental study. When the cylinder is cooled to its original temperature, it has a modified torque-twist response. This is discussed in Sects. 5 and 6. Section 5 is concerned with twisting while the length is held fixed by application of an axial force. In Sect. 6, the axial force and length can vary. Residual twist and length are determined when the elastomeric networks are modeled as Mooney-Rivlin materials.

2 Constitutive equation

Tobolsky [1] discussed experiments on rubber strips at elevated temperatures that led to the conclusion that the rubber had undergone chemical changes in its macromolecular 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 decrease with time. At the end of the time interval, the specimen was unloaded and returned to its original temperature. The specimen was observed to have a permanent stretch. Tests were carried out for different applied stretches, temperatures, and time intervals. It was concluded that the decrease in stress was due to scission within the macromolecular network. The permanent stretch was attributed to a new network that formed when the macromolecules crosslinked in the stretched state of the original material. Tobolsky [1] implied that these events are significant for temperatures greater than a temperature T_{cr}, the onset of the 'chemorheological range'.

In the experimental work discussed by Tobolsky, specimens were generally subjected to fixed uniaxial stretch at different constant temperatures. The purpose was to understand the physical and chemical processes involved in scission and crosslinking. Recently, a program has been underway to develop a constitutive framework for rubber undergoing scission and crosslinking while subjected to arbitrary homogeneous deformation and temperature histories. The constitutive equation is based on the two-network model of Tobolsky [1] and an extension to arbitrary homogeneous deformations by Fong and Zapas [6]. A brief summary of the constitutive framework is presented here. For a detailed discussion, see Wineman and Min [2], Jones [3] and Shaw, Jones and Wineman [4].

Consider a rubbery material in a stress free reference configuration at a temperature T_0. It is assumed that there is a range of deformations and temperatures in which the material response can be regarded as mechanically incompressible at a fixed temperature, isotropic and nonlinearly elastic. For brevity, explicit notational dependence on the current time t is generally omitted. If $\mathbf{x}$ is the position at current time t of a particle located at $\mathbf{X}$ in the reference configuration, the deformation gradient is $\mathbf{F} = \partial\mathbf{x}/\partial\mathbf{X}$. The left Cauchy-Green tensor is $\mathbf{B} = \mathbf{F}\mathbf{F}^T$ and $\mathbf{B}^{-1}$ denotes its inverse. Then the Cauchy stress σ is given by

$$\boldsymbol{\sigma}^{(1)} = -p^{(1)}\mathbf{I} + 2\frac{\partial W^{(1)}}{\partial I_1}\mathbf{B} - 2\frac{\partial W^{(1)}}{\partial I_2}\mathbf{B}^{-1}, \tag{1}$$

where $p^{(1)}$ arises from the constraint that deformations are isochoric, $I_1,\ \ I_2$ are invariants of $\mathbf{B}$, $W^{(1)}(I_1, I_2, T)$ is the Helmholtz free energy density associated with the original material and T is the temperature, and the notation $(-)^{(1)}$ denotes a quantity associated with the original material network.

No scission occurs for temperatures $T < T_{\text{cr}}$. All of the material is in its original state and the total stress is given by (1). For temperatures $T \geq T_{\text{cr}}$, scission of the original microstructural network is assumed to occur continuously in time. Let $b^{(1)}$ denote the volume fraction of the original network remaining at time t. $b^{(1)} = 1$ at $t = 0$, monotonically decreases with t when $T \geq T_{\text{cr}}$ and is constant when $T < T_{\text{cr}}$. Tobolsky's experiments indicated that $b^{(1)}$ does not depend on the uniaxial stretch provided that it is less than 3–4. This was supported by the experimental results of Scanlan and Watson [7] and Jones [3]. For the sake of simplicity and in consideration of these experimental results, it is assumed that $b^{(1)}$ depends only on the temperature history and time, i.e., $b^{(1)} = b^{(1)}[T(s)|_0^t, t]$.

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 crosslinks, a network is formed during the interval from $\hat{t}$ to $\hat{t} + d\hat{t}$ whose reference configuration is the configuration of the original material at time $\hat{t}$. As suggested by Tobolsky [1] and Tobolsky, Prettyman and Dillon [8], this is assumed to be an unstressed configuration for the newly formed network. During subsequent deformation, the configurations of the newly formed material network coincide with the configurations of the original material network. Stress arises in this newly formed material network due to its deformation relative to its unstressed configuration at time $\hat{t}$. At time $t > \hat{t}$, the material formed at time $\hat{t}$ has the relative deformation gradient $\hat{\mathbf{F}} = \partial\mathbf{x}/\partial\hat{\mathbf{x}}$, where $\hat{\mathbf{x}}$ is the position of the particle in the configuration corresponding to time $\hat{t}$ and $\mathbf{x}$ is its position at time t. For simplicity, the new network is also assumed to be mechanically incompressible at a fixed temperature, isotropic and nonlinearly elastic. Let the left Cauchy-Green tensor $\hat{\mathbf{B}} = \hat{\mathbf{F}}\hat{\mathbf{F}}^T$ be introduced for deformations of this network. The Cauchy stress $\sigma^{(2)}$ at time t in the network formed at time $\hat{t}$ is then given by

$$\boldsymbol{\sigma}^{(2)} = -p^{(2)}\mathbf{I} + 2\frac{\partial W^{(2)}}{\partial \hat{I}_1}\hat{\mathbf{B}} - 2\frac{\partial W^{(2)}}{\partial \hat{I}_2}\hat{\mathbf{B}}^{-1}, \tag{2}$$

where $p^{(2)}$ arises from the constraint that deformations are isochoric and $\hat{I}_1,\ \ \hat{I}_2$ are invariants of $\hat{\mathbf{B}}$. $W^{(2)}(\hat{I}_1,\ \hat{I}_2,\ T)$ is the Helmholtz free energy density associated with the newly formed network and can differ from that associated with the original material.

Let $a(\hat{t})$ be a scalar-valued function that gives the rate at which crosslink density of new network is formed at time $\hat{t}$. Thus, $a(\hat{t}) > 0$ and $a(\hat{t})\,d\hat{t}$ is interpreted as the amount of new network that is formed during the time interval from $\hat{t}$ to $\hat{t} + d\hat{t}$. Recent experimental results of Jones [3] indicate that the new network undergoes scission. Let $b^{(2)}(t, \hat{t})$ denote the volume fraction of the network formed at time $\hat{t}$ that is remaining at time t. The properties of $b^{(2)}$ are similar to those of $b^{(1)}$: $b^{(2)}(\hat{t}, \hat{t}) = 1$ and $b^{(2)}(t, \hat{t})$ decreases monotonically with t for fixed $\hat{t}$ when $T \geq T_{\text{cr}}$ and is unchanged when $T < T_{\text{cr}}$. It is assumed that $b^{(2)}(t, \hat{t})$ is independent of the deformation of the new network and depends on the temperature history from the time it has formed, i.e., $b^{(2)} = b^{(2)}[T(s)|_{\hat{t}}^t, t]$. The crosslink density at time t in the network that was formed in the interval from $\hat{t}$ to $\hat{t} + d\hat{t}$ is $a(\hat{t})b^{(2)}(t, \hat{t})\,d\hat{t}$.

The time-dependent functions $a(\hat{t}), b^{(1)}(t), b^{(2)}(t, \hat{t})$ describe the kinetics of scission and re-crosslinking for a particular rubber. They are assumed to be continuous functions of time whose mathematical properties are summarized as follows:

(i) $\quad b^{(1)}(0) = 1, b^{(2)}(\hat{t}, \hat{t}) = 1, a(0) = 0,$

(ii) $\quad$ When $T > T_{\text{cr}}$:

$$db^{(1)}/dt < 0, \quad a > 0, \quad \partial b^{(2)}(t,\hat{t})/\partial t < 0, \tag{3}$$

(iii) When $T < T_{\mathrm{cr}}$,

$$db^{(1)}/dt = 0, \quad a = 0, \quad \partial b^{(2)}(t,\hat{t})/\partial t = 0.$$

Specific forms for $a(\hat{t}), b^{(1)}(t), b^{(2)}(t,\hat{t})$ are not presented here because they are not required for the development of the results in the subsequent sections.

The total current stress in the macromolecular system is taken as the superposition of the stress in the remaining portion of the original network and the stresses in the networks that formed during the process of scission and crosslinking. Then, by (1) and (2),

$$\begin{aligned}\boldsymbol{\sigma}(t) = -p(t)\mathbf{I} + 2b^{(1)}(t)\left(\frac{\partial W^{(1)}}{\partial I_1}\mathbf{B}(t) - \frac{\partial W^{(1)}}{\partial I_2}\mathbf{B}(t)^{-1}\right)\\ +2\int_0^t a(\hat{t})b^{(2)}(t,\hat{t})\left(\frac{\partial W^{(2)}}{\partial \hat{I}_1}\hat{\mathbf{B}}(t,\hat{t}) - \frac{\partial W^{(2)}}{\partial \hat{I}_2}\hat{\mathbf{B}}(t,\hat{t})^{-1}\right)d\hat{t}\end{aligned} \tag{4}$$

The term $-p\mathbf{I}$ is an isotropic stress that combines contributions from $p^{(1)}$ and $p^{(2)}$.

3 Formulation of the boundary value problem

A solid circular cylinder of radius R_0 and length L_0 is composed of an elastomeric material that can be described by the constitutive equation presented in Sect. 2. In the first part of this study the cylinder is twisted while its length is maintained at L_0. Twisting moments and axial forces are applied to its end surfaces and the cylindrical surface is traction free.

Let (R, Θ, Z) and (r, θ, z) be the cylindrical coordinates of a material particle of the original network in the reference and current configurations, respectively. The motion of the original network is assumed to have the form

$$r = R, \quad \theta = \Theta + \psi(t)Z, \quad z = Z, \tag{5}$$

where $\psi(t)$ is the angle of twist per unit length at time t. Let $(r(\hat{t}), \theta(\hat{t}), z(\hat{t}))$ be the cylindrical coordinates of a material particle of the network formed at time $\hat{t}$ in its reference configuration. The motion of this network is given by

$$r = r(\hat{t}), \quad \theta = \theta(\hat{t}) + (\psi(t) - \psi(\hat{t}))z(\hat{t}), \quad z = z(\hat{t}). \tag{6}$$

The temperature on the cylindrical surface is uniform and is a prescribed function of time, $T(R_0, t) = \tilde{T}(t)$. The ends of the cylinder are insulated so only radial heat conduction exists. For the present purposes, it is not necessary to consider a specific law of heat conduction. It is sufficient to note that heat conduction results in a radial and time varying temperature $T(R, t)$. As a result, scission and crosslinking within the cylinder vary with radial position. The kinetics of scission and crosslinking are now denoted by the spatially dependent functions $a(R, \hat{t}), b^{(1)}(R, t), b^{(2)}(R, t, \hat{t})$.

It has been shown [9] that motion (5) is possible (controllable) in every material described by the constitutive equation (4) for any variation of the properties with R. That is, the equations of motion (neglecting inertia) are satisfied. The conditions defined here are thus very useful for a study of the interaction of scission and crosslinking processes with an inhomogeneous deformation that describes a common experimental configuration.

The components of the deformation gradient $\mathbf{F}$, with respect to orthonormal basis vectors oriented along a cylindrical coordinate system, are

$$\mathbf{F} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & R\psi(t) \\ 0 & 0 & 1 \end{bmatrix}, \tag{7}$$

from which are found

$$\mathbf{B}=\begin{bmatrix}1 & 0 & 0\\ 0 & 1+(R\psi(t))^2 & R\psi(t)\\ 0 & R\psi(t) & 1\end{bmatrix},\qquad \mathbf{B}^{-1}=\begin{bmatrix}1 & 0 & 0\\ 0 & 1 & -R\psi(t)\\ 0 & -R\psi(t) & 1+(R\psi(t))^2\end{bmatrix},\tag{8}$$

and the invariants

$$I_1=I_2=3+(R\psi(t))^2.\tag{9}$$

The deformation gradient $\hat{\mathbf{F}}$ is calculated using the definition

$$\hat{\mathbf{F}}=\frac{\partial\mathbf{x}(t)}{\partial\mathbf{x}(\hat{t})}=\frac{\partial\mathbf{x}(t)}{\partial\mathbf{X}}\left(\frac{\partial\mathbf{x}(\hat{t})}{\partial\mathbf{X}}\right)^{-1}.\tag{10}$$

$\hat{\mathbf{F}}$ has the same form as $\mathbf{F}$ in (7), but with $R\psi(t)$ replaced by $R(\psi(t)-\psi(\hat{t}))$. Hence, $\hat{\mathbf{B}}$, $\hat{\mathbf{B}}^{-1}$ and their invariants are given by (8) and (9), respectively, with $R\psi(t)$ replaced by $R(\psi(t)-\psi(\hat{t}))$.

The stresses are found to be $\sigma_{r\theta}=\sigma_{rz}=0$,

$$\begin{aligned}\sigma_{\theta z}(R,t)&=2b^{(1)}(R,t)\big[W_1^{(1)}+W_2^{(1)}\big]R\psi(t)\\ &\quad+2\int_0^t a(R,\hat{t})b^{(2)}(R,t,\hat{t})\big[W_1^{(2)}+W_2^{(2)}\big](R(\psi(t)-\psi(\hat{t})))d\hat{t},\end{aligned}\tag{11}$$

$$\sigma_{rr}=-p+F_{rr},\ F_{rr}(R,t)=2b^{(1)}(R,t)\big[W_1^{(1)}-W_2^{(1)}\big]+2\int_0^t a(R,\hat{t})b^{(2)}(R,t,\hat{t})\big[W_1^{(2)}-W_2^{(2)}\big]d\hat{t},\tag{12a}$$

$$\begin{aligned}\sigma_{\theta\theta}&=-p+F_{\theta\theta},\\ F_{\theta\theta}(R,t)&=2b^{(1)}(R,t)\big[W_1^{(1)}(1+(R\psi(t))^2)-W_2^{(1)}\big]\\ &\quad+2\int_0^t a(R,\hat{t})b^{(2)}(R,t,\hat{t})\big[W_1^{(2)}(1+(R(\psi(t)-\psi(\hat{t})))^2)-W_2^{(2)}\big]d\hat{t},\end{aligned}\tag{12b}$$

$$\begin{aligned}\sigma_{zz}&=-p+F_{zz},\\ F_{zz}(R,t)&=2b^{(1)}(R,t)\big[W_1^{(1)}-W_2^{(1)}(1+(R\psi(t))^2)\big]\\ &\quad+2\int_0^t a(R,\hat{t})b^{(2)}(R,t,\hat{t})\big[W_1^{(2)}-W_2^{(2)}(1+(R(\psi(t)-\psi(\hat{t})))^2)\big]d\hat{t},\end{aligned}\tag{12c}$$

where the notation $W_\alpha^{(1)}=\partial W^{(1)}/\partial I_\alpha$ and $W_\alpha^{(2)}=\partial W^{(2)}/\partial\hat{I}_\alpha$, $\alpha=1,2$ is now used. $W_1^{(1)}$, $W_2^{(1)}$ are evaluated at $I_1=I_2=3+(R\psi(t))^2$ and $W_1^{(2)}$, $W_2^{(2)}$ are evaluated at $\hat{I}_1=\hat{I}_2=3+(R(\psi(t)-\psi(\hat{t})))^2$.

The equilibrium equations imply that $p=p(R,t)$. An expression for $p(R,t)$ is obtained by substituting (12a) and (12b) into the radial equilibrium equation,

$$\frac{\partial\sigma_{rr}}{\partial R}+\frac{\sigma_{rr}-\sigma_{\theta\theta}}{R}=0,\quad 0\le R\le R_0,\tag{13}$$

integrating from R to R_0 and using the condition that the lateral surface of the cylinder be traction free,

$$-p(R,t)=-F_{rr}(R,t)+\int_R^{R_0}\frac{F_{rr}(\bar{R},t)-F_{\theta\theta}(\bar{R},t)}{\bar{R}}d\bar{R}.\tag{14}$$

Then

$$\sigma_{zz}(R,t)=F_{zz}(R,t)-F_{rr}(R,t)+\int_R^{R_0}\frac{F_{rr}(\bar{R},t)-F_{\theta\theta}(\bar{R},t)}{\bar{R}}d\bar{R}.\tag{15}$$

The resultant twisting moment is

$$M(t) = 2\pi \int_0^{R_0} \sigma_{z\theta}(R,t) R^2 dR. \tag{16}$$

The resultant axial force is

$$N(t) = 2\pi \int_0^{R_0} \sigma_{zz}(R,t) R dR. \tag{17}$$

Substituting (15) into (17) and integrating by parts gives

$$N(t) = 2\pi \int_0^{R_0} \left[(F_{zz}(R,t) - F_{rr}(R,t)) + \frac{1}{2}(F_{rr}(R,t) - F_{\theta\theta}(R,t)) \right] R dR. \tag{18}$$

From (12a,b,c),

$$F_{zz}(R,t) - F_{rr}(R,t) = -2b^{(1)}(R,t) W_2^{(1)}(R\psi(t))^2 - 2\int_0^t a(R,\hat{t}) b^{(2)}(R,t,\hat{t}) W_2^{(2)}(R(\psi(t) - \psi(\hat{t})))^2 d\hat{t}, \tag{19a}$$

$$F_{rr}(R,t) - F_{\theta\theta}(R,t) = -2b^{(1)}(R,t) W_1^{(1)}(R\psi(t))^2 - 2\int_0^t a(R,\hat{t}) b^{(2)}(R,t,\hat{t}) W_1^{(2)}(R(\psi(t) - \psi(\hat{t})))^2 d\hat{t}. \tag{19b}$$

It is usually assumed that $W_\alpha^{(\beta)} > 0$. It is seen from (19a, b) that $F_{zz}(R,t) - F_{rr}(R,t) < 0$ and $F_{rr}(R,t) - F_{\theta\theta}(R,t) < 0$ and from (18) that $N < 0$, i.e., a compressive axial force is required for all twisting and thermal processes.

4 Response during scission and crosslinking

The cylinder is initially untwisted and at a uniform temperature $T_0 < T_{\text{cr}}$, i.e. $\psi(t) = 0$ and $T(R,t) = T_\text{o} < T_{\text{cr}}$, $0 \le R \le R_\text{o}$, $t < 0$. The twist and surface temperature histories for $t \ge 0$, shown in Fig. 1, are:

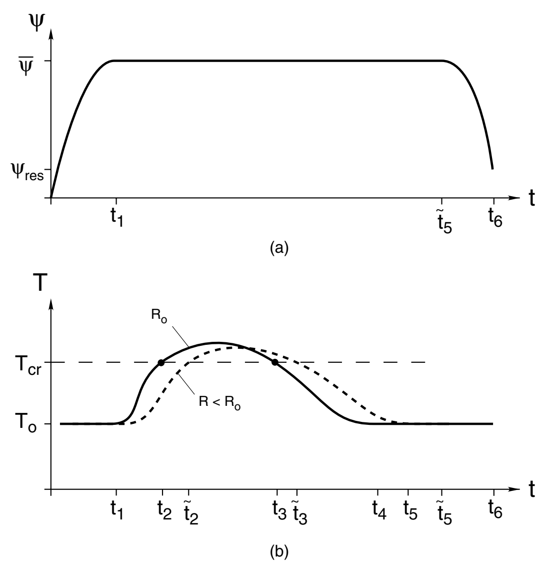

Fig. 1 **a** Prescribed twist history. **b** Temperature history

Surface temperature $0 \le t \le t_1$, $T(R_0, t) = T_0$,
$t_1 \le t < t_2$, $T(R_0, t)$ increases, $T(R_0, t_2) = T_{\text{cr}}$,
$t_2 \le t < t_3$, $T(R_0, t) > T_{\text{cr}}$, $T(R_0, t_3) = T_{\text{cr}}$,
$t_3 \le t < t_4$, $T(R_0, t)$ decreases, $T(R_0, t_4) = T_0$
$t_4 \le t$, $T(R_0, t) = T_0$.
Twist $0 \le t \le t_1$, $\psi(t)$ increases, $\psi(t_1) \equiv \bar{\psi}$
$t_1 \le t \le \tilde{t}_5$, $\psi(t) = \bar{\psi}$
$\tilde{t}_5 \le t$, $\psi(t)$ arbitrary

The actual determination of the conduction of heat into the interior of the cylinder would require a heat conduction law and it could depend on temperature, deformation and scission and crosslinking. For present purposes, these issues need not be considered. It is sufficient to assume only that heat conduction into the cylinder occurs and that it is radial. The interior temperature at $R < R_0$ can be expected to vary as shown in Fig. 1. It starts to increase at a time $\tilde{t}_1 > t_1$ and exceeds T_{cr} at a time $\tilde{t}_2 > t_2$. It may reach the maximum surface temperature if the surface temperature is held fixed for a sufficiently long time. The temperature at R begins to decrease after the surface temperature does, decreases below T_{cr} at a time $\tilde{t}_3 > t_3$ and returns to T_0 at a time $\tilde{t}_4 > t_4$. It is assumed that there is a sufficiently large time $t_5 > t_4$ such that when $t > t_5$ the cylinder is again at an essentially uniform temperature, i.e., $T(R, t) = T_0 < T_{\text{cr}}$, $0 \le R \le R_0$.

The cylinder is maintained at a fixed twist $\bar{\psi}$ until the cylinder is again at a uniform temperature. The twist is allowed to vary after a time $\tilde{t}_5 \ge t_5$. The remainder of this section is concerned with the cylinder preceding and during scission at a fixed $\bar{\psi}$, $0 \le t < t_3$. The post-scission response to arbitrary twists, $\tilde{t}_5 \le t$, is given in the next section.

Consider the initial time interval $0 \le t \le t_1$. Since the surface temperature is T_0, there is no conduction of heat into the interior of the cylinder and $T(R, t) = T_0$, $0 \le R \le R_0$. Then, $b^{(1)}(R, t) = 1$ and $a(R, t) = 0$, $0 \le R \le R_0$. By (11) and (16)

$$M(t) = 4\pi \int_0^{R_0} \left[W_1^{(1)} + W_2^{(1)}\right] R^3 \psi(t) dR \tag{20a}$$

and by (18) and (19a, b)

$$N(t) = -4\pi \int_0^{R_0} \left[\frac{1}{2} W_1^{(1)} + W_2^{(1)}\right] R^3 \psi^2(t) dR, \tag{20b}$$

where $W_\alpha^{(1)} = W_\alpha^{(1)}(3 + (R\psi(t))^2, 3 + (R\psi(t))^2, T_0)$, $\alpha = 1, 2$. These are the well-known torque-twist and axial force-twist relations for an isotropic nonlinear elastic cylinder. The twisting moment and axial force vary with time due to the twist $\psi(t)$.

Consider the next time interval $t_1 \le t < t_2$. The surface temperature increases and there is heat conduction into the cylinder, yet the temperature throughout is below the chemorheological temperature, $T_0 \le T(R, t) \le T_{\text{cr}}$, $0 \le R \le R_0$. Since $b^{(1)}(R, t) = 1$, $a(R, t) = 0$, $0 \le R \le R_0$ and $\psi(t) = \bar{\psi}$, (11) and (16) give

$$M(t) = 4\pi \int_0^{R_0} \left[W_1^{(1)} + W_2^{(1)}\right] R^3 \bar{\psi} dR \tag{21a}$$

and (18) and (19a, b) give

$$N(t) = -4\pi \int_0^{R_0} \left[\frac{1}{2} W_1^{(1)} + W_2^{(1)}\right] R^3 \bar{\psi}^2 dR, \tag{21b}$$

where now $W_\alpha^{(1)} = W_\alpha^{(1)}(3 + (R\bar{\psi})^2, 3 + (R\bar{\psi})^2, T(R, t))$, $\alpha = 1, 2$. The twisting moment and axial force vary with time due to the dependence of $W_\alpha^{(1)}$ on the temperature.

Consider the third time interval $t_2 \le t < t_3$. Now $T(R_0, t) \ge T_{\text{cr}}$, and owing to heat conduction, $T(R, t) \ge T_{\text{cr}}$ for some set of radii and times. It follows that $b^{(1)}(R, t)$ decreases with time at these radii. Since $a(R, \hat{t}) = 0$ for $0 \le \hat{t} \le t_1$ and $\psi(t) - \psi(\hat{t}) = 0$ for $t_1 \le \hat{t} \le t$, the integrals in (11) and (19a,

b) vanish. In effect, the new networks are formed in a stress free state and are not sheared. Thus, by (11) and (16)

$$M(t) = 4\pi \int_0^{R_0} b^{(1)}(R,t)\big[W_1^{(1)} + W_2^{(1)}\big] R^3 \bar{\psi}\, dR, \tag{22a}$$

and by (18) and (19a,b)

$$N(t) = -4\pi \int_0^{R_0} b^{(1)}(R,t)\left[\frac{1}{2}W_1^{(1)} + W_2^{(1)}\right] R^3 \bar{\psi}^2 dR, \tag{22b}$$

where $W_\alpha^{(1)} = W_\alpha^{(1)}(3 + (R\bar{\psi})^2, 3 + (R\bar{\psi})^2, T(R,t))$, $\alpha = 1, 2$. The twisting moment and axial force vary with time due to the decrease of $b^{(1)}(R,t)$ with time on some set of radii and the dependence of $W_\alpha^{(1)}$ on the temperature.

For many models of rubber elasticity proposed in the literature, the response is assumed to be entropic, i.e., $W^{(1)}(I_1, I_2, T) = n_0 k T W^0(I_1, I_2)$, where n_0 is the initial crosslink density, k is the Boltzmann constant and $W^0(I_1, I_2)$ depends on the particular model under consideration. The twisting moment and axial force in the initial time interval $0 \le t \le t_1$, given by (20a, b), become

$$M(t) = 4\pi n_0 k T_0 \int_0^{R_0} \big[W_1^0 + W_2^0\big] R^3 \psi\, dR, \tag{23a}$$

and

$$N(t) = -4\pi n_0 k T_0 \int_0^{R_0} \left[\frac{1}{2}W_1^0 + W_2^0\right] R^3 \psi^2 dR, \tag{23b}$$

where $W_\alpha^0 = \partial W^0/\partial I_\alpha$ and $W_\alpha^0 = W_\alpha^0(3 + (R\psi)^2, 3 + (R\psi)^2)$, $\alpha = 1, 2$. Note that M/N is independent of T_0.

The twisting moment and axial force in the second time interval $t_1 \le t < t_2$, given by (21a, b) become

$$M(t) = 4\pi n_0 k \int_0^{R_0} \big[W_1^0 + W_2^0\big] T(R,t) R^3 \bar{\psi}\, dR \tag{24a}$$

and

$$N(t) = -4\pi n_0 k \int_0^{R_0} \left[\frac{1}{2}W_1^0 + W_2^0\right] T(R,t) R^3 \bar{\psi}^2 dR \tag{24b}$$

Although the twist is fixed, the twisting moment and axial force increase as the temperature increases due to entropic stiffening at each radius.

The twisting moment and axial force in the third time interval $t_2 \le t < t_3$, given by (22a, b) become

$$M(t) = 4\pi n_0 k \int_0^{R_0} b^{(1)}(R,t) T(R,t) \big[W_1^0 + W_2^0\big] R^3 \bar{\psi}\, dR, \tag{25a}$$

and

$$N(t) = -4\pi n_0 k \int_0^{R_0} b^{(1)}(R,t) T(R,t) \left[\frac{1}{2}W_1^0 + W_2^0\right] R^3 \bar{\psi}^2 dR. \tag{25b}$$

Although the temperature may increase at some radii causing entropic stiffening, when $T(R,t) > T_{\mathrm{cr}}$ there may be a rapid decrease in $b^{(1)}(R,t)$ due to scission. The net effect is that the twisting moment and axial force can be expected to increase and then decrease. This effect is similar to that observed in experiments on rubber strips in fixed uniaxial extension (see Jones [3] and Shaw, Jones and Wineman [4]). The force required to hold the strip increases with temperature due to entropic stiffening and then, while $T > T_{\mathrm{cr}}$, decreases due to scission.

The remainder of this section is concerned with the third time interval $t_2 \le t < t_3$, when scission and crosslinking occur. Several results about the relation between $M(t)$ and $N(t)$ can be deduced from (22a, b) and (25a, b).

(1) When $W_1^{(1)} \neq 0$ and $W_2^{(1)} \neq 0$ and they depend on both invariants, there is no apparent relation between the time variations of $M(t)$ and $N(t)$.

(2) When $W^{(1)}$ depends only on I_1 and T, $W_2^{(1)} = 0$, (as in the case of the neo-Hookean, Arruda-Boyce [10], Gent [11] and general average-stretch full-network model discussed by Beatty [12]), $M(t)$ and $N(t)$ are related by

$$\frac{N(t)}{M(t)} = -\frac{\bar{\psi}}{2}. \tag{26}$$

Thus, $N(t)/M(t)$ is independent of time, i.e., the time variations of $M(t)$ and $N(t)$ differ by a scale factor that depends only on the twist. A plot of $N(t)/M(t)$ vs. $\bar{\psi}$ would be a straight line with a slope of -0.5. Relation (26) is independent of the particular dependence of $W^{(1)}$ on I_1 and T and is an extension of a universal relation discovered by Horgan and Saccomandi [13] for generalized neo-Hookean materials and later discussed by Wineman [14].

(3) When the network materials are of Mooney-Rivlin type, i.e., $W_\alpha^{(1)} = TC_\alpha^{(1)}$, $\alpha = 1, 2$, where $C_\alpha^{(1)}$ are constant. the time variations of $M(t)$ and $N(t)$ again differ by a scale factor

$$\frac{N(t)}{M(t)} = -\frac{\bar{\psi}}{2}\frac{C_1^{(1)} + 2C_2^{(1)}}{C_1^{(1)} + C_2^{(1)}}, \tag{27}$$

$N(t)/M(t)$ is independent of time, but the plot of $N(t)/M(t)$ vs. $\bar{\psi}$ would be a straight line with a slope of that depends on the material properties.

(4) When the material response is entropic and the characteristic time for heat conduction is small compared to the characteristic time for scission processes, the temperature is approximately uniform, that is, $T(R,t) \approx T(R_0,t)$, and $b^{(1)}(R,t) \approx b^{(1)}(R_0,t)$, $R \leq R_0$. In this case, (22a, b) give

$$M(t) = b^{(1)}(R_0,t)T(R_0,t)4\pi n_0 k \int_0^{R_0} \left[W_1^0 + W_2^0\right] R^3 \bar{\psi}\, dR, \tag{28a}$$

$$N(t) = -b^{(1)}(R_0,t)T(R_0,t)4\pi n_0 k \int_0^{R_0} \left[\frac{1}{2}W_1^0 + W_2^0\right] R^3 \bar{\psi}^2 dR. \tag{28b}$$

Once again, $N(t)/M(t)$ is independent of time, but the plot of $N(t)/M(t)$ vs. $\bar{\psi}$ need not be a straight line.

5 Modified elastic response: post-scission twist

Consider times $t > t_5$ after scission has stopped throughout the cylinder. During scission, new networks were formed at each radius, but were not sheared and did not contribute to the axial force or the twisting moment. There are now two networks at each radius, the remaining portion of the original network and the newly formed network. Each responds elastically on further loading. This section presents the post-scission elastic response for $t > \tilde{t}_5$ when the cylinder is subjected to an arbitrary twist ψ while being kept at its initial length L_0, thereby causing each network to undergo simple shear.

Since for $t_1 \leq \hat{t} \leq t_5$, $\psi(\hat{t}) = \bar{\psi}$, and for $t > t_5$, $b^{(1)}(R,t) = b^{(1)}(R,t_5)$, $a(R,t) = 0$, and $b^{(2)}(R,t,\hat{t}) = b^{(2)}(R,t_5,\hat{t})$, $0 \leq R \leq R_0$, (11), (19a, b) can be written as

$$\sigma_{\theta z}(R,t) = 2n_1(R)\left[W_1^{(1)} + W_2^{(1)}\right]R\psi + 2n_2(R)\left[W_1^{(2)} + W_2^{(2)}\right]R(\psi - \bar{\psi}), \tag{29}$$

$$F_{zz}(R,t) - F_{rr}(R,t) = -2n_1(R)W_2^{(1)}R^2\psi^2 - 2n_2(R)W_2^{(2)}R^2(\psi - \bar{\psi})^2, \tag{30a}$$

$$F_{rr}(R,t) - F_{\theta\theta}(R,t) = -2n_1(R)W_1^{(1)}R^2\psi^2 - 2n_2(R)W_1^{(2)}R^2(\psi - \bar{\psi})^2. \tag{30b}$$

where

$$n_1(R) = b^{(1)}(R, t_5) \tag{31a}$$

$$n_2(R) = \int_0^{t_5} a(R, \hat{t}) b^{(2)}(R, t_5, \hat{t}) d\hat{t}. \tag{31b}$$

$n_1(R)$ and $n_2(R)$ represent the influence of the radially dependent scission kinetics within the cylinder. Equations (29) and (30a, b), being independent of time and varying with ψ, represent the post-scission elastic response.

By use of (16) and (29), the torque-twist relation is found to be

$$M = 4\pi \int_0^{R_0} \left\{ n_1(R)\left[W_1^{(1)} + W_2^{(1)}\right]\psi + n_2(R)\left[W_1^{(2)} + W_2^{(2)}\right](\psi - \bar{\psi}) \right\} R^3 dR. \tag{32}$$

By use of (18) and (30a, b), the axial force is given by

$$N = -4\pi \int_0^{R_0} \left\{ n_1(R)\left(\frac{1}{2}W_1^{(1)} + W_2^{(1)}\right)\psi^2 + n_2(R)\left(\frac{1}{2}W_1^{(2)} + W_2^{(2)}\right)(\psi - \bar{\psi})^2 \right\} R^3 dR. \tag{33}$$

Intuition suggests that the pre-scission and post-scission torque-twist relations will be different. It is also suggests that the cylinder will have a permanent twist if the torque is removed. In principle, these phenomena could be illustrated for any choices of the hyperelastic models $W^{(1)}$ and $W^{(2)}$ for the individual networks, and in general, this would require the use of numerical examples. Alternatively, we assume that each network acts as a Mooney-Rivlin material, i.e., $W_\beta^{(\alpha)} = C_\beta^{(\alpha)}$ are non-negative constants, in order to capture the same phenomena qualitatively without excessive complexity. Let the following notation be introduced

$$N_1 = \int_0^{R_0} b^{(1)}(R, t) R^3 dR, \tag{34a}$$

$$N_2 = \int_0^{R_0} R^3 \int_0^{t_5} a(R, \hat{t}) b^{(2)}(R, t_5, \hat{t}) d\hat{t} dR. \tag{34b}$$

Then

$$\frac{M}{4\pi} = \left(C_1^{(1)} + C_2^{(1)}\right) N_1 \psi + \left(C_1^{(2)} + C_2^{(2)}\right) N_2 (\psi - \bar{\psi}) \tag{35}$$

and

$$\frac{N}{4\pi} = -\left(\frac{1}{2}C_1^{(1)} + C_2^{(1)}\right) N_1 \psi^2 - \left(\frac{1}{2}C_1^{(2)} + C_2^{(2)}\right) N_2 (\psi - \bar{\psi})^2. \tag{36}$$

When $M = 0$, there is a residual twist ψ_{res} given by

$$\psi_{\text{res}} = \frac{\left(C_1^{(2)} + C_2^{(2)}\right) N_2}{\left(C_1^{(1)} + C_2^{(1)}\right) N_1 + \left(C_1^{(2)} + C_2^{(2)}\right) N_2} \bar{\psi}. \tag{37}$$

Now letting $\psi = \Delta\psi + \psi_{\text{res}}$, (35) reduces to the $M - \Delta\psi$ relation

$$M = 4\pi \left\{ \left(C_1^{(1)} + C_2^{(1)}\right) N_1 + \left(C_1^{(2)} + C_2^{(2)}\right) N_2 \right\} \Delta\psi. \tag{38}$$

This relation is linear in $\Delta\psi$ and independent of the twist $\bar{\psi}$ imposed on the cylinder during scission. An expression can be derived for the axial force at ψ_{res}, but it is lengthy and therefore omitted. It can be seen from (36) and (37) that the axial force at ψ_{res} is compressive and proportional to $\bar{\psi}^2$.

Figure 2 shows the torque-twist response when the networks act as Mooney-Rivlin materials. Figure 3 shows the corresponding axial force-twist response. Note that the axial force need not be zero when the torque is zero:

OA - the pre-scission response given by (23a, b) during time interval $0 \le t \le t_1$,

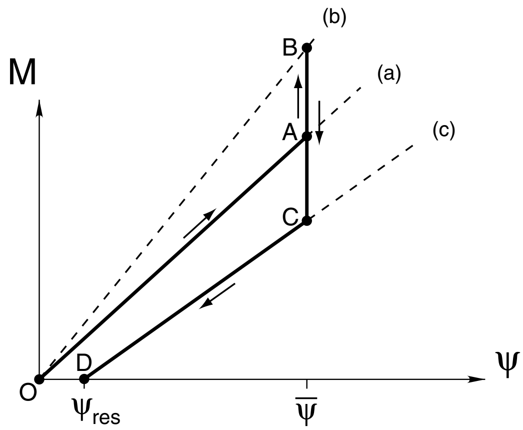

Fig. 2 Moment-twist response proceeding in sequence from points O, A($t = t_1$), B, C($t = \tilde{t}_3$), and D: **a** Initial elastic curve for $T(R, t) = T_0$. **b** Elevated temperature elastic curve for $T_0 < T(R, t) < T_{cr}$ (no scission). **c** Elastic curve after scission and $T(R, t) = T_0$, showing reduced stiffness and permanent set

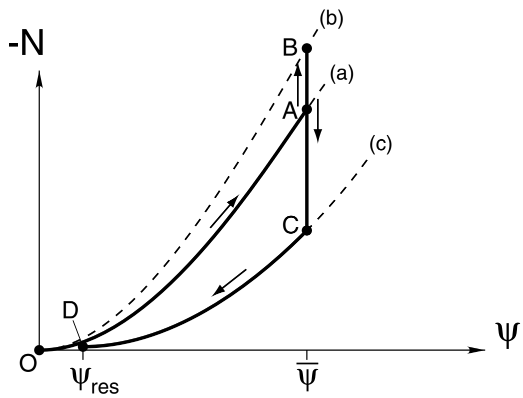

Fig. 3 Compressive normal force response corresponding to Fig. 2

AB - the increase in $M(t)$ and $|N(t)|$ at constant twist $\bar{\psi}$ due to entropic stiffening at each radius. These are given by (24a,b) during time interval $t_1 \le t \le t_2$ and by (25a, b) during time interval $t_2 \le t \le t_3$.
BC - the decrease of $M(t)$ and $|N(t)|$ at constant twist $\bar{\psi}$ due to scission. These are given by (25a, b) during time interval $t_2 \le t \le \tilde{t}_3$.
CD - the post-scission response given by (36) and (38) for times $t > t_5$.
D - the residual twist ψ_{res} given by (37).

There is a residual shear stress distribution when $M = 0$ that is obtained by substituting (37) into (29),

$$\sigma_{\theta z,\mathrm{res}} = 2\left\{ \frac{\left(C_1^{(1)} + C_2^{(1)}\right)n_1(R) + \left(C_1^{(2)} + C_2^{(2)}\right)n_2(R)}{\left(C_1^{(1)} + C_2^{(1)}\right)N_1 + \left(C_1^{(2)} + C_2^{(2)}\right)N_2} - \frac{n_2(R)}{N_2} \right\}\left(C_1^{(2)} + C_2^{(2)}\right)N_2 R\bar{\psi}. \qquad (39)$$

Suppose the networks are of Mooney-Rivlin type, but $\psi(t)$ varies during $t_2 \le t \le \tilde{t}_3$. An expression for ψ_{res} and an $M - \Delta\psi$ relation that are analogous to (37) and (38) could be obtained, but these are omitted for the sake of brevity of presentation. Suppose $W_\beta^{(\alpha)}$ depend on the strain invariants. Then ψ_{res} must be determined numerically in general. The $M - \Delta\psi$ relation will depend on $\psi(t)$ during $t_2 \le t \le \tilde{t}_3$ and will be nonlinear in $\Delta\psi$. Since each network could be sheared about a nonzero shear state, the resultant $M - \Delta\psi$ relation need not be an odd function of $\Delta\psi$.

6 Modified elastic response: post-scission twist and stretch

Section 5 treated the post-scission elastic twist of a cylinder that was kept at its initial length with an appropriate axial force being applied to maintain this condition. Now, consider the more general post-scission elastic response in which there is both stretch and twist.

The current configuration is assumed to be a cylinder with length $\tilde{L}$ and radius $\tilde{r}_0$.

The coordinates of a particle of the original network in the current configuration are denoted by $(\tilde{r}, \tilde{\theta}, \tilde{z})$. These are related to its coordinates in the reference configuration by

$$\tilde{r} = \frac{1}{\sqrt{\mu}} R, \qquad \tilde{\theta} = \Theta + \tilde{\phi} Z, \qquad \tilde{z} = \mu Z, \tag{40}$$

in which $\mu = \tilde{L} \big/ L_0$ is the axial stretch ratio and $\tilde{\phi}$ is the twist per unit initial length. By the assumption of incompressibility, $\tilde{r}_0 \big/ R_0 = 1 \big/ \sqrt{\mu}$.

The deformation gradient and its inverse associated with the remaining portion of the original network are

$$\mathbf{F} = \begin{bmatrix} 1/\sqrt{\mu} & 0 & 0 \\ 0 & 1/\sqrt{\mu} & \tilde{r}\tilde{\phi} \\ 0 & 0 & \mu \end{bmatrix}, \qquad \mathbf{F}^{-1} = \begin{bmatrix} \sqrt{\mu} & 0 & 0 \\ 0 & \sqrt{\mu} & -\tilde{r}\tilde{\phi}/\sqrt{\mu} \\ 0 & 0 & 1/\mu \end{bmatrix}. \tag{41}$$

The corresponding left Cauchy-Green tensor and its inverse are

$$\mathbf{B} = \begin{bmatrix} 1/\mu & 0 & 0 \\ 0 & 1/\mu + \left(\tilde{r}\tilde{\phi}\right)^2 & \mu\tilde{r}\tilde{\phi} \\ 0 & \mu\tilde{r}\tilde{\phi} & \mu^2 \end{bmatrix}, \qquad \mathbf{B}^{-1} = \begin{bmatrix} \mu & 0 & 0 \\ 0 & \mu & -\tilde{r}\tilde{\phi} \\ 0 & -\tilde{r}\tilde{\phi} & 1/\mu^2 + (\tilde{r}\tilde{\phi})^2/\mu \end{bmatrix}. \tag{42}$$

The deformation gradient associated with the network formed at $\hat{t}$ is determined using (10). The left factor in (10), $\partial\mathbf{x}(t) \big/ \partial\mathbf{X} = \partial\tilde{\mathbf{x}} \big/ \partial\mathbf{X}$, is given by (41). The right factor, $[\partial\mathbf{x}(\hat{t}) \big/ \partial\mathbf{X}]^{-1}$ is determined from (7) and the fact that $\psi(\hat{t}) = \bar{\psi}$ during scission. Then

$$\hat{\mathbf{F}} = \begin{bmatrix} 1/\sqrt{\mu} & 0 & 0 \\ 0 & 1/\sqrt{\mu} & \tilde{r}(\tilde{\phi} - \bar{\psi}) \\ 0 & 0 & \mu \end{bmatrix}, \qquad \hat{\mathbf{F}}^{-1} = \begin{bmatrix} \sqrt{\mu} & 0 & 0 \\ 0 & \sqrt{\mu} & -\tilde{r}(\tilde{\phi} - \bar{\psi})/\sqrt{\mu} \\ 0 & 0 & 1/\mu \end{bmatrix}. \tag{43}$$

The corresponding left Cauchy-Green tensor and its inverse are

$$\hat{\mathbf{B}} = \begin{bmatrix} 1/\mu & 0 & 0 \\ 0 & 1/\mu + \tilde{r}^2(\tilde{\phi} - \bar{\psi})^2 & \mu\tilde{r}(\tilde{\phi} - \bar{\psi}) \\ 0 & \mu\tilde{r}(\tilde{\phi} - \bar{\psi}) & \mu^2 \end{bmatrix} \tag{44a}$$

and

$$\hat{\mathbf{B}}^{-1} = \begin{bmatrix} \mu & 0 & 0 \\ 0 & \mu & -\tilde{r}(\tilde{\phi} - \bar{\psi}) \\ 0 & -\tilde{r}(\tilde{\phi} - \bar{\psi}) & 1/\mu^2 + \tilde{r}^2(\tilde{\phi} - \bar{\psi})^2/\mu \end{bmatrix}. \tag{44b}$$

Since $\hat{\mathbf{B}}$ and $\hat{\mathbf{B}}^{-1}$ are independent of $\hat{t}$ for $t_1 \le \hat{t} \le t_5$, and $b^{(1)}(R, t) = b^{(1)}(R, t_5)$, $a(R, t) = 0$, $b^{(2)}(R, t, \hat{t}) = b^{(2)}(R, t_5, \hat{t})$ for $t_5 < t$, the constitutive equation (4) reduces to

$$\sigma = -p\mathbf{I} + 2n_1(R)\big(W_1^{(1)}\mathbf{B} - W_2^{(1)}\mathbf{B}^{-1}\big) + 2n_2(R)\big(W_1^{(2)}\hat{\mathbf{B}} - W_2^{(2)}\hat{\mathbf{B}}^{-1}\big), \tag{45}$$

where $n_1(R)$ and $n_2(R)$ were defined in (31a, b).

Using (42) and (44a, b) in (45) gives the shear stress

$$\sigma_{\theta z} = 2n_1(R)\big(\mu W_1^{(1)} + W_2^{(1)}\big)\tilde{r}\tilde{\phi} + 2n_2(R)\big(\mu W_1^{(2)} + W_2^{(2)}\big)\tilde{r}(\tilde{\phi} - \bar{\psi}), \tag{46}$$

and the normal stresses

$$\begin{aligned}\sigma_{rr} &= -p + F_{rr}\\ F_{rr}(R,t) &= 2n_1(R)\left[\frac{1}{\mu}W_1^{(1)} - \mu W_2^{(1)}\right] + 2n_2(R)\left[\frac{1}{\mu}W_1^{(2)} - \mu W_2^{(2)}\right],\end{aligned} \tag{47a}$$

$$\begin{aligned}\sigma_{\theta\theta} &= -p + F_{\theta\theta}\\ F_{\theta\theta}(R,t) &= 2n_1(R)\left[W_1^{(1)}\left(\frac{1}{\mu} + (\tilde{r}\tilde{\phi})^2\right) - \mu W_2^{(1)}\right]\\ &\quad +2n_2(R)\left[W_1^{(2)}\left(\frac{1}{\mu} + \tilde{r}^2(\tilde{\phi} - \bar{\psi})^2\right) - \mu W_2^{(2)}\right]\end{aligned} \tag{47b}$$

$$\begin{aligned}\sigma_{zz} &= -p + F_{zz}\\ F_{zz}(R,t) &= 2n_1(R)\left[\mu^2 W_1^{(1)} - W_2^{(1)}\left(\frac{1}{\mu^2} + \frac{(\tilde{r}\tilde{\phi})^2}{\mu}\right)\right]\\ &\quad +2n_2(R)\left[\mu^2 W_1^{(2)} - W_2^{(2)}\left(\frac{1}{\mu^2} + \frac{\tilde{r}^2(\tilde{\phi} - \bar{\psi})^2}{\mu}\right)\right],\end{aligned} \tag{47c}$$

The equilibrium equations imply $p = \tilde{p}(\tilde{r}, t)$ and

$$\frac{\partial \sigma_{rr}}{\partial \tilde{r}} + \frac{\sigma_{rr} - \sigma_{\theta\theta}}{\tilde{r}} = 0, \quad 0 \le \tilde{r} \le \tilde{r}_0. \tag{48}$$

Since $\tilde{r} = R/\sqrt{\mu}$, $p = \tilde{p}(\tilde{r}, t) = p(R, t)$. Let (48) be transformed to the reference configuration. Using (40) and the condition that the cylindrical surface is traction free, it is again found that p is given by (14) and hence σ_{zz} is given by (15).

The resultant axial force is

$$N = 2\pi \int_0^{\tilde{r}_0} \sigma_{zz}\tilde{r}\,d\tilde{r}. \tag{49}$$

and, on transforming to the reference configuration, becomes

$$N = \frac{2\pi}{\mu}\int_0^{R_0} \sigma_{zz} R\,dR. \tag{50}$$

When σ_{zz} from (15) is substituted into the integral in (50), the latter reduces to the same integral as in (18). Next, let expressions for $F_{zz} - F_{rr}$ and $F_{rr} - F_{\theta\theta}$ be calculated from (47a, b, c), let $\tilde{r} = R/\sqrt{\mu}$ and substitute the results into (18). Then

$$\begin{aligned}\frac{N}{(2\pi/\mu)} &= \left(\mu^2 - \frac{1}{\mu}\right)\int_0^{R_0}\left[2n_1(R)\left(W_1^{(1)} + \frac{1}{\mu}W_2^{(1)}\right) + 2n_2(R)\left[\left(W_1^{(2)} + \frac{1}{\mu}W_2^{(2)}\right)\right]\right]R\,dR\\ &\quad - \int_0^{R_0}\left[2n_1(R)\left(\frac{1}{\mu}W_2^{(1)} + \frac{1}{2}W_1^{(1)}\right)\tilde{\phi}^2 + 2n_2(R)\left(\frac{1}{\mu}W_2^{(2)} + \frac{1}{2}W_1^{(2)}\right)(\tilde{\phi} - \bar{\psi})^2\right]\frac{R^3}{\mu}dR\end{aligned} \tag{51}$$

The resultant twisting moment is

$$M = 2\pi \int_0^{\tilde{r}_0} \sigma_{z\theta}\tilde{r}^2 d\tilde{r} \tag{52}$$

which transforms to

$$M = \frac{2\pi}{\mu\sqrt{\mu}}\int_0^{R_0} \sigma_{z\theta} R^2 dR. \tag{53}$$

By (46)

$$M = \frac{4\pi}{\mu^2} \int_0^{R_0} \left[n_1(R) \left(\mu W_1^{(1)} + W_2^{(1)} \right) \tilde{\phi} + n_2(R) \left(\mu W_1^{(2)} + W_2^{(2)} \right) (\tilde{\phi} - \bar{\psi}) \right] R^3 dR \tag{54}$$

Suppose that $W_\beta^{(\alpha)} = C_\beta^{(\alpha)}$ are constants. (54) reduces to

$$M = \frac{4\pi}{\mu^2} \left\{ \left(\mu C_1^{(1)} + C_2^{(1)} \right) \tilde{\phi} \int_0^{R_0} n_1(R) R^3 dR + \left(\mu C_1^{(2)} + C_2^{(2)} \right) (\tilde{\phi} - \bar{\psi}) \int_0^{R_0} n_2(R) R^3 dR \right\} \tag{55}$$

By (34a,b), this can be rewritten as

$$M = \frac{4\pi}{\mu^2} \left\{ \left[\left(\mu C_1^{(1)} + C_2^{(1)} \right) N_1 + \left(\mu C_1^{(2)} + C_2^{(2)} \right) N_2 \right] \tilde{\phi} - \left(\mu C_1^{(2)} + C_2^{(2)} \right) N_2 \bar{\psi} \right\}. \tag{56}$$

In a similar manner, the expression for the axial force in (51) reduces to

$$\frac{N}{(4\pi/\mu)} = \left(\mu^2 - \frac{1}{\mu} \right) \left\{ \left(C_1^{(1)} + \frac{1}{\mu} C_2^{(1)} \right) \int_0^{R_0} n_1(R) R dR + \left(C_1^{(2)} + \frac{1}{\mu} C_2^{(2)} \right) \int_0^{R_0} n_2(R) R dR \right\}$$
$$- \left(\frac{1}{\mu} C_2^{(1)} + \frac{1}{2} C_1^{(1)} \right) \frac{N_1}{\mu} \tilde{\phi}^2 - \left(\frac{1}{\mu} C_2^{(2)} + \frac{1}{2} C_1^{(2)} \right) \frac{N_2}{\mu} (\tilde{\phi} - \bar{\psi})^2 \tag{57}$$

Equations (56) and (57) express M and N in terms of $\tilde{\phi}$ and μ. Two equations for the residual twist $\tilde{\phi}_{\mathrm{res}}$ and the residual stretch μ_{res} are obtained by letting $M = N = 0$. An expression for the twist at $M = 0$ and at any stretch is found from (56)

$$\tilde{\phi}_{M=0} = \frac{\left(\mu C_1^{(2)} + C_2^{(2)} \right) N_2}{\left(\mu C_1^{(1)} + C_2^{(1)} \right) N_1 + \left(\mu C_1^{(2)} + C_2^{(2)} \right) N_2} \bar{\psi}. \tag{58}$$

Substituting (58) into (57) and setting $N = 0$ gives a nonlinear equation for the residual stretch μ_{res}. $\tilde{\phi}_{\mathrm{res}}$ and μ_{res} are related by

$$\tilde{\phi}_{\mathrm{res}} = \frac{\left(\mu_{\mathrm{res}} C_1^{(2)} + C_2^{(2)} \right) N_2}{\left(\mu_{\mathrm{res}} C_1^{(1)} + C_2^{(1)} \right) N_1 + \left(\mu_{\mathrm{res}} C_1^{(2)} + C_2^{(2)} \right) N_2} \bar{\psi}. \tag{59}$$

A number of comments can now be made.

(1) (37) is a special case of (58) when $\mu = 1$. A comparison of (58) and (59) shows that the residual twist when $M = 0$ and $N \neq 0$ differs, in general, from that when $M = N = 0$. In any case, the residual twist is less than $\bar{\psi}$.

(2) If $C_\beta^{(1)} = C_\beta^{(2)}$, $\tilde{\phi}$ becomes independent of μ when $M = 0$,

$$\tilde{\phi}_{\mathrm{res}} = \frac{N_2}{N_1 + N_2} \bar{\psi}. \tag{60}$$

(3) Let $\tilde{\phi} = \Delta\tilde{\phi} + \tilde{\phi}_{M=0}$ in (56) and make use of (58). Then (56) reduces to a linear torque-twist relation,

$$M = \frac{4\pi}{\mu^2} \left\{ \left[\left(\mu C_1^{(1)} + C_2^{(1)} \right) N_1 + \left(\mu C_1^{(2)} + C_2^{(2)} \right) N_2 \right] \Delta\tilde{\phi}. \right. \tag{61}$$

(4) Let $\tilde{\phi} = \tilde{\phi}_{\text{res}}$ and $\mu = \mu_{\text{res}}$. Suppose the cylinder tested by someone who is unaware of its torsional or thermal history. If the cylinder is kept at the fixed length $\mu_{\text{res}} L_0$, the torque-twist relation that would be found is given by (61) with $\mu = \mu_{\text{res}}$. The axial force would be given by (57). Since the axial force was compressive during scission, it is reasonable to assume $\mu_{\text{res}} > 1$. As the first term in (57) is positive, while the other terms are negative, the post-scission axial force may or may not be compressive.

(5) The torque-twist relation for the cylinder in its initial state is

$$M = 2\big(C_1^{(1)} + C_2^{(1)}\big)\frac{\pi R_0^4}{2}\tilde{\phi} \tag{62}$$

The ratio of the post-scission torsional stiffness and pre-scission torsional stiffness is

$$\frac{(M/\Delta\tilde{\phi})_{\text{post}}}{(M/\tilde{\phi})_{\text{pre}}} = \frac{4}{\mu_{\text{res}}^2 R_0^4}\frac{\big[\big(\mu_{\text{res}} C_1^{(1)} + C_2^{(1)}\big)N_1 + \big(\mu_{\text{res}} C_1^{(2)} + C_2^{(2)}\big)N_2\big]}{\big(C_1^{(1)} + C_2^{(1)}\big)}. \tag{63}$$

7 Concluding remarks

This work is concerned with the thermo-mechanical response of elastomers over a range of temperatures from below T_{cr}, when there is no microstructural change, to above T_{cr} when there are microstructural changes due to scission and crosslinking. Using a constitutive equation that describes this range of response, the consequences of these microstructural changes are studied in the context of the torsion of a circular elastomeric cylinder when it has a temperature distribution that varies with radius and time. This deformation is possible in every material represented by the constitutive equation and for any such temperature distribution. It thus provides a convenient platform for studying torsion when microstructural changes interact with the deformation and temperature, and it enables results to be obtained that are expressed in terms of general material properties and kinetics of scission and crosslinking.

The cylinder is first twisted while the cylinder is at a constant temperature below T_{cr}. The well-known torque-twist and axial force twist relations from nonlinear elasticity are developed. The cylinder is then held at a fixed twist and the surface temperature is increased to above T_{cr}. Because of heat conduction through the surface, there is radial and time-dependent scission and crosslinking within the cylinder. Since the newly crosslinked material is not deformed, the torque and axial force depend only on scission. It is shown that there can be two competing effects resulting from the temperature increase, an initial increase in torque and axial force due to entropic stiffening in their elastic response and then a subsequent decrease due to scission based stress relaxation. Even though the torque and axial force vary with time when the temperature exceeds T_{cr}, it is shown that their ratio can be independent of time provided the material properties satisfy certain conditions. This result should be useful in an experimental program.

Finally, the surface temperature is reduced to its initial value T_0, the temperature distribution in the cylinder becomes uniform at T_0 and the scission and crosslinking processes have stopped. Because of scission and crosslinking that occurred when the cylinder was twisted and the temperature exceeded T_{cr}, the cylinder now has a modified torque-twist and axial force-twist response. Expressions are developed for these in terms of general material properties and scission kinetics. When the networks can be described by the Mooney-Rivlin strain energy function, explicit expressions are obtained for the modified torsional stiffness and the permanent set upon removal of torque and axial force.

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