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Influence of Thermally Induced Chemorheological Changes on the Inflation of Spherical Elastomeric Membranes

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Abstract. When an elastomeric material is deformed and subjected to temperatures above some chemorheological 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 (often a reduced stiffness) and permanent set on removal of the applied load. A recently proposed constitutive theory is used to study the influence of chemorheological changes on the inflation of an initially isotropic spherical rubber membrane. The membrane is inflated while at a temperature below T_{cr}. We then look at the pressure response assuming the sphere's radius is held fixed while the temperature is increased above T_{cr} for a period of time and then returned to its original value. The inflation pressure during this process is expressed in terms of the temperature, representing entropic stiffening of the elastomer, and a time dependent property that represents the kinetics of the chemorheological change in the elastomer. When the membrane has been returned to its original temperature, it is shown to have a permanent set and a modified pressure-inflated radius relation. Their dependence on the initial inflated radius, material properties and kinetics of chemorheological change is studied when the underlying elastomeric networks are neo-Hookean or Mooney–Rivlin.

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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 macromolecular 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.

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Tobolsky [11] presented results of experiments that provided significant insight into this process. It occurs at elevated temperatures, is faster at higher temperatures and stops when the temperature drops below some level. If the material is stretched 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 accounting for two material networks, the remainder of the original material molecular network and a newly formed network. An extension of this constitutive equation to arbitrary deformation and temperature histories to account for continuous destruction and growth of material network has been proposed and studied by Jones [6] and Shaw et al. [9].

Jones [6] demonstrated a facility to study the high temperature inflation of an initially flat circular elastomeric membrane undergoing non-uniform deformation, and experimental work is ongoing. The results will be used to further develop the constitutive model and are planned to be published separately.

The purpose of the present paper, however, is to illustrate the type of phenomena that are expected in a simpler context (i.e., uniform biaxial deformation) without the need to specify material parameters and their evolution laws. In particular, the constitutive theory is used to study the influence of scission and crosslinking on the inflation of an initially isotropic spherical rubber membrane. The membrane is inflated while at a temperature below T_{cr}. We analyze the pressure response assuming the sphere's radius is held fixed while the temperature is increased above T_{cr} for a period of time and then returned to its original value. The inflation pressure during this process is expressed in terms of the temperature, representing entropic stiffening of the elastomer, and a time dependent property that represents the kinetics of scission in the elastomer. When the membrane has been returned to its original temperature, it is shown to have a permanent set and a modified pressure-inflated radius relation. In the case of neo-Hookean response of the original and newly formed networks, explicit expressions are obtained for the dependence of permanent set and the modified pressure-inflated radius relation on the initial inflated radius, material properties and kinetics of scission and crosslinking. In the case of Mooney–Rivlin response, a numerical study is presented.

The constitutive model is outlined in Section 2. The problem of the inflation of a spherical membrane undergoing chemorheological changes is formulated in Section 3. Section 4 discusses the response while the membrane is at a fixed radius during time varying temperature and scission. After the membrane is cooled to its original temperature, it has permanent set and a modified pressure-inflated radius relation, which is developed in Section 5 for the case of Mooney–Rivlin networks. Section 6 discusses this relation for neo-Hookean material networks. It is shown that the pre-scission and post-scission pressure-inflated radius relations have the same form, but differ by a scale factor. Section 7 treats Mooney–Rivlin networks. Although not addressed explicitly, other more realistic hyperelastic models for rubber behaviour could also be used in the framework developed. It is shown that the pre-scission and post-scission pressure-inflated radius relations have different forms. In an Appendix, the difference is shown to be a result of the membrane material becoming transversely isotropic. A numerical study for Mooney–Rivlin materials is carried out in Section 8. Concluding comments are given in Section 9.

2. Constitutive Equation

Tobolsky [11] 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 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. A brief summary of the constitutive framework is presented here. The underlying constitutive framework was developed by Wineman and Rajagopal [12] and Rajagopal and Wineman [7] for deformation induced scission and crosslinking. For a detailed discussion of the subsequent application of this framework to thermally induced scission and crosslinking, see Jones [6] and Shaw et al. [9].

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

$$\sigma^{(1)} = -p^{(1)}\mathbf{I} + 2\frac{\partial W^{(1)}}{\partial I_1}\mathbf{B} - 2\frac{\partial W^{(1)}}{\partial I_2}\mathbf{B}^{-1}, \tag{2.1}$$

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. For brevity, explicit notational dependence on the current time t is omitted.

No scission occurs for temperatures $T < T_{cr}$. All of the material is in its original state and the total stress is given by (2.1). For temperatures $T \geq T_{cr}$, scission of the original microstructural network is assumed to occur continuously in time. Let $b^{(1)}(t)$ denote the volume fraction of the original network remaining at time t. Its properties are $b^{(1)}(0) = 1$, $\mathrm{d}b^{(1)}/\mathrm{d}t < 0$ when $T \geq T_{cr}$ and $\mathrm{d}b^{(1)}/\mathrm{d}t = 0$ when $T < T_{cr}$. Tobolsky's experiments indicated that $b^{(1)}(t)$ does not depend on the uniaxial stretch provided that it is less than 3 to 4. This was supported by the experimental results of Scanlan and Watson [8] and Jones [6]. For the sake of simplicity and in consideration of these experimental results, it is assumed that $b^{(1)}(t)$ depends only on the temperature history and time, i.e., $b^{(1)}(t) = \tilde{b}^{(1)}\left[T(s)\big|_0^t, t\right]$.

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 $\hat{t} + \mathrm{d}\hat{t}$ whose reference configuration is the configuration of the original material at time $\hat{t}$. As suggested by Tobolsky et al. [10] and Tobolsky [11], 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 $\hat{\mathbf{G}} = \partial \mathbf{x}/\partial \hat{\mathbf{x}}$, 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 $\hat{\mathbf{B}} = \hat{\mathbf{G}}\hat{\mathbf{G}}^T$ 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

$$\sigma^{(2)} = -p^{(2)}\mathbf{I} + 2\frac{\partial W^{(2)}}{\partial \hat{\mathrm{I}}_1}\hat{\mathbf{B}} - 2\frac{\partial W^{(2)}}{\partial \hat{\mathrm{I}}_2}\hat{\mathbf{B}}^{-1}, \tag{2.2}$$

where $p^{(2)}$ arises from the constraint that deformations are isochoric and $\hat{\mathrm{I}}_1$, $\hat{\mathrm{I}}_2$ are invariants of $\hat{\mathbf{B}}$. $W^{(2)}(\hat{\mathrm{I}}_1, \hat{\mathrm{I}}_2, T)$ 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 new network is formed at time $\hat{t}$. Thus, $a(0) = 0$, $a(\hat{t}) > 0$ when $T \geq T_{cr}$ and $a(\hat{t}) = 0$ when $T < T_{cr}$. The amount of new network that is formed during the time interval from $\hat{t}$ to $\hat{t} + \mathrm{d}\hat{t}$ is $a(\hat{t})\mathrm{d}\hat{t}$. Recent experimental results of Jones [6] indicate that the new network also undergoes scission. Let $b^{(2)}(t, \hat{t})$ denote the volume fraction of the network formed at time $\hat{t}$ that is remaining at time t. The properties of $b^{(2)}$ are similar to those of $b^{(1)}$: $b^{(2)}(\hat{t}, \hat{t}) = 1$, $\partial b^{(2)}(t, \hat{t})/\partial t < 0$ when $T \geq T_{cr}$ and $\partial b^{(2)}(t, \hat{t})/\partial t = 0$ when $T < T_{cr}$. 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. $b^{(2)} = \tilde{b}^{(2)}\left[T(s)\big|_{\hat{t}}^{t}, t\right]$. The amount of crosslinks at time t in the network that was formed at time $\hat{t}$ is $a(\hat{t})b^{(2)}(t, \hat{t})\mathrm{d}\hat{t}$. The time dependent functions $a(\hat{t})$, $b^{(1)}(t)$, $b^{(2)}(t, \hat{t})$ describe the kinetics of scission and crosslinking for a particular rubber. 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 qualitative 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, combining (2.1) and (2.2),

$$\sigma(t) = -p(t)\mathbf{I} + 2b^{(1)}(t)\left(\frac{\partial W^{(1)}}{\partial I_1}\mathbf{B}(t) - \frac{\partial W^{(1)}}{\partial I_2}\mathbf{B}(t)^{-1}\right) + 2\int_0^t a(\hat{t})b^{(2)}(t,\hat{t})\left(\frac{\partial W^{(2)}}{\partial \hat{I}_1}\hat{\mathbf{B}}(t,\hat{t}) - \frac{\partial W^{(2)}}{\partial \hat{I}_2}\hat{\mathbf{B}}(t,\hat{t})^{-1}\right)\mathrm{d}\hat{t}. \tag{2.3}$$

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

This constitutive framework defines a class of materials that have evolving natural configurations. It has been presented without providing a corresponding thermodynamic framework. In particular, specific kinetic laws are not provided here for the evolution of $a(\hat{t})$, $b^{(1)}(t)$ and $b^{(2)}(t, \hat{t})$. The importance of placing the theory in such a thermodynamically consistent framework is recognized and is left for future work.

3. Formulation

The theory of nonlinear elastic membranes has been presented by Green and Adkins [4]. The formulation for spherical membranes contained therein is extended here to materials described by the constitutive equation of Section 2. Consider a spherical membrane in its reference state, where it is assumed to be stress free and at a uniform temperature $T_o < T_{cr}$. The radius of its mid-surface is R_o and its wall thickness is h_o, with $h_o/R_o << 1$. A time dependent pressure, $p(t)$, acts on the inner surface of the membrane causing it to inflate. At times $t > 0$, it is assumed that the membrane is spherically symmetric, the current radius of the mid-surface is $r(t)$ and the wall thickness is $h(t)$. The condition $h_o/R_o << 1$ implies that the value of a physical variable on the mid-surface is the same as that at any point through the thickness to within order $O(h_o/R_o)$.

At each point in the deformed membrane, the principal directions of stretch of the original membrane network are tangent to the coordinate lines of a spherical coordinate system. The principal stretches in a radial surface are equal and are given by $\lambda(t) = r(t)/R_o$. For notational convenience, henceforth $\lambda(t) = \lambda$, $r(t) = r$, etc. The membrane material is assumed to be incompressible so that the radial principal stretch is given by

$$\lambda_r = h/h_o = 1/\lambda^2. \tag{3.1}$$

The stretch tensors $\mathbf{B}$ for the original network and $\hat{\mathbf{B}}$ for the network formed at time $\hat{t}$ are,

$$\mathbf{B} = \begin{bmatrix} 1/\lambda^4 & 0 & 0 \\ 0 & \lambda^2 & 0 \\ 0 & 0 & \lambda^2 \end{bmatrix}, \quad \hat{\mathbf{B}} = \begin{bmatrix} \lambda^4(\hat{t})/\lambda^4 & 0 & 0 \\ 0 & \lambda^2/\lambda^2(\hat{t}) & 0 \\ 0 & 0 & \lambda^2/\lambda^2(\hat{t}) \end{bmatrix}, \tag{3.2}$$

from which it is seen that the principal stretch directions of the network formed at time $\hat{t}$ coincide with the principal stretch directions of the original network.

On substituting (3.2) into (2.3), it is found that the principal directions of stress and stretch coincide. The principal stresses on surfaces in the membrane normal to the coordinate directions are equal and are denoted by σ. Assuming quasi-static motion, the balance between the forces arising from the internal pressure and from the tensile stresses in the membrane wall gives

$$p = \frac{2\sigma h}{r}. \tag{3.3}$$

On using (3.1), (3.3) can be re-written as

$$\frac{pR_o}{2h_o} = \frac{\sigma}{\lambda^3}. \tag{3.4}$$

Each material element of the membrane is in an approximate state of plane stress and equal biaxial extension. It follows from (2.3) and (3.2) that the relation between the membrane stress and mid-surface stretch history is given by

$$\sigma = 2b^{(1)}\left(\lambda^2 - \frac{1}{\lambda^4}\right)\left(W_1^{(1)} + \lambda^2 W_2^{(1)}\right) + 2\int_0^t a(\hat{t})b^{(2)}(t,\hat{t})\left(\frac{\lambda^2}{\lambda^2(\hat{t})} - \frac{\lambda^4(\hat{t})}{\lambda^4}\right)\left(W_1^{(2)} + \frac{\lambda^2}{\lambda^2(\hat{t})})W_2^{(2)}\right)\mathrm{d}\hat{t}, \tag{3.5}$$

where $W_\alpha^{(1)} = \partial W^{(1)} / \partial I_\alpha$, $W_\alpha^{(2)} = \partial W^{(2)} / \partial \hat{I}_\alpha$, α = 1,2. $W_\alpha^{(2)}$ is evaluated at

$$I_1 = 2\lambda^2 + \frac{1}{\lambda^4},\; I_2 = \frac{2}{\lambda^2} + \lambda^4 \tag{3.6$_1$}$$

and T. $W_\alpha^{(2)}$ is evaluated at

$$\hat{I}_1 = 2\frac{\lambda^2}{\lambda^2(\hat{t})} + \frac{\lambda^4(\hat{t})}{\lambda^4}, \quad \hat{I}_2 = 2\frac{\lambda^2(\hat{t})}{\lambda^2} + \frac{\lambda^4}{\lambda^4(\hat{t})} \tag{3.6$_2$}$$

and T.

Let it now be assumed that $W^{(1)}(I_1, I_2, T) = T\boldsymbol{W}^{(1)}(I_1, I_2)$ and $W^{(2)}(\hat{I}_1, \hat{I}_2, T) = T\boldsymbol{W}^{(2)}(\hat{I}_1, \hat{I}_2)$, which is the case for a number of strain energy density functions presented in the literature that exhibit entropic stiffening [5]. Then, $\boldsymbol{W}_\alpha^{(1)} = \partial \boldsymbol{W}^{(1)} / \partial I_\alpha$ and $\boldsymbol{W}_\alpha^{(2)} = \partial \boldsymbol{W}^{(2)} / \partial \hat{I}_\alpha$, α = 1, 2. Let $C_o = 2\boldsymbol{W}_1^{(1)}(3, 3, T_o) = 2T_o\boldsymbol{W}_1^{(1)}(3, 3)$ be a constant having the dimension of stress. The dimensionless strain energy derivatives and pressure are defined as

$$w_\alpha^{(\beta)} = \boldsymbol{W}_\alpha^{(\beta)} \Big/ \boldsymbol{W}_1^{(1)}(3,3), \quad P = \frac{pR_o}{2h_oC_o}. \tag{3.7}$$

Then, by (3.4) and (3.7),

$$P = \frac{1}{\lambda^3}\frac{\sigma}{C_o}. \tag{3.8}$$

Equations (3.5) and (3.8) give the dimensionless pressure–stretch–temperature relation for the membrane,

$$\begin{aligned} P = {} & b^{(1)}(t)\frac{T(t)}{T_o}\frac{1}{\lambda^3}\left(\lambda^2 - \frac{1}{\lambda^4}\right)\left(w_1^{(1)} + \lambda^2 w_2^{(1)}\right) \\ & + \frac{T(t)}{T_o}\frac{1}{\lambda^3}\int_0^t a(\hat{t})b^{(2)}(t,\hat{t})\left(\frac{\lambda^2}{\lambda^2(\hat{t})} - \frac{\lambda^4(\hat{t})}{\lambda^4}\right)\left(w_1^{(2)} + \frac{\lambda^2}{\lambda^2(\hat{t})}w_2^{(2)}\right)\mathrm{d}\hat{t}. \end{aligned} \tag{3.9}$$

4. Response During Scission and Re-Crosslinking

The membrane is assumed to contain an incompressible liquid that is used to control its inflation and heating. Specifying the time dependence of the volume of the contained liquid is equivalent to specifying $r(t)$, assuming spherical symmetry is maintained. Specifying the time dependence of the temperature of the liquid is equivalent to specifying the temperature of the inner surface of the membrane. Since $h_o/R_o \ll 1$, it is assumed that the temperature in the membrane is uniform and is the same as that at the inner surface at each instant.

The temperature and inflation histories, shown in Figure 1, are:

Temperature	$0 \leq t \leq t_1$, $T(t) = T_o$, $t_1 \leq t < t_2$, $T(t)$ increases, $T(t_2) = T_{cr}$, $t_2 \leq t < t_3$, $T(t) > T_{cr}$, $T(t_3) = T_{cr}$, $t_3 \leq t < t_4$, $T(t)$ decreases, $T(t_4) = T_o$, $t_4 \leq t$, $T(t) = T_o$.
Inflation	$0 \leq t < t_1$, $\lambda(t)$ increases, $\lambda(\bar{t}) = \bar{\lambda}$, $\bar{t} \leq t < t_1$, $\bar{t} \leq t < t_4$, $\lambda(t) = \bar{\lambda}$, $t_4 \leq t$, $\lambda(t)$ arbitrary.

The remainder of this section is concerned with the response of the membrane preceding and during scission, when $0 \leq t < t_4$. The post-scission response when $t_4 \leq t$ is discussed in later sections.

<u>$0 \leq t < t_1$</u> : $T(t) = T_o$, $b^{(1)} = 1$, $a = 0$ and (3.9) reduces to

$$P(t) = \frac{1}{\lambda^3}\left(\lambda^2 - \frac{1}{\lambda^4}\right)\left(w_1^{(1)} + \lambda^2 w_2^{(1)}\right). \tag{4.1}$$

This is the well known pressure–stretch relation for an isotropic membrane and relates the time variation of the pressure to that of the stretch.

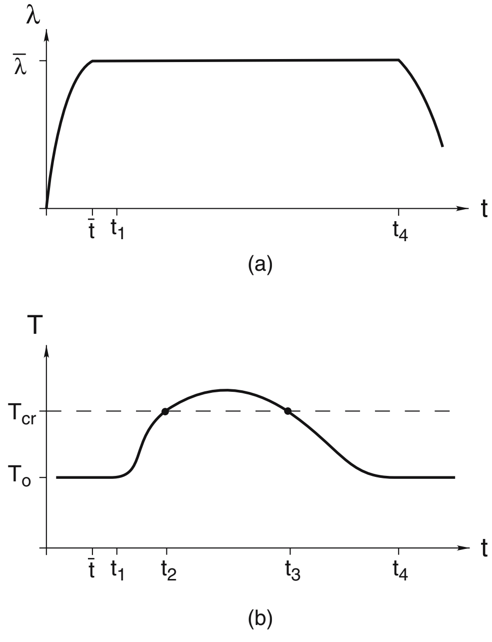

Figure 1. a) Prescribed stretch history, b) Temperature history.

$\underline{t_1 \le t < t_2}$: $T(t) \le T_{cr}$, $b^{(1)} = 1$, $a = 0$, and $\lambda = \lambda(\hat{t}) = \bar{\lambda} = \bar{r}/R_o$. Then (3.9) reduces to

$$P(t) = \frac{T(t)}{T_o} \frac{1}{\bar{\lambda}^3} \left(\bar{\lambda}^2 - \frac{1}{\bar{\lambda}^4} \right) \left(w_1^{(1)} + \bar{\lambda}^2 w_2^{(1)} \right). \tag{4.2}$$

The pressure required to hold the membrane at a fixed radius increases with the temperature. This is a consequence of entropic stiffening of the original network.

$\underline{t_2 \le t < t_3}$: $T(t) > T_{cr}$ and $b^{(1)}(t)$ decreases with time. Since $a(\hat{t}) = 0$ for $0 \le \hat{t} \le t_2$ and $\lambda = \lambda(\hat{t}) = \bar{\lambda}$ for $\bar{t} \le \hat{t} \le t$, the integral in (3.9) vanishes. Equation (3.9) becomes

$$P(t) = b^{(1)}(t) \frac{T(t)}{T_o} \frac{1}{\bar{\lambda}^3} \left(\bar{\lambda}^2 - \frac{1}{\bar{\lambda}^4} \right) \left(w_1^{(1)} + \bar{\lambda}^2 w_2^{(1)} \right). \tag{4.3}$$

$P(t)$ varies with time in a manner determined by that of $b^{(1)}(t)T(t)$. Its variation would be similar to that observed in experiments on rubber strips in fixed uniaxial extension (see Jones [6] and Shaw et al. [9]). For a constant uniaxial stretch ratio, the force required to hold the strip increased at first with temperature $T(t)$ due to entropic stiffening, but then reached a maximum and decreased as the response became dominated by the decrease of $b^{(1)}(t)$ due to scission while $T > T_{cr}$.

$\underline{t_3 \le t < t_4}$: $T(t) < T_{cr}$, $b^{(1)}(t) = b^{(1)}(t_3)$. As before, the integral in (3.9) vanishes because λ is held fixed and (3.9) reduces to

$$P(t) = b^{(1)}(t_3) \frac{T(t)}{T_o} \frac{1}{\bar{\lambda}^3} \left(\bar{\lambda}^2 - \frac{1}{\bar{\lambda}^4} \right) \left(w_1^{(1)} + \bar{\lambda}^2 w_2^{(1)} \right). \tag{4.4}$$

$t_4 < t$: The temperature has returned to T_o and the pressure required to maintain the membrane at the fixed stretch $\bar{\lambda}$ is

$$P = b^{(1)}(t_3) \frac{1}{\bar{\lambda}^3} \left(\bar{\lambda}^2 - \frac{1}{\bar{\lambda}^4} \right) \left(w_1^{(1)} + \bar{\lambda}^2 w_2^{(1)} \right). \tag{4.5}$$

5. Post-Scission Response

During scission at constant stretch, a new network was formed in the fixed inflated state of the membrane, but was not stretched and did not contribute to the stress. When $t > t_4$, there are two networks, one associated with the undeformed membrane and one associated with its fixed inflated state during scission. If λ and P are now changed, both networks respond elastically. The membrane has a new elastic regime, and a new P–λ relation can be obtained from (3.9) by incorporating the following: $a(t) = 0$ for $0 \le t \le t_2$ and $t_3 < t$; $b^{(1)} = b^{(1)}(t_3)$ and

$b^{(2)} = b^{(2)}(t_3, \hat{t})$ for $t_3 < t$; $\lambda(\hat{t}) = \bar{\lambda}$ for $t_1 \leq \hat{t} \leq t_4$; and $T(t) = T_o$ for $t_4 < t$. Then, (3.9) reduces to

$$P = b^{(1)}(t_3)\frac{1}{\lambda^3}\left(\lambda^2 - \frac{1}{\lambda^4}\right)\left(w_1^{(1)} + \lambda^2 w_2^{(1)}\right)$$

$$+ \int_{t_2}^{t_3} a\left(\hat{t}\right) b^{(2)}(t_3, \hat{t})\mathrm{d}\hat{t} \cdot \frac{1}{\lambda^3}\left(\frac{\lambda^2}{\bar{\lambda}^2} - \frac{\bar{\lambda}^4}{\lambda^4}\right)\left(w_1^{(2)} + \frac{\lambda^2}{\bar{\lambda}^2} w_2^{(2)}\right), \tag{5.1}$$

the post-scission P–λ relation for $T = T_o$. Note that (5.1) reduces to (4.5) when $\lambda = \bar{\lambda}$. In other words, (4.5) gives one point on the post-scission plot of P vs. λ determined from (5.1).

In the remainder of this study, it is assumed that the original and newly formed networks have strain energy density functions of Mooney–Rivlin type, that is $\boldsymbol{W}_\beta^{(\alpha)}$ are constants that are denoted by $C_\beta^{(\alpha)}$. Since $C_1^{(1)} = \boldsymbol{W}_1^{(1)}(3,3)$, (5.1) becomes

$$P = b^{(1)}(t_3)\frac{1}{\lambda^3}\left(\lambda^2 - \frac{1}{\lambda^4}\right)\left(1 + \lambda^2\alpha^{(1)}\right)$$

$$+ \frac{C_1^{(2)}}{C_1^{(1)}}\int_{t_2}^{t_3} a\left(\hat{t}\right) b^{(2)}(t_3, \hat{t})\mathrm{d}\hat{t} \cdot \frac{1}{\lambda^3}\left(\frac{\lambda^2}{\bar{\lambda}^2} - \frac{\bar{\lambda}^4}{\lambda^4}\right)\left(1 + \frac{\lambda^2}{\bar{\lambda}^2}\alpha^{(2)}\right), \tag{5.2}$$

where

$$\alpha^{(1)} = \frac{C_2^{(1)}}{C_1^{(1)}}, \quad \alpha^{(2)} = \frac{C_2^{(2)}}{C_1^{(2)}} \tag{5.3}$$

are the ratios of the Mooney–Rivlin constants for the respective networks. Let

$$N_1 = b^{(1)}(t_3) \tag{5.4$_1$}$$

$$N_2 = \frac{C_1^{(2)}}{C_1^{(1)}}\int_{t_2}^{t_3} a\left(\hat{t}\right) b^{(2)}(t_3, \hat{t})\mathrm{d}\hat{t}, \tag{5.4$_2$}$$

be dimensionless measures of the amount of original and new networks, respectively. Then (5.2) can be written as

$$P = N_1\frac{1}{\lambda^3}\left(\lambda^2 - \frac{1}{\lambda^4}\right)\left(1 + \alpha^{(1)}\lambda^2\right) + N_2\frac{1}{\lambda^3}\left(\frac{\lambda^2}{\bar{\lambda}^2} - \frac{\bar{\lambda}^4}{\lambda^4}\right)\left(1 + \alpha^{(2)}\frac{\lambda^2}{\bar{\lambda}^2}\right). \tag{5.5}$$

This can be written more tersely as

$$P = \frac{1}{\lambda^3}\left[A_1\lambda^2 + A_2\lambda^4 - A_3\frac{1}{\lambda^4} - A_4\frac{1}{\lambda^2}\right]. \tag{5.6}$$

in which

$$\begin{aligned} A_1 &= N_1 + \frac{N_2}{\bar{\lambda}^2}, \quad A_2 = N_1\alpha^{(1)} + \frac{N_2\alpha^{(2)}}{\bar{\lambda}^4}, \\ A_3 &= N_1 + N_2\bar{\lambda}^{-4} \quad A_4 = N_1\alpha^{(1)} + N_2\alpha^{(2)}\bar{\lambda}^{-2}. \end{aligned} \tag{5.7}$$

Note that $A_i > 0$, $i = 1, 2, 3, 4$ if $\alpha^{(1)} > 0$ and $\alpha^{(2)} > 0$.

6. Neo-Hookean Networks

It is instructive to study the post-scission membrane response when both networks are neo-Hookean. In this case, $\alpha^{(1)} = \alpha^{(2)} = 0$ and (5.5) reduces to

$$P = N_1 \frac{1}{\lambda^3}\left(\lambda^2 - \frac{1}{\lambda^4}\right) + N_2 \frac{1}{\lambda^3}\left(\frac{\lambda^2}{\bar{\lambda}^2} - \frac{\bar{\lambda}^4}{\lambda^4}\right). \tag{6.1}$$

When $P = 0$, the membrane has a permanent set at a new radius r_{set} and a corresponding stretch ratio $\lambda_{set} = r_{set}/R_o$ given by

$$\lambda_{set} = \left[\frac{1 + \frac{N_2}{N_1}\bar{\lambda}^4}{1 + \frac{N_2}{N_1}\frac{1}{\bar{\lambda}^2}}\right]^{1/6}, \tag{6.2}$$

from which it follows that

$$\frac{\lambda_{set}}{\bar{\lambda}} = \left[\frac{\frac{1}{\bar{\lambda}^6} + \frac{N_2}{N_1}\frac{1}{\bar{\lambda}^2}}{1 + \frac{N_2}{N_1}\frac{1}{\bar{\lambda}^2}}\right]^{1/6}. \tag{6.3}$$

Since N_1 and N_2 are positive quantities and $\bar{\lambda} > 1$, Equations (6.2) and (6.3) imply

$$1 < \lambda_{set} < \bar{\lambda}. \tag{6.4}$$

The P–λ relation (6.1) can be rewritten in the form

$$P = K\left(\frac{1}{\mu} - \frac{1}{\mu^7}\right), \tag{6.5}$$

where $\mu = \lambda/\lambda_{set} = r/r_{set}$ is the stretch measured from permanent set and

$$K = N_1 \frac{\left(1 + \frac{N_2}{N_1}\frac{1}{\bar{\lambda}^2}\right)^{7/6}}{\left(1 + \frac{N_2}{N_1}\bar{\lambda}^4\right)^{1/6}}. \tag{6.6}$$

The pre-scission pressure-stretch relation can be obtained by letting $N_1 = 1$ and $N_2 = 0$ in (6.1). It is given by (6.5) with $K = 1$ and μ replaced by λ, or equivalently, $\lambda_{set} = 1$. The coefficient K acts as a scale factor that depends on the scission kinetics, the relative stiffnesses of the networks and the stretch of the original membrane during scission. It is straightforward to show that the pre-scission pressure–stretch relation has a local maximum of $6/\left(7^{7/6}\right) = 0.6197$ at a stretch ratio of $\lambda = 7^{1/6}$ corresponding to a radius of $7^{1/6}R_o$, while the post-scission pressure–stretch relation has a local maximum of

$$N_1 \frac{\left(1 + \frac{N_2}{N_1}\frac{1}{\overline{\lambda}^2}\right)^{7/6}}{\left(1 + \frac{N_2}{N_1}\overline{\lambda}^4\right)^{1/6}} \frac{6}{7^{7/6}} \tag{6.7}$$

at a stretch ratio of $\mu = 7^{1/6}$, corresponding to a radius of $7^{1/6}r_{set}$.

Calculations show that K is less than one for many values of $N_1 < 1$, $\overline{\lambda} > 1$, and N_2/N_1. This is seen to be the case as N_2/N_1 increases, since K approaches $N_2/\overline{\lambda}^3 < 1$. Note also that K decreases as $\overline{\lambda}$ increases for fixed values of N_1 and N_2. These results imply that the pressure needed after scission to inflate the membrane to a stretch of $\mu = \lambda_o$ would be less than that needed before scission to inflate it to a stretch of $\lambda = \lambda_o$. Stated differently, consider two spherical membranes: membrane 1 was not subjected to an inflation and scission history and membrane 2 was. Suppose both membranes were given to someone who was unaware of the difference between them. They would find it easier to inflate membrane 2 to a stretch ratio of λ_o.

Figure 2 shows results of a simulation that illustrate the process discussed in Sections 4 and 5. The upper curve (a) is a P–λ plot for a neo-Hookean membrane before scission. The membrane is inflated to $\overline{\lambda} = 1.2$, corresponding to point A. The pressure increases to point B as the temperature increases during $t_1 \le t < t_2$ and then decreases as a result of the scission during $t_2 \le t < t_3$. Point C corresponds to the pressure given by (4.5) when the temperature has returned to T_o at time t_4. Suppose scission was stopped at time t_3 with $N_1 = N_2 = 0.5$. The lower curve (b) is the P–λ plot for the membrane after scission. The residual stretch ratio is $\lambda_{set} = 1.104$, and the local maximum has decreased from 0.6197 on the pre-scission P–λ plot to 0.4754 on the post-scission P–λ plot (open circles). The dashed portions of the curves indicate the negative sloping portions where the response is unstable.

The similarity of the pre- and post-scission pressure-stretch relations follows from a remarkable result for neo-Hookean materials obtained by Berry, Scanlan and Watson [2] and later by Zimmermann and Wineman [13]. They showed that when a neo-Hookean material has undergone scission and a new network forms that is also neo-Hookean, the resultant material is isotropic and responds as a neo-Hookean material with respect to the new stress free reference configuration.

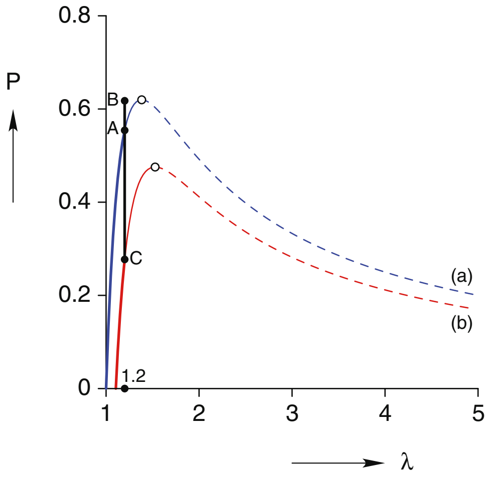

Figure 2. (a) Neo-Hookean pre-scission P–λ relation, (b) neo-Hookean post-scission P–λ relation following scission at $\overline{\lambda} = 1.2$. AB: Increase in pressure with increasing temperature as a result of entropic stiffening, BC: Decay of pressure as a result of scission.

However, as will be seen in the next section, this is not generally true for other hyperelastic models.

7. Mooney–Rivlin Networks

Now consider the post-scission P–λ relation (5.5) when both networks respond as Mooney–Rivlin materials, that is $\alpha^{(1)} \neq 0$, $\alpha^{(2)} \neq 0$. A number of analytical results can be established that correspond to those of Section 6.

Let $P = 0$ in (5.5). The membrane has a permanent stretch λ_{set} that satisfies the equation obtained by setting

$$N_1\left(\lambda_{\text{set}}^2 - \frac{1}{\lambda_{\text{set}}^4}\right)\left(1 + \alpha^{(1)}\lambda_{\text{set}}^2\right) + N_2\left(\frac{\lambda_{\text{set}}^2}{\overline{\lambda}^2} - \frac{\overline{\lambda}^4}{\lambda_{\text{set}}^4}\right)\left(1 + \alpha^{(2)}\frac{\lambda_{\text{set}}^2}{\overline{\lambda}^2}\right) = 0. \tag{7.1}$$

It is useful to recall that N_1, N_2, $\alpha^{(1)}$ and $\alpha^{(2)}$ are positive and $\overline{\lambda} > 1$ Thus, if $\lambda_{\text{set}} < 1$, both terms in (7.1) are negative and the equation cannot be satisfied. Likewise, if $\lambda_{\text{set}} > \overline{\lambda}$, both terms are positive and the equation cannot be satisfied. Hence, a solution λ_{set} of (7.1) must satisfy the condition $1 \leq \lambda_{\text{set}} \leq \overline{\lambda}$. The equality at the lower end occurs if $N_2 = 0$ and at the upper end if $N_1 = 0$, i.e., all of the original network has undergone scission. Equation (7.1) can be written as a quartic equation for λ_{set}^2. An expression for λ_{set} in terms of N_1, N_2, $\alpha^{(1)}$, $\alpha^{(2)}$ and $\overline{\lambda}$, corresponding to (6.2), could be constructed from the formulae for the roots of a quartic. The expression is very complicated, and as it would not appear to lead to useful insight, is not presented here.

Recalling that $\mu = r/r_{set}$ is the stretch measured from the permanent set, let $\lambda = \mu\lambda_{set}$ be substituted into (5.5). The P–λ relation in (5.5) becomes a P–μ relation analogous to that in (6.5) for neo-Hookean networks.

$$P = \frac{1}{\mu^3\lambda_{set}^3}\left\{N_1\left(\mu^2\lambda_{set}^2 - \frac{1}{\mu^4\lambda_{set}^4}\right)\left(1+\alpha^{(1)}\mu^2\lambda_{set}^2\right)\right.$$
$$\left. + N_2\left(\mu^2\frac{\lambda_{set}^2}{\bar{\lambda}^2} - \frac{1}{\mu^4}\frac{\bar{\lambda}^4}{\lambda_{set}^4}\right)\left(1+\alpha^{(2)}\mu^2\frac{\lambda_{set}^2}{\bar{\lambda}^2}\right)\right\}. \tag{7.2}$$

This is not in a form that is convenient for comparison with the pre-scission P–λ relation obtained by setting $N_1 = 1$ and $N_2 = 0$ in (5.5). However, as shown in the Appendix, (7.2) can be restated as follows,

$$P = \left(N_1 + \frac{N_2}{\bar{\lambda}^2}\right)\frac{1}{\lambda_{set}}\left(\frac{1}{\mu} - \frac{1}{\mu^7}\right)\left(1+\alpha_{eq}\mu^2\right)$$
$$-\left[\frac{1}{\lambda_{set}}\left(N_1 + \frac{N_2}{\bar{\lambda}^2}\right) - \frac{1}{\lambda_{set}^7}\left(N_1 + N_2\bar{\lambda}^4\right)\right]\left(\mu - \frac{1}{\mu^7}\right), \tag{7.3}$$

where

$$\alpha_{eq} = \frac{N_1\alpha^{(1)} + N_2\alpha^{(2)}\bar{\lambda}^2}{N_1 + \dfrac{N_2}{\bar{\lambda}^2}}\frac{1}{\lambda_{set}^4}. \tag{7.4}$$

The first term in (7.3) is analogous to (6.5), namely it is a scale factor times a function of μ that has the same form as that in the pre-scission P–λ relation, but with λ and $\alpha^{(1)}$ replaced by μ and α_{eq}. However, because of the presence of the second term in (7.3), known analytical results for the pre-scission P–λ relation cannot be extended to the post-scission relation. For this reason, all further discussion will be carried out using (5.6).

It is worth noting the reason for the presence of the second term in (7.3). As shown by Zimmermann and Wineman [13], the post-scission material is transversely isotropic with respect to the permanent set state, with the axis of transverse isotropy in the radial direction. Thus, (7.3) is the pressure–stretch relation for a membrane composed of a transversely isotropic material while the pre-scission pressure–stretch is that for an isotropic material.

Conditions can be developed for determining when the post-scission P vs. λ curve has an up-down-up shape similar that for the pre-scission P vs. λ curve. The following analysis follows that of Adkins and Rivlin [1] for the pre-scission response. From (5.6)

$$\frac{dP}{d\lambda} = \frac{1}{\lambda^8}\left[A_2\lambda^8 - A_1\lambda^6 + 5A_4\lambda^2 + 7A_3\right]. \tag{7.5}$$

$dP/d\lambda > 0$ as λ approaches zero or becomes large. The polynomial in square brackets in (7.5) has two sign alternations. According to Descarte's rule of signs [3], there are either two or zero values of λ at which $dP/d\lambda = 0$. If there are no values, then $dP/d\lambda > 0$ for all λ and P vs. λ is monotonic. If there are two values, say λ_1 and $\lambda_2 > \lambda_1$, then $dP/d\lambda < 0$ for $\lambda_1 < \lambda < \lambda_2$. By (5.7) and (7.5), the condition that $dP/d\lambda < 0$ becomes

$$1 < \frac{\left(1 + \frac{N_2}{N_1}\frac{1}{\bar{\lambda}^2}\right)\lambda^6 - 7\left(1 + \frac{N_2}{N_1}\bar{\lambda}^4\right)}{\left(\alpha^{(1)} + \frac{N_2}{N_1}\frac{\alpha^{(2)}}{\bar{\lambda}^4}\right)\lambda^8 + 5\left(\alpha^{(1)} + \frac{N_2}{N_1}\alpha^{(2)}\bar{\lambda}^2\right)\lambda^2}. \tag{7.6}$$

Let the right hand side of (7.6) be written in the form

$$m(x) = \frac{A_1 x^3 - 7A_3}{A_2 x^4 + 5A_4 x}, \tag{7.7}$$

where A_i, $i = 1, 2, 3, 4$ are defined in (5.7) and $x = \lambda^2$. By a straightforward analysis, it can be shown that $m(x)$ has a local maximum at

$$x^3 = \lambda^6$$
$$= \frac{(10A_1A_4 + 28A_2A_3) + \sqrt{(10A_1A_4 + 28A_2A_3)^2 + 140A_1A_2A_3A_4}}{2A_1A_2}. \tag{7.8}$$

This maximum, obtained by substituting x from (7.8) into (7.7), is given by

$$m_{\max} = \frac{A_1^2(7A_2A_3 + 5A_1A_4 + D)}{(A_1A_2)^{2/3}(14A_2A_3 + 5A_1A_4 + D)^{1/3}(14A_2A_3 + 10A_1A_4 + D)}, \tag{7.9}$$

where

$$D = \frac{1}{2}\sqrt{(10A_1A_4 + 28A_2A_3)^2 + 140A_1A_2A_3A_4}\Bigg]. \tag{7.10}$$

By (5.7) this maximum can be written as $m_{\max}$ (N_2/N_1, $\alpha^{(1)}$, $\alpha^{(2)}$, $\bar{\lambda}$) Condition (7.6) for a negative sloping part of the P vs. λ curve can be restated as

$$1 < m_{\max}\left(N_2/N_1,\ \alpha^{(1)}, \alpha^{(2)}, \bar{\lambda}\right). \tag{7.11}$$

In the pre-scission case when $N_2 = 0$, (7.11) reduces to

$$1 < \frac{0.214458}{\alpha^{(1)}}. \tag{7.12}$$

This gives the previously established result [1] that the P–λ curve has an up-down-up shape if $\alpha^{(1)} < 0.214458$ and is monotonic if $\alpha^{(1)} > 0.214458$.

Suppose $\alpha^{(1)} = \alpha^{(2)} = \alpha$. The expressions in (5.7) can be written as

$$A_1 = N_1M_1,\ A_2 = \alpha N_1M_2,\ A_3 = N_1M_3,\ A_4 = \alpha N_1M_4, \tag{7.13}$$

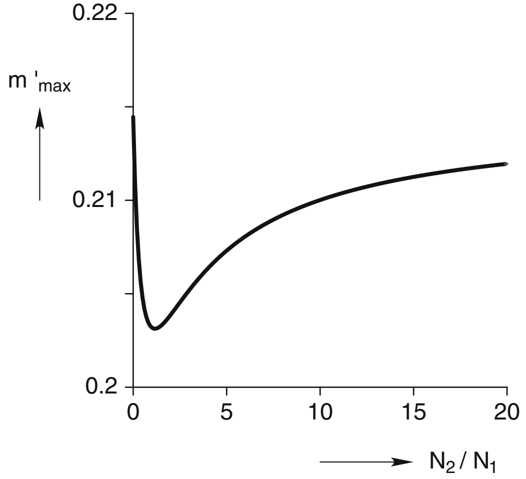

Figure 3. $m'_{\max}$ versus N_2/N_1 at $\overline{\lambda} = 1.2$.

where

$$M_1 = 1 + \frac{N_2}{N_1}\frac{1}{\overline{\lambda}^2}, M_2 = 1 + \frac{N_2}{N_1}\frac{1}{\overline{\lambda}^4},$$

$$M_3 = 1 + \frac{N_2}{N_1}\overline{\lambda}^4 \quad M_4 = 1 + \frac{N_2}{N_1}\overline{\lambda}^2. \tag{7.14}$$

Equation (7.9) reduces to

$$m_{\max} = \frac{m'_{\max}}{\alpha}, \tag{7.15}$$

where

$$m'_{\max} = \frac{M_1^2\left(7M_2M_3 + 5M_1M_4 + D'\right)}{(M_1M_2)^{2/3}(14M_2M_3 + 5M_1M_4 + D')^{1/3}(14M_2M_3 + 10M_1M_4 + D')} \tag{7.16}$$

and

$$D' = \frac{1}{2}\sqrt{(10M_1M_4 + 28M_2M_3)^2 + 140M_1M_2M_3M_4}\Bigg]. \tag{7.17}$$

Equation (7.11) now has the form

$$1 < \frac{m'_{\max}\left(N_2/N_1, \overline{\lambda}\right)}{\alpha}. \tag{7.18}$$

Figure 3 shows a plot of $m'_{\max}$ vs. N_2/N_1 with $\overline{\lambda} = 1.2$. The initial value is $m'_{\max}\left(0, \overline{\lambda}\right) = 0.214458$ and (7.18) reduces to (7.12) because only the original

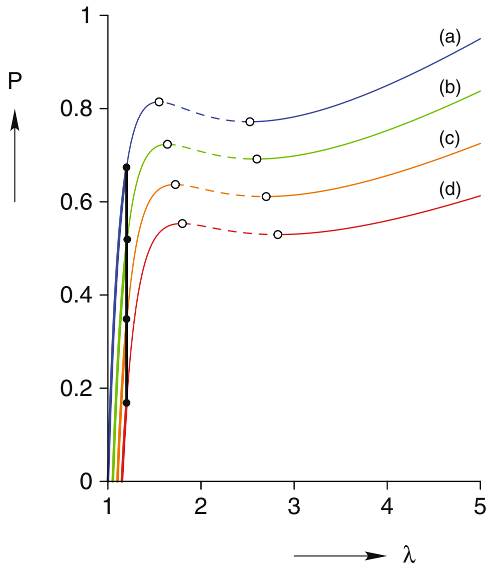

Figure 4. Influence of N_1 and N_2 on the P–λ relation for Mooney–Rivlin materials with $\alpha^{(1)} = \alpha^{(2)} = 0.15$ and $\overline{\lambda} = 1.2$. (a) Pre-scission P–λ relation, $N_1 = 1$, $N_2 = 0$, (b) post-scission P–λ relation, $N_1 = 0.75$, $N_2 = 0.25$, (c) post-scission P–λ relation, $N_1 = 0.5$, $N_2 = 0.5$, (d) post-scission P–λ relation, $N_1 = 0.25$, $N_2 = 0.75$.

network exists. $m'_{\max}(N_2/N_1, \overline{\lambda})$ decreases slightly as N_2/N_1 increases, has a minimum of 0.20314 at $N_2/N_1 = 1.16$ and approaches 0.214458 as N_2/N_1 becomes large, when only the new network exists. (7.18) again reduces to (7.12). Since $m'_{\max}$ only changes by about 5% over its entire range of N_2/N_1, scission has only a slight influence on the monotonicity of the pressure–stretch relation when $\alpha^{(1)} = \alpha^{(2)}$.

8. Numerical Examples

The analytical results in Section 7 provide insight into the influence of N_1, N_2, $\alpha^{(1)}$, $\alpha^{(2)}$ and $\overline{\lambda}$ on the post-scission pressure–stretch relation. This section contains numerical results to investigate the trends of these parameters.

Figures 4 and 5 show plots of P vs. λ as N_1 decreases and N_2 increases for two values of $\alpha^{(1)} = \alpha^{(2)}$, respectively. Figure 4 shows four cases for $\overline{\lambda} = 1.2$ and $\alpha^{(1)} = \alpha^{(2)} = 0.15$. As shown in Section 7, when $\alpha^{(1)} = \alpha^{(2)} = 0.15$, the plots have the up-down-up character for all choices of N_1, N_2. The dashed portions of the curves indicate the negatively sloping portions where the response is unstable. As N_1 decreases and N_2 increases, the response softens, i.e., the pressure required to achieve a given stretch decreases. In addition, the permanent stretch increases, the local maximum decreases and occurs at a larger stretch. Figure 5 shows three cases for $\overline{\lambda} = 1.2$ and $\alpha^{(1)} = \alpha^{(2)} = 0.3$. The P vs. λ plots are now monotonic, as

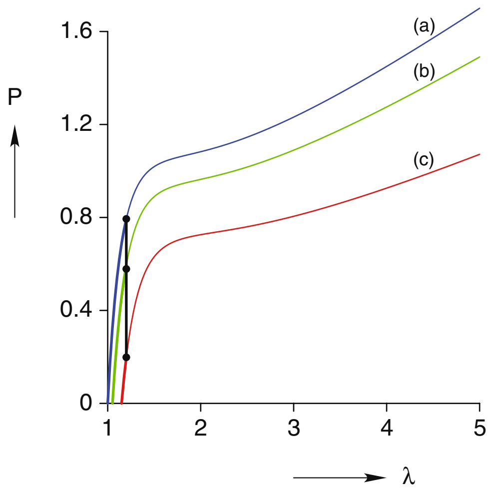

Figure 5. Influence of N_1 and N_2 on the P–λ relation for Mooney–Rivlin materials with $\alpha^{(1)} = \alpha^{(2)} = 0.3$ and $\overline{\lambda} = 1.2$ (a) Pre-scission P–λ relation, $N_1 = 1$, $N_2 = 0$, (b) post-scission P–λ relation, $N_1 = 0.75$, $N_2 = 0.25$, (c) post-scission P–λ relation, $N_1 = 0.25$, $N_2 = 0.75$.

expected from the results in Section 7. The response is again seen to soften as N_1 decreases and N_2 increases.

Figure 6 shows plots of P vs. λ for $\overline{\lambda} = 1.2$ and $\overline{\lambda} = 1.4$. Results are presented for $N_1 = 0.75$, $N_2 = 0.25$ and $\alpha^{(1)} = \alpha^{(2)} = 0.15$. Once again, the response softens as $\overline{\lambda}$ increases, the permanent stretch increases and the local maximum decreases and

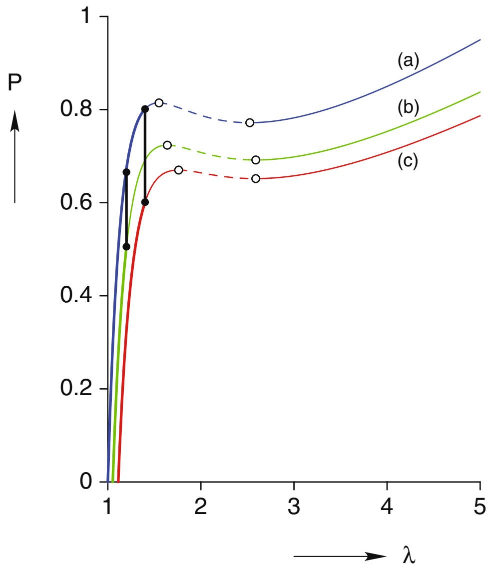

Figure 6. Influence of $\overline{\lambda}$, on the P–λ relation for Mooney–Rivlin materials with $\alpha^{(1)} = \alpha^{(2)} = 0.15$. (a) Pre-scission P–λ relation, (b) post-scission P–λ relation, $\overline{\lambda} = 1.2$, $N_1 = 0.75$, $N_2 = 0.25$, (c) post-scission P–λ relation, $\overline{\lambda} = 1.4$, $N_1 = 0.75$, $N_2 = 0.25$.

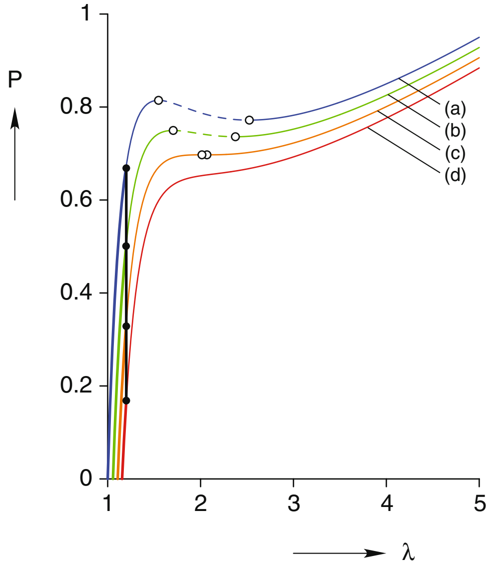

Figure 7. Influence of N_1 and N_2 on the P–λ relation for Mooney-Rivlin materials with $\alpha^{(1)} = 0.15$, $\alpha^{(2)} = 0.3$ and $\overline{\lambda} = 1.2$. (a) Pre-scission P–λ relation, $N_1 = 1$, $N_2 = 0$, (b) post-scission P–λ relation, $N_1 = 0.75$, $N_2 = 0.25$, (c) post-scission P–λ relation, $N_1 = 0.5$, $N_2 = 0.5$, (d) post-scission P–λ relation, $N_1 = 0.25$, $N_2 = 0.75$.

occurs at a larger stretch. Although not shown, similar results are obtained when $\alpha^{(1)} = \alpha^{(2)} = 0.3$, when the plots of P vs. λ are monotonic.

Figure 7 shows plots of P vs. λ for decreasing N_1 and increasing N_2 when $\alpha^{(1)} = 0.15$, $\alpha^{(2)} = 0.3$ and $\overline{\lambda} = 1.2$. In addition to the softening of response, the size of the negatively sloping portion decreases and eventually vanishes. That is, there is a transition from an up-down-up shape to a monotonic one. Although not shown, results for $\alpha^{(1)} = 0.3$ and $\alpha^{(2)} = 0.15$ show softening and a transition from a monotonic shape to an up-down-up one. Interestingly, depending on the Mooney–Rivlin parameters of the new network, scission and crosslinking can apparently stabilize or destabilize the post-scission membrane response compared to the pre-scission one.

9. Concluding Comments

This work is concerned with the thermo-mechanical response of elastomers over a range of temperatures from below a chemorheological temperature, T_{cr}, when no microstructural changes occur, to above T_{cr} when microstructural changes occur due to scission and crosslinking. A constitutive model is used to explore the effects of these microstructural changes on the response of a spherical elastomeric membrane that has first been inflated to a fixed state. It is then subjected to a temperature history that is increased from below T_{cr} to above T_{cr} and then returned to its initial value. The pre-scission pressure–radius relation is compared to the post-scission one for a variety of conditions and material properties. It is shown that there is permanent set when the inflating pressure is removed and softening of the subsequent response. The permanent set and softening of response are shown to increase with both the amount of scission and the prescribed radius during scission.

In addition, it is shown that the shape of the pressure–radius relation evolves due to scission. It may have an up-down-up shape whose local maximum and minimum decrease with both the amount of scission and the prescribed radius during scission. Depending on the relative properties of the networks, an up-down-up shape may become monotonic or a monotonic shape may develop into an up-down-up shape. The local maxima and minima are limit load instabilities. Although not studied here, bifurcation points may also exist that lead to non-spherical deformations. Thus, a spherical membrane that is initially stable in its virgin state may become unstable after scission and crosslinking. This interesting question of how scission affects the stability of a spherical membrane is left to future work. In summary, a membrane that meets a set of operating criteria under pre-scission conditions may, as a result of microstructural changes, fail to meet those criteria under post-scission conditions.

Appendix

Consider the expression for stress in (2.3) for times $t > t_4$ with $W^{(1)}(I_1, I_2, T) = TW^{(1)}(I_1, I_2)$, $W^{(2)}(\hat{\mathrm{I}}_1, \hat{\mathrm{I}}_2, T) = TW^{(2)}(\hat{\mathrm{I}}_1, \hat{\mathrm{I}}_2)$. The deformation is assumed to be unchanged for times $\bar{t} \le \hat{t} \le t_4$, i.e., $\mathbf{x}(\hat{t}) = \mathbf{x}(\bar{t})$, and is arbitrary for times $t > t_4$, i.e., $\mathbf{x} = \mathbf{x}(t)$ is unspecified. The temperature history is assumed to be that described in Section 4. Then, $\hat{\mathbf{G}} = \partial\mathbf{x}(t)/\partial\mathbf{x}(\hat{t}) = \partial\mathbf{x}(t)/\partial\mathbf{x}(\bar{t})$, i.e., the deformation gradient of configurations for $t > t_4$ with respect to configurations for $\bar{t} < \hat{t} < t_4$ is independent of $\hat{t}$.

For notational convenience, let $\mathbf{x}(\bar{t}) = \bar{\mathbf{x}}$ and $\mathbf{x}(\hat{t}) = \hat{\mathbf{x}}$. Then, $\hat{\mathbf{G}} = \partial\mathbf{x}/\partial\hat{\mathbf{x}}$ is now denoted by $\overline{\mathbf{G}} = \partial\mathbf{x}/\partial\bar{\mathbf{x}}$. The tensor $\hat{\mathbf{B}}$ in the integrand of (2.3), now denoted by $\overline{\mathbf{B}}$, is given by $\overline{\mathbf{B}} = \overline{\mathbf{G}}\overline{\mathbf{G}}^T$, and is independent of $\hat{t}$, $\bar{t}. < \hat{t} < t_4$ On using the assumption that both networks are Mooney–Rivlin materials, along with (5.3) and (5.4), the expression for stress in (2.3) becomes

$$\frac{\sigma}{C_o} = -\frac{p}{C_o}\mathbf{I} + N_1\left(\mathbf{B} - \alpha^{(1)}\mathbf{B}^{-1}\right) + N_2\left(\overline{\mathbf{B}} - \alpha^{(2)}\overline{\mathbf{B}}^{-1}\right). \tag{A.1}$$

The stress can now be related to deformation from the permanent set state. Let $\mathbf{F} = \mathbf{G}_{set}\mathbf{F}_{set}$, where $\mathbf{F}_{set} = \partial\mathbf{x}_{set}/\partial\mathbf{X}$ is the deformation gradient of the permanent set configuration with respect to the reference configuration and $\mathbf{G}_{set} = \partial\mathbf{x}/\partial\mathbf{x}_{set}$ is the deformation gradient of a configuration at time $t > t_4$ with respect to the permanent set configuration. Then

$$\mathbf{B} = \mathbf{G}_{set}\mathbf{F}_{set}\mathbf{F}_{set}^T\mathbf{G}_{set}^T. \tag{A.2}$$

Next, let $\overline{\mathbf{F}} = \partial\overline{\mathbf{x}}/\partial\mathbf{X}$ be the deformation gradient of the configuration held fixed during $\bar{t} \le \hat{t} \le t_4$ with respect to the reference configuration. Then $\overline{\mathbf{G}} = \partial\mathbf{x}/\partial\overline{\mathbf{x}}$ can be expressed as $\overline{\mathbf{G}} = \mathbf{G}_{\text{set}}\mathbf{F}_{\text{set}}\overline{\mathbf{F}}^{-1}$ and

$$\overline{\mathbf{B}} = \mathbf{G}_{\text{set}}\mathbf{F}_{\text{set}}\overline{\mathbf{F}}^{-1}\overline{\mathbf{F}}^{-T}\mathbf{F}_{\text{set}}{}^{T}\mathbf{G}_{\text{set}}{}^{T}. \tag{A.3}$$

For the inflated spherical membrane, the deformation at each material element is an equal biaxial stretch. Thus,

$$\mathbf{F}_{\text{set}} = \begin{bmatrix} \frac{1}{\lambda_{\text{set}}^2} & 0 & 0 \\ 0 & \lambda_{\text{set}} & 0 \\ 0 & 0 & \lambda_{\text{set}} \end{bmatrix}, \qquad \overline{\mathbf{F}} = \begin{bmatrix} \frac{1}{\bar{\lambda}^2} & 0 & 0 \\ 0 & \bar{\lambda} & 0 \\ 0 & 0 & \bar{\lambda} \end{bmatrix}. \tag{A.4}$$

Then

$$\mathbf{F}_{\text{set}}\mathbf{F}_{\text{set}}^{T} = \lambda_{\text{set}}^2\mathbf{I} + \left(\frac{1}{\lambda_{\text{set}}^4} - \lambda_{\text{set}}^2\right)\mathbf{I}^{(1)} \tag{A.5}$$

and

$$\mathbf{F}_{\text{set}}\overline{\mathbf{F}}^{-1}\overline{\mathbf{F}}^{-T}\mathbf{F}_{\text{set}}{}^{T} = \frac{\lambda_{\text{set}}^2}{\bar{\lambda}^2}\mathbf{I} + \left(\frac{\bar{\lambda}^4}{\lambda_{\text{set}}^4} - \frac{\lambda_{\text{set}}^2}{\bar{\lambda}^2}\right)\mathbf{I}^{(1)}, \tag{A.6}$$

where

$$\mathbf{I}^{(1)} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}. \tag{A.7}$$

By (A.2) and (A.5),

$$\mathbf{B} = \lambda_{\text{set}}^2\mathbf{G}_{\text{set}}\mathbf{G}_{\text{set}}^{T} + \left(\frac{1}{\lambda_{\text{set}}^4} - \lambda_{\text{set}}^2\right)\mathbf{G}_{\text{set}}\mathbf{I}^{(1)}\mathbf{G}_{\text{set}}^{T}. \tag{A.8}$$

By (A.3) and (A.6),

$$\overline{\mathbf{B}} = \frac{\lambda_{\text{set}}^2}{\bar{\lambda}^2}\mathbf{G}_{\text{set}}\mathbf{G}_{\text{set}}{}^{T} + \left(\frac{\bar{\lambda}^4}{\lambda_{\text{set}}^4} - \frac{\lambda_{\text{set}}^2}{\bar{\lambda}^2}\right)\mathbf{G}_{\text{set}}\mathbf{I}^{(1)}\mathbf{G}_{\text{set}}{}^{T}. \tag{A.9}$$

In a similar manner, it can be shown that

$$\mathbf{B}^{-1} = \frac{1}{\lambda_{\text{set}}^2}\mathbf{G}_{\text{set}}^{-T}\mathbf{G}_{\text{set}}^{-1} + \left(\lambda_{\text{set}}^4 - \frac{1}{\lambda_{\text{set}}^2}\right)\mathbf{G}_{\text{set}}^{-T}\mathbf{I}^{(1)}\mathbf{G}_{\text{set}}^{-1} \tag{A.10}$$

and

$$\overline{\mathbf{B}}^{-1} = \frac{\bar{\lambda}^2}{\lambda_{\text{set}}^2}\mathbf{G}_{\text{set}}^{-T}\mathbf{G}_{\text{set}}^{-1} + \left(\frac{\lambda_{\text{set}}^4}{\bar{\lambda}^4} - \frac{\bar{\lambda}^2}{\lambda_{\text{set}}^2}\right)\mathbf{G}_{\text{set}}^{-T}\mathbf{I}^{(1)}\mathbf{G}_{\text{set}}^{-1}. \tag{A.11}$$

Substitution of (A.8)–(A.11) into (A.1) gives

$$\frac{\sigma}{C_o} = -\frac{p}{C_o}\mathbf{I} + \left(N_1 + \frac{N_2}{\overline{\lambda}^2}\right)\lambda_{\text{set}}^2 \mathbf{G}_{\text{set}}\mathbf{G}_{\text{set}}^T - \frac{1}{\lambda_{set}^2}\left(N_1\alpha^{(1)} + N_2\alpha^{(2)}\overline{\lambda}^2\right)\mathbf{G}_{\text{set}}^{-T}\mathbf{G}_{\text{set}}^{-1} + \left[-\left(N_1 + \frac{N_2}{\overline{\lambda}^2}\right)\lambda_{\text{set}}^2 + \frac{1}{\lambda_{\text{set}}^4}\left(N_1 + N_2\overline{\lambda}^4\right)\right]\mathbf{G}_{\text{set}}\mathbf{I}^{(1)}\mathbf{G}_{\text{set}}^T + \left[-\lambda_{\text{set}}^4\left(N_1\alpha^{(1)} + \frac{N_2\alpha^{(2)}}{\overline{\lambda}^4}\right) + \frac{1}{\lambda_{\text{set}}^2}\left(N_1\alpha^{(1)} + N_2\alpha^{(2)}\overline{\lambda}^2\right)\right]\mathbf{G}_{\text{set}}^{-T}\mathbf{I}^{(1)}\mathbf{G}_{\text{set}}^{-1}. \tag{A.12}$$

This gives the stress in terms of the deformation gradient $\mathbf{G}_{\text{set}}$ from the permanent set configuration. It has the form of a constitutive equation for a material that is transversely isotropic about the radial direction.

When the membrane is inflated from its permanent set configuration and remains spherical,

$$\mathbf{G}_{\text{set}} = \begin{bmatrix} \frac{1}{\mu^2} & 0 & 0 \\ 0 & \mu & 0 \\ 0 & 0 & \mu \end{bmatrix}, \tag{A.13}$$

where $\mu = \lambda/\lambda_{\text{set}}$. From (A.12)

$$\frac{\sigma_{33} - \sigma_{11}}{C_o} = \left(\mu^2 - \frac{1}{\mu^4}\right)\left[\left(N_1 + \frac{N_2}{\overline{\lambda}^2}\right)\lambda_{\text{set}}^2 + \frac{\mu^2}{\lambda_{\text{set}}^2}\left(N_1\alpha^{(1)} + N_2\alpha^{(2)}\overline{\lambda}^2\right)\right] + \left[\left(N_1 + \frac{N_2}{\overline{\lambda}^2}\right)\lambda_{\text{set}}^2 - \frac{1}{\lambda_{\text{set}}^4}\left(N_1 + N_2\overline{\lambda}^4\right)\right]\frac{1}{\mu^4} + \left[\lambda_{\text{set}}^4\left(N_1\alpha^{(1)} + \frac{N_2\alpha^{(2)}}{\overline{\lambda}^4}\right) - \frac{1}{\lambda_{\text{set}}^2}\left(N_1\alpha^{(1)} + N_2\alpha^{(2)}\overline{\lambda}^2\right)\right]\mu^4. \tag{A.14}$$

Since σ_{11} is considered negligible compared to σ_{33} in membrane theory, the membrane stress is given by $(\sigma_{33} - \sigma_{11})/C_o \approx \sigma_{33}/C_o = \sigma/C_o$.

When $\mu = 1$, the membrane is in the permanent set state with $\sigma = 0$. (A.14) reduces to

$$\left(N_1 + \frac{N_2}{\overline{\lambda}^2}\right)\lambda_{\text{set}}^2 - \frac{1}{\lambda_{\text{set}}^4}\left(N_1 + N_2\overline{\lambda}^4\right) + \lambda_{\text{set}}^4\left(N_1\alpha^{(1)} + \frac{N_2\alpha^{(2)}}{\overline{\lambda}^4}\right) - \frac{1}{\lambda_{\text{set}}^2}\left(N_1\alpha^{(1)} + N_2\alpha^{(2)}\overline{\lambda}^2\right) = 0, \tag{A.15}$$

which is a restatement of (7.1). (A.14) then simplifies to

$$\sigma = \left(\mu^2 - \frac{1}{\mu^4}\right)\left[\left(N_1 + \frac{N_2}{\bar{\lambda}^2}\right)\lambda_{set}^2 + \frac{\mu^2}{\lambda_{set}^2}\left(N_1\alpha^{(1)} + N_2\alpha^{(2)}\bar{\lambda}^2\right)\right]$$
$$- \left[\left(N_1 + \frac{N_2}{\bar{\lambda}^2}\right)\lambda_{set}^2 - \frac{1}{\lambda_{set}^4}\left(N_1 + N_2\bar{\lambda}^4\right)\right]\left(\mu^4 - \frac{1}{\mu^4}\right). \tag{A.16}$$

Finally, substituting (A.16) and $\lambda = \mu\lambda_{set}$ into (3.8) gives (7.3) and (7.4).

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