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Modeling the thermomechanical effects of crystallization in natural rubber: I. The theoretical structure

Mehrdad Negahban*

Department of Engineering Mechanics and The Center for Materials Research and Analysis, PO Box 880526, W317-4 Nebraska Hall, The University of Nebraska–Lincoln, Lincoln, NE 68588-0526, USA

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Abstract

Using the theoretical framework introduced in a previous work (Negahban, M., 1997. Thermodynamic modeling of the thermomechanical effects of polymer crystalliation: A general theoretical structure. International Journal of Engineering Science 35, 277–298), a model is proposed for capturing the thermomechanical response of natural rubber during and after crystallization. The model is given in a form which will allow the incorporation of both the known mechanical response and the known thermal response observed before, during, and after crystallization in natural rubber. In particular, one can include in this model known experimental results characterizing the stress relaxation due to crystallization, increase in rigidity with crystallization, heat capacity, heat of crystallization, and the melting temperature. In this first article, a basic overview is presented of the model, and the thermal expansion of the amorphous and crystalline phases of natural rubber are incorporated into the model. The specific form of the free energy used to characterize the response of natural rubber is presented in the following articles. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Interest in crystallization of polymers, and in particular natural rubber, has a long history. This interest was motivated by the large thermal and mechanical effects associated with this phase transition. The early works of Bekkedahl (1934) and, later, of Wood and Bekkedahl (1946) give a clear

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* Fax: +001-402-472-8292.
E-mail address: mnegahban@unl.edu (M. Negahban).

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Nomenclature

a	Rate of crystallization in mass per unit time
b	Mass fraction of amorphous material ($= 1 - \int_{t_s}^{t} a(s)\mathrm{d}s$)
$\mathbf{B}$	Left Cauchy stretch tensor ($=\mathbf{F}\mathbf{F}^T$)
$\mathbf{C}$	Right Cauchy stretch tensor ($=\mathbf{F}^T\mathbf{F}$)
$\mathbf{F}(t)$	Deformation gradient at current time t
$\mathbf{F}_s(t)$	Relative deformation gradient comparing the configuration at time t to the configuration at time s
$\mathbf{F}^*(t)$	$= \frac{1}{J^{1/3}(t)}\mathbf{F}(t)$
$\mathbf{F}_s^*(t)$	$= \frac{J^{1/3}(s)}{J^{1/3}(t)}\mathbf{F}_s(t)$
$I_1, \ldots, I_{10}$	isotropic invariants of $\mathbf{B}(t)$ and $\mathbf{B}_s(t)$
$\mathbf{I}$	Second order tensor identity
J	Volume ratio ($=\det[\mathbf{F}]$)
J_A	Volume ratio of the amorphous polymer
J_C	Volume ratio of the fully crystalline polymer
$\mathbf{L}$	Velocity gradient ($= \dot{\mathbf{F}}(t)\mathbf{F}^{-1}(t)$)
p	Indeterminate scalar associated with incompressibility
t	Current time
t_s	Starting time of crystallization
$\mathbf{T}$	Cauchy stress tensor (true stress)
η	Entropy per unit mass
θ	Temperature
ρ_0	Mass density in reference configuration
ρ	Mass density
ρ_A	Mass density of the amorphous polymer
ρ_C	Mass density of the fully crystalline polymer
σ_ave	Average principal Cauchy (true) stress ($=1/3\ \mathrm{tr}(\mathbf{T})$)
ψ	Free energy per unit mass
$\psi_\mathrm{A}(t)$	Effective free energy of the amorphous part
$\psi_\mathrm{C}(t, s)$	Effective free energy at the current time of the crystals (or parts of crystals) formed at time 's'
'∂_A'	Partial derivative with respect to 'A'
'$\dot{\overline{\ \ }}$'	Material time derivative of overlined quantity

experimental description of the time dependant change in volume due to gradual crystallization as a function of temperature in isothermal conditions. The early work of Treloar (1941) shows that the change in volume, and hence crystallization, is strongly influenced by stretching as he presents experiments showing the change in density as a function of time for different stretches. The work of Gent (1954) clearly demonstrates that there is a linear relation between stress relaxation and volume reduction (crystallization) in natural rubber. Leitner (1955) and, later, Stevenson (1983, 1989) clearly demonstrate that crystallization has a strong effect on the elastic moduli of natural rubber, to the extent of increasing it by a factor of several hundred.

Crystallization in natural rubber is a gradual phase transition which may occur over a large interval of time and is accompanied by many thermomechanical events, as described above. In this and in the following articles, a theoretical structure for modeling this phase transition is proposed and specific material functions are evaluated to reproduce known experimental results. This proposed structure models crystallization as a continuous process of transformation from one elastic solid to another.

The goal of these articles is to phenomenologically characterize the transition seen when amorphous natural rubber transforms into a semi-crystalline material, by capturing *in a single model* the thermal and mechanical events which accompany each stage of this gradual transformation. This is motivated by the recent resurgence of interest to develop constitutive equations capable of capturing more accurately the thermal and/or mechanical behavior of polymers under varying external conditions (Chew et al., 1988; Ziabicki, 1996a; Ziabicki, 1996b; Ding and Spruiell, 1997; Phillips and Manson, 1997; Hoffman and Miller, 1997), as is characteristic of most manufacturing and design conditions. In turn, this drive may be fueled by an increase in computational capability that allows the simulation of more complex processes.

The model proposed in this article is based on using a mathematical structure introduced by Negahban (1997). This structure captures the effects of crystallization by modeling the polymer at each stage of its transformation as a composite of an amorphous phase and an array of different crystals. The current free energy, $\psi(t)$, of this composite is modeled by

$$\psi(t) = b(t)\psi_{\mathrm{A}}(t) + \int_{t_{\mathrm{s}}}^{t} \psi_{\mathrm{C}}(t, s)a(s)\mathrm{d}s, \tag{1}$$

where $b(t)$ is the current mass fraction of amorphous material, $a(s)$ is the rate of crystallization at time s, t_{s} is the time crystallization starts, t is the current time, $\psi_{\mathrm{A}}(t)$ is the effective free energy per unit mass in the amorphous fraction and $\psi_{\mathrm{C}}(t, s)$ is the effective current free energy per unit mass in the crystal created at time s. Since it is assumed that there is no third phase in the material, the relation between the fraction of amorphous material and the rate of crystallization is given by

$$b(t) = 1 - \int_{t_{\mathrm{s}}}^{t} a(s)\mathrm{d}s. \tag{2}$$

The effective free energy in the amorphous portion is assumed to be a function of the deformation gradient, temperature and the extent of the amorphous material. This is written as

$$\psi_{\mathrm{A}}(t) = \psi_{\mathrm{A}}^{\dagger}[\mathbf{F}(t), \theta(t), b(t)], \tag{3}$$

where $\mathbf{F}(t)$ is the current value of the deformation gradient, $\theta(t)$ is the current value of the temperature, and '†' refers to the mathematical function describing this physical quantity.

The effective current free energy of the crystal created at time s is assumed to depend on the conditions at the time of crystallization and the conditions imposed on the crystal since crystallization. This is mathematically characterized by the expression

$$\psi_{\mathrm{C}}(t, s) = \psi_{\mathrm{C}}^{\dagger}[\mathbf{F}(t), \theta(t), b(t), \mathbf{F}(s), \theta(s), b(s)]. \tag{4}$$

Similar assumptions to those presented in Eqs. (1), (3) and (4) are made for the expressions for stress and for entropy, with the addition of an indeterminate scalar $p(t)$ associated with an assumption made in regards to the incompressibility of each phase, as will be described in detail in a following section.

In addition to developing a model for the free energy of natural rubber, to obtain a complete model one needs to provide a model for the unconstrained thermal expansion of the amorphous and crystalline phases. One also needs to provide a model for the rate of crystallization and for the heat flux. The way in which one incorporates the information on thermal expansion into the model is described in Section

3. The model for the rate of crystallization must depend on the history of the events occurring during crystallization, and also must depend on the indeterminate scalar associated with the incompressibility described in Section 3. This is described by

$$a(t) = a^{\dagger}\left[\mathop{\mathbf{F}(s)}_{s=t_{\mathrm{s}}}^{t},\ \mathop{\theta(s)}_{s=t_{\mathrm{s}}}^{t},\ \mathop{b(s)}_{s=t_{\mathrm{s}}}^{t},\ p(t)\right]. \tag{5}$$

As is described in Negahban (1997), each of the constitutive models must satisfy the assumption of material frame indifference, and also must be constrained to be consistent with the initial isotropy of the undeformed amorphous material before crystallization.

It will be shown that within the proposed structure, in a single model one can capture both the thermal and mechanical effects associated with crystallization of natural rubber. These effects include:

1. Thermal expansion of unconstrained natural rubber at constant crystallinity,
2. The melting temperature of unconstrained natural rubber,
3. The dependence of the melting temperature on pressure and extension,
4. Heat capacity of unconstrained natural rubber at constant crystallinity,
5. The heat of fusion for crystals of natural rubber at the melting temperature,
6. The initial rubbery response of the amorphous material,
7. The increase in elastic modulus during unconstrained crystallization of natural rubber,
8. Stress relaxation in stretched natural rubber during crystallization.

Also, as a result of the general structure of the model, one can relate or simulate thermal and mechanical characteristics of crystallization under different thermomechanical loading conditions. For example, by simulating crystallization under stretch, one can evaluate the relation between residual stretch and temperature, and, as a result, evaluate the effect of crystallization under stretch on the anisotropic thermal expansion of natural rubber.

The model proposed in this article differs from the microstructural model proposed by Ahzi et al. (1995) and Parks (1995) in that the current model attempts to characterize both the thermal and the mechanical events occurring during the process of crystallization, but the mentioned microstructural models only predict mechanical response *after* crystallization, and only when given the existing microstructure. Unlike the proposed model, these models are not designed to predict the effects of processing on the current response of the polymer. Yet, the microstructural model proposed by Ahzi et al. (1995) and Parks (1995) are developed to predict the elastic–plastic response of a semi-crystalline polymer after crystallization if one assumes the microstructure, a feature not included in the current model. The current model also differs from many of the other phenomenological fits to experimental results in that the current model incorporates the initial isotropic character of the undeformed amorphous natural rubber as a constraint, it is consistent with continuum thermodynamics and it fits all the different thermal and mechanical results *within a single model*.

As in other polymers, crystallization in natural rubber occurs in the rubbery range of its material response. This range is characterized at the lower limit by the glass transition temperature and at the higher limit by the melting temperature. For natural rubber this range is from about −50°C to about 36°C. As will be shown in the following articles, this range is not fixed and changes with changes in loading conditions. A recent review article by Magill (1995) provides an overview of the research conducted to date on the response of natural rubber. Also, the books by Treloar (1975), Mandelkern (1964) and Wunderlich (1973, 1976, 1980) contain invaluable information on crystallization of polymers.

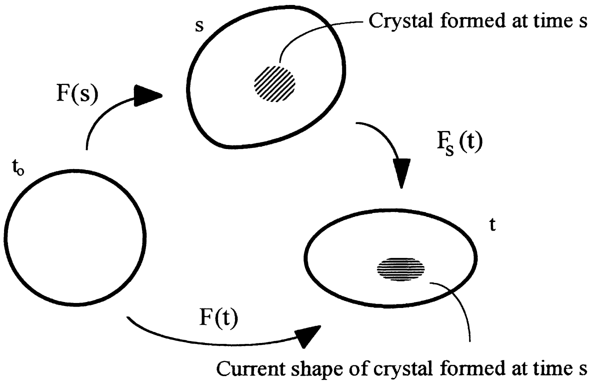

Fig. 1. Reference configuration, intermediate configuration, current configuration, and kinematical variables.

2. Kinematics and notation

On a macroscopic level the kinematics of deformation of the material body is characterized by a reference configuration and a function describing the motion of each point in this configuration. The deformation gradient will be denoted by $\mathbf{F}$, which is the first gradient of this function with respect to changes in position in the reference configuration. Fig. 1 shows a schematic of three configurations:

(a) the reference configuration κ_0,
(b) the current configuration $\kappa(t)$, and
(c) an intermediate configuration $\kappa(s)$.

Also, in this same figure is shown the deformation gradient at time t, $\mathbf{F}(t)$, the deformation gradient at time s, $\mathbf{F}(s)$ and the relative deformation gradient comparing the change in configuration between time s and time t, $\mathbf{F}_s(t)=\mathbf{F}(t)\mathbf{F}^{-1}(s)$, where the superscript ‘−1’ refers to the inverse. From each of these deformation gradients one can obtain a left Cauchy stretch tensor $\mathbf{B}=\mathbf{F}\mathbf{F}^{\mathrm{T}}$, and a right Cauchy stretch tensor $\mathbf{C}=\mathbf{F}^{\mathrm{T}}\mathbf{F}$, where the superscript ‘T’ refers to the transpose. The velocity gradient will be denoted by $\mathbf{L}=\dot{\mathbf{F}}\mathbf{F}^{-1}$, where ‘˙’ denotes the material time derivative. The volume ratio $J(s)$ is the ratio of volume of the neighborhood of a material point at time s to its volume in the reference configuration, and is calculated from the deformation gradient using $J(s)=\det[\mathbf{F}(s)]$, where det[.] denotes the determinant operation. The operator ‘·’ between two vectors denotes the dot product. The operator ‘:’ between second order tensors $\mathbf{A}$ and $\mathbf{B}$ is defined as $\mathbf{A}:\mathbf{B}=\mathrm{tr}(\mathbf{A}\mathbf{B}^{\mathrm{T}})$, where tr(.) denotes the trace operation. The operation ‘∂_A’ will denote the partial derivative with respect to ‘A’, where ‘A’ may be a scalar or tensor quantity. For example, the partial derivative $\partial_{\mathbf{A}}$ of the function $\phi(\mathbf{A})$ of the single second order tensor argument $\mathbf{A}$ will be defined by the relation

$$\dot{\phi}=\partial_{\mathbf{A}}\phi:\dot{\mathbf{A}}. \tag{6}$$

3. Assumption of incompressibility of each phase

It is common in the literature on polymer crystallization to directly relate the change in volume under isothermal conditions to the extent of crystallinity (Gent, 1954). This is done by assuming each phase of the polymer to be incompressible, therefore, allowing changes in volume to occur only when matter transforms from one phase to the other.

Even though this is not an essential assumption, it allows one to simplify the resulting model by clearly decoupling volumetric changes due to crystallization from the volumetric changes due to thermal expansion. On the macroscopic level, the material is assumed to be a continuum that follows the basic laws of continuum thermodynamics, and as a result must satisfy the law of conservation of mass. This requires that the current mass density, $\rho(t)$, and the current volume ratio, $J(t)$, be related by the relation

$$\rho(t)J(t) = \rho_0, \tag{7}$$

where ρ_0 is the mass density in the reference configuration (for which the volume ratio is, by definition, equal to unity).

At each material point on the macroscopic scale (the continuum scale), one may have both amorphous rubber and crystalline rubber. Each one of these two phases is assumed to obey a similar law of conservation of mass as the macroscopic continuum, but with the stipulation that the volume of each phase is controlled entirely by temperature. The result is that each phase of the material becomes incompressible if the temperature is held constant. Therefore, in isothermal processes volume change on the macroscopic level may be accommodated only through phase transition. The relation between the density and volume ratio of each phase will be

$$\rho_{\mathrm{A}}(\theta)J_{\mathrm{A}}(\theta) = \rho_{\mathrm{A}_0},\ \rho_{\mathrm{C}}(\theta)J_{\mathrm{C}}(\theta) = \rho_{\mathrm{C}_0}, \tag{8}$$

where $\rho_{\mathrm{A}}(\theta)$ and $\rho_{\mathrm{C}}(\theta)$ are the densities as a function of temperature of the amorphous and crystalline rubber, respectively, $J_{\mathrm{A}}(\theta)$ and $J_{\mathrm{C}}(\theta)$ are the volume ratios as a function of temperature of the amorphous and crystalline rubber, respectively, and ρ_{A_0} and ρ_{C_0} are the densities at the reference temperature (in the reference configuration) of the amorphous and crystalline rubber, respectively.

Following the preceding assumptions and the hypothesis that at each material point, the total macroscopic volume is the sum of the volume of the amorphous part and the crystals, one will arrive at the relation

$$\frac{1}{\rho(\theta,\ b)} = \frac{1}{\rho_{\mathrm{A}}(\theta)}b + \frac{1}{\rho_{\mathrm{C}}(\theta)}(1-b), \tag{9}$$

where $\rho(\theta,\ b)$ is the macroscopic density. Invoking conservation of mass, as given in Eq. (7), one obtains

$$J(\theta,\ b) = \frac{\rho_0}{\rho_{\mathrm{A}}(\theta)}b + \frac{\rho_0}{\rho_{\mathrm{C}}(\theta)}(1-b), \tag{10}$$

where $J(\theta,\ b)$ is the macroscopic volume ratio. Introduction of Eq. (8) results in

$$J(\theta,\ b) = \frac{\rho_0}{\rho_{\mathrm{A}_0}}J_{\mathrm{A}}(\theta)b + \frac{\rho_0}{\rho_{\mathrm{C}_0}}J_{\mathrm{C}}(\theta)(1-b). \tag{11}$$

Since $J = \det(\mathbf{F})$, Eq. (10) is a restriction on how $\mathbf{F}$ may change. The relation between the rate of change of volume, crystallinity and temperature is obtained by taking the derivative of Eq. (10) to get

$$\dot{J} = -\left[\frac{\rho_0 b}{\rho_{\mathrm{A}}^2}\frac{\mathrm{d}\rho_{\mathrm{A}}}{\mathrm{d}\theta} + \frac{\rho_0(1-b)}{\rho_{\mathrm{C}}^2}\frac{\mathrm{d}\rho_{\mathrm{C}}}{\mathrm{d}\theta}\right]\dot{\theta} - \left[\frac{\rho_0}{\rho_{\mathrm{A}}} - \frac{\rho_0}{\rho_{\mathrm{C}}}\right]a, \tag{12}$$

or one can rewrite this in the form

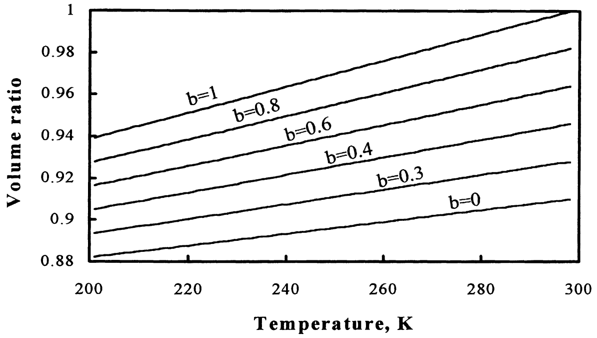

Fig. 2. Volume ratio as a function of temperature for natural rubber at different degrees of crystallinity.

$$\dot{J} = \left[\frac{\rho_0 b}{\rho_{A_0}} \frac{dJ_A}{d\theta} + \frac{\rho_0 (1-b)}{\rho_{C_0}} \frac{dJ_C}{d\theta} \right] \dot{\theta} - \left[\frac{\rho_0}{\rho_{A_0}} J_A - \frac{\rho_0}{\rho_{C_0}} J_C \right] a, \tag{13}$$

where use is made of the relation

$$\dot{b}(t) = -a(t). \tag{14}$$

For natural rubber, one can use the following approximate expressions for $J_A(\theta)$ and $J_C(\theta)$:

$$J_A(\theta) = 1 + \frac{dJ_A}{d\theta}(\theta - \theta_0) \tag{15}$$

and

$$J_C(\theta) = 1 + \frac{dJ_C}{d\theta}(\theta - \theta_0), \tag{16}$$

where θ_0 is the reference temperature. The values provided by Van Krevelen and Hoftyzer (1976) for $\theta_0 = 298°\mathrm{K}$ yields

$$\frac{dJ_A}{d\theta} = 6.249 \times 10^{-4}\ 1/\mathrm{K}, \quad \frac{dJ_C}{d\theta} = 3.132 \times 10^{-4}\ 1/\mathrm{K}. \tag{17}$$

For natural rubber, one can take $\rho_0 = \rho_{A_0} = 910\,\mathrm{kg/m^3}$ and $\rho_{C_0} = 1000\,\mathrm{kg/m^3}$. Fig. 2 shows the volume ratio (evaluated relative to the volume at 298°K) as a function of temperature for natural rubber. Each graph represents a different constant degree of crystallinity. During a normal cooling process, which includes crystallization, the volume ratio would actually be changing more rapidly as the material crystallizes and, therefore, moves from the curve for one degree of crystallinity to another. As can be seen, the volume changes due to crystallization are comparable to those associated with thermal expansion.

4. The constraints on the free energy

As described in Negahban (1997), the model for the free energy must satisfy the constraints imposed upon it by material frame indifference and also by the initial isotropy of the undeformed amorphous rubber before crystallization. The result of imposing these restrictions is that the model for the free energy must be of the form

$$\psi_A(t) = \psi_A^{\dagger\dagger}[I_1, I_2, I_3, \theta(t), b(t), p(t)] \tag{18}$$

$$\psi_C(t,s) = \psi_C^{\dagger\dagger}[I_1, \ldots, I_{10}, \theta(t), \theta(s), b(t), b(s), p(t)], \tag{19}$$

where

$$I_1 = \mathrm{tr}[\mathbf{B}(t)],$$

$$I_2 = \mathrm{tr}[\mathbf{B}^2(t)],$$

$$I_3 = \mathrm{tr}[\mathbf{B}^3(t)],$$

$$I_4 = \mathrm{tr}[\mathbf{B}_s(t)],$$

$$I_5 = \mathrm{tr}\left[\mathbf{B}_s^2(t)\right],$$

$$I_6 = \mathrm{tr}\left[\mathbf{B}_s^3(t)\right],$$

$$I_7 = \mathrm{tr}[\mathbf{B}(t)\mathbf{B}_s(t)],$$

$$I_8 = \mathrm{tr}\left[\mathbf{B}(t)\mathbf{B}_s^2(t)\right],$$

$$I_9 = \mathrm{tr}\left[\mathbf{B}^2(t)\mathbf{B}_s(t)\right],$$

$$I_{10} = \mathrm{tr}\left[\mathbf{B}^2(t)\mathbf{B}_s^2(t)\right]. \tag{20}$$

I_1,..., I_{10} represent the ten isotropic invariants of the two tensors $\mathbf{B}(t)$ and $\mathbf{B}_s(t)$. As a result of the constraint introduced in the last section, volumetric changes are either a result of thermal expansion or of phase transition. As such, they should not influence the free energy. To avoid unnecessary complications, without loss of generality, one can replace the above set of invariants given in Eq. (20) by ones constructed from deformation gradients which have had the volumetric changes extracted from them. To this end, the deformation gradients $\mathbf{F}^*(t)$ and $\mathbf{F}_s^*(t)$ will be introduced which are obtained from the deformation gradients $\mathbf{F}(t)$ and $\mathbf{F}_s(t)$ by the relations

$$\mathbf{F}^*(t) = \frac{1}{J^{1/3}(t)}\mathbf{F}(t)$$

and

$$\mathbf{F}_s^*(t) = \frac{J^{1/3}(s)}{J^{1/3}(t)}\mathbf{F}_s(t). \tag{21}$$

Without any loss of generality, one can replace $I_1,..., I_{10}$ in Eq. (20) by $I^*_1, \ldots, I^*_{10}$, which are obtained by replacing in Eq. (20) the tensor $\mathbf{B}(t)$ by $\mathbf{B}*(t)=\mathbf{F}*(t)\mathbf{F}^{*\mathrm{T}}(t)$ and $\mathbf{B}_s(t)$ by $\mathbf{B}*_s(t)=\mathbf{F}*_s(t)\mathbf{F}_s^{*\mathrm{T}}(t)$.

The entropy production inequality, also known as the Clausius–Duhem inequality, requires that at each material point, one has

$$\rho\dot{\psi}-\mathrm{tr}(\mathbf{TL})+\rho\eta\dot{\theta}+\frac{1}{\theta}\mathbf{q}\cdot\mathbf{g}\leq 0 \tag{22}$$

for every possible process, where η is entropy density, $\mathbf{T}$ is the Cauchy stress tensor, $\mathbf{q}$ is the heat flux, and $\mathbf{g}$ is the temperature gradient. Imposing this constraint on the material response results in the relations

$$\mathbf{T}(t)=p(t)\mathbf{I}+\rho(t)\left\{b(t)\partial_{\mathbf{F}(t)}\psi_{\mathrm{A}}(t)+\int_{t_{\mathrm{s}}}^{t}\left[\partial_{\mathbf{F}(t)}\psi_{\mathrm{C}}(t,s)+\partial_{\mathbf{F}_s(t)}\psi_{\mathrm{C}}(t,s)\mathbf{F}^{-\mathrm{T}}(s)\right]a(s)\mathrm{d}s\right\}\mathbf{F}^{\mathrm{T}}(t), \tag{23}$$

$$\eta(t)=-b(t)\partial_{\theta(t)}\psi_{\mathrm{A}}(t)-\int_{t_{\mathrm{s}}}^{t}\partial_{\theta(t)}\psi_{\mathrm{C}}(t,s)a(s)\mathrm{d}s-p(t)\left[\frac{b(t)}{\rho_{\mathrm{A}}^2(t)}\frac{\mathrm{d}\rho_{\mathrm{A}}}{\mathrm{d}\theta}+\frac{1-b(t)}{\rho_{\mathrm{C}}^2(t)}\frac{\mathrm{d}\rho_{\mathrm{C}}}{\mathrm{d}\theta}\right], \tag{24}$$

$$-\xi(t)a(t)\leq 0 \tag{25}$$

and

$$-\rho(t)\xi(t)a(t)+\frac{1}{\theta(t)}\mathbf{q}(t)\cdot\mathbf{g}(t)\leq 0, \tag{26}$$

where $p(t)$ is an indeterminate scalar resulting from the incompressibility assumption presented in Section 3 and $\xi(t)$ denotes the current value of the ‘thermodynamic force of crystallization’ given by

$$\xi(t)=\psi_{\mathrm{A}}(t)-\psi_{\mathrm{C}}(t,t)+b(t)\partial_{b(t)}\psi_{\mathrm{A}}(t)+\int_{t_{\mathrm{s}}}^{t}\partial_{b(t)}\psi_{\mathrm{C}}(t,s)a(s)\mathrm{d}s-p(t)\left[\frac{1}{\rho_{\mathrm{A}}(t)}-\frac{1}{\rho_{\mathrm{C}}(t)}\right]. \tag{27}$$

Since the indeterminate scalar p does not, in general, have any physical meaning, it is appropriate to replace it by a more physically based quantity. This will also shorten the expressions derived in the following papers. The parameter selected to replace p is the average principal stress, σ_{ave}, given by

$$\sigma_{\mathrm{ave}}=\frac{1}{3}\,\mathrm{tr}(\mathbf{T}). \tag{28}$$

The average principal stress is *negative the hydrostatic pressure*. Solving for p using Eq. (23) results in

$$p(t)=\sigma_{\mathrm{ave}}(t)-\frac{\rho(t)}{3}\left\{b(t)\mathrm{tr}\left[\partial_{\mathbf{F}(t)}\psi_{\mathrm{A}}(t)\mathbf{F}^{\mathrm{T}}(t)\right]+\int_{t_{\mathrm{s}}}^{t}\left[\mathrm{tr}\left[\partial_{\mathbf{F}(t)}\psi_{\mathrm{C}}(t,s)\mathbf{F}^{\mathrm{T}}(t)\right]\right.\right.$$
$$\left.\left.+\mathrm{tr}\left[\partial_{\mathbf{F}_s(t)}\psi_{\mathrm{C}}(t,s)\mathbf{F}_s^{\mathrm{T}}(t)\right]\right]a(s)\mathrm{d}s\right\}. \tag{29}$$

This relation can be substituted into the above to eliminate p in favor of the more physically based average principal stress.

It should now be noted that even though it is assumed that each phase of natural rubber is incompressible, after substituting Eq. (29) into Eqs. (23)–(26), one can see that both entropy and the thermodynamic force of crystallization depend linearly on hydrostatic pressure. The coefficient of the hydrostatic pressure term in the expression for entropy is fully determined by the extent of crystallization and knowledge of the thermal expansion of the amorphous and crystalline phases, while the coefficient of the hydrostatic pressure in the expression for the thermodynamic force of crystallization is fully obtained from the knowledge of the current values of the density of the two phases.

5. The proposed form of the free energy for natural rubber

Even though the general form of the free energy as described in the last section allows for arbitrary dependence on the isotropic invariants of $\mathbf{B}^*(t)$ and $\mathbf{B}_s^*(t)$, it is convenient to select a simpler dependence. As will be shown in the coming articles, the following form for the free energy is sufficient to describe all of the observed response for natural rubber. The aim is to select the simplest model which will also capture all the observed behaviors.

The free energy for natural rubber in the following articles will be taken to be given by

$$\psi_{\mathrm{A}}(t)=\sum_{i=0}^{2}A_i\left(I_1^*-3\right)^i \tag{30}$$

and

$$\psi_{\mathrm{C}}(t,s)=\sum_{i=0}^{2}C_i\left(I_4^*-3\right)^i, \tag{31}$$

where each A_i is a function of $b(t)$ and $\theta(t)$, and each C_i is a function of $b(t)$, $b(s)$, $\theta(t)$ and $\theta(s)$. There are the following relationships between the invariants

$$I_1^*=\frac{1}{J^{2/3}(t)}I_1,\ I_4^*=\frac{J^{2/3}(s)}{J^{2/3}(t)}I_4, \tag{32}$$

where, from Eq. (10), it is clear that $J(t)$ depends only on $\theta(t)$ and $b(t)$, and $J(s)$ only depends on $\theta(s)$ and $b(s)$. The invariant I_1 is only a function of $\mathbf{F}(t)$ and the invariant I_4 is only a function of $\mathbf{F}_s(t)$.

The following are the partial derivatives of the two invariants used in the model with respect to their respective variables

$$\partial_{\mathbf{F}(t)}I_1=2\mathbf{F}(t),\ \partial_{\mathbf{F}_s(t)}I_4=2\mathbf{F}_s(t). \tag{33}$$

Using the chain rule, one obtains

$$\partial_{\mathbf{F}(t)}\psi_{\mathrm{A}}(t)=\frac{2}{J^{2/3}(t)}\left[A_1+2A_2\left(I_1^*-3\right)\right]\mathbf{F}(t), \tag{34}$$

$$\partial_{\mathbf{F}_s(t)}\psi_{\mathrm{C}}(t,s)=2\frac{J^{2/3}(s)}{J^{2/3}(t)}\left[C_1+2C_2\left(I_4^*-3\right)\right]\mathbf{F}_s(t), \tag{35}$$

and $\partial_{\mathbf{F}(t)}\psi_{\mathrm{C}}(t,s)=0$. Using these derivatives and substitution for p from Eq. (29) results in the following expression for the Cauchy stress tensor

$$\mathbf{T} = \sigma_{\text{ave}}(t)\mathbf{I} + 2\rho(t)b(t)\left[A_1 + 2A_2\left(I_1^* - 3\right)\right]\left[\mathbf{B}^*(t) - \frac{I_1^*}{3}\mathbf{I}\right] + 2\rho(t)\int_{t_s}^{t}\left[C_1 + 2C_2(I^{*_4} - 3)\right]$$

$$\left[\mathbf{B}_s^*(t) - \frac{I_4^*}{3}\mathbf{I}\right]a(s)\mathrm{d}s. \tag{36}$$

Using Eq. (10), one can obtain the partial derivative of $J(t)$ with respect to $\theta(t)$ as

$$\partial_{\theta(t)}J(t) = -\left[\frac{\rho_0 b(t)}{\rho_{\mathrm{A}}^2(t)}\frac{\mathrm{d}\rho_{\mathrm{A}}}{\mathrm{d}\theta}(t) + \frac{\rho_0[1-b(t)]}{\rho_{\mathrm{C}}^2(t)}\frac{\mathrm{d}\rho_{\mathrm{C}}}{\mathrm{d}\theta}(t)\right], \tag{37}$$

where $\rho_{\mathrm{A}}(t)$ and $\rho_{\mathrm{C}}(t)$ are functions only of current temperature. Starting from Eq. (32), using the chain rule and noting that I_1 and I_4 are not explicit functions of temperature, one will have the relations

$$\partial_{\theta(t)}I_1^* = \frac{2\rho_0 I_1^*}{3J(t)}\left[\frac{b(t)}{\rho_{\mathrm{A}}^2(t)}\frac{\mathrm{d}\rho_{\mathrm{A}}}{\mathrm{d}\theta}(t) + \frac{1-b(t)}{\rho_{\mathrm{C}}^2(t)}\frac{\mathrm{d}\rho_{\mathrm{C}}}{\mathrm{d}\theta}(t)\right] \tag{38}$$

and

$$\partial_{\theta(t)}I_4^* = \frac{2\rho_0 I_4^*}{3J(t)}\left[\frac{b(t)}{\rho_{\mathrm{A}}^2(t)}\frac{\mathrm{d}\rho_{\mathrm{A}}}{\mathrm{d}\theta}(t) + \frac{1-b(t)}{\rho_{\mathrm{C}}^2(t)}\frac{\mathrm{d}\rho_{\mathrm{C}}}{\mathrm{d}\theta}(t)\right]. \tag{39}$$

Substitution for p from Eq. (29) into Eq. (24), introduction of the expressions for free energy given in Eqs. (30) and (31), and use of the partial derivatives as given in Eq. (38) results in the expression for entropy given as

$$\eta(t) = -b(t)\sum_{i=0}^{2}\frac{\partial A_i}{\partial\theta(t)}\left(I_1^* - 3\right)^i - \sum_{i=0}^{2}\int_{t_s}^{t}\frac{\partial C_i}{\partial\theta(t)}\left(I_4^* - 3\right)^i a(s)\mathrm{d}s -$$

$$\sigma_{\text{ave}}\left[\frac{b(t)}{\rho_{\mathrm{A}}^2(t)}\frac{\mathrm{d}\rho_{\mathrm{A}}}{\mathrm{d}\theta}(t) + \frac{1-b(t)}{\rho_{\mathrm{C}}^2(t)}\frac{\mathrm{d}\rho_{\mathrm{C}}}{\mathrm{d}\theta}(t)\right], \tag{40}$$

where $A_i[\theta(t), b(t)]$ and $C_i[\theta(t), b(t), \theta(s), b(s)]$.

Using Eq. (10), one can obtain the partial derivative of $J(t)$ with respect to $b(t)$ as

$$\partial_{b(t)}J(t) = \frac{\rho_0}{\rho_{\mathrm{A}}} - \frac{\rho_0}{\rho_{\mathrm{C}}}, \tag{41}$$

where ρ_{A} and ρ_{C} are functions only of temperature. Starting from Eq. (32), using the chain rule and noting that I_1 and I_4 are not explicit functions of $b(t)$, one obtain the relations

$$\partial_{b(t)}I_1^* = -\frac{2\rho_0 I_1^*}{3J(t)}\left(\frac{1}{\rho_{\mathrm{A}}} - \frac{1}{\rho_{\mathrm{C}}}\right),\ \partial_{b(t)}I_4^* = -\frac{2\rho_0 I_4^*}{3J(t)}\left(\frac{1}{\rho_{\mathrm{A}}} - \frac{1}{\rho_{\mathrm{C}}}\right). \tag{42}$$

Substitution for p from Eq. (29) into Eq. (27), introduction of the expressions for free energy given in Eqs. (30) and (31), and use of the partial derivatives as given in Eq. (42) results in the expression for the thermodynamic force of crystallization to be given as

$$\xi(t) = \sum_{i=0}^{2} A_i\left(I_1^* - 3\right)^i - C_0|_{s=t} + b(t)\sum_{i=0}^{2}\frac{\partial A_i}{\partial b(t)}\left(I_1^* - 3\right)^i + \sum_{i=0}^{2}\int_{t_s}^{t}\frac{\partial C_i}{\partial b(t)}\left(I_4^* - 3\right)^i a(s)\,\mathrm{d}s - \sigma_{\mathrm{ave}}\left[\frac{1}{\rho_{\mathrm{A}}(t)} - \frac{1}{\rho_{\mathrm{C}}(t)}\right], \quad (43)$$

where, as noted, in the second term on the right, C_0 is evaluated at $s = t$.

6. Summary and conclusion

In this article, which is the first in a series, a general description is provided of the model proposed for capturing the thermomechanical response of natural rubber. This model is a specific example of a more general model described in Negahban (1997). Eqs. (9)–(17) describe how one captures thermal expansion in the model. Eqs. (30) and (31) describe the basic form used for modeling the free energy. Eq. (36) presents the resulting expression for Cauchy stress. Eq. (40) provides the expression obtained for entropy. Eq. (43) presents the resulting expression for the thermodynamic force of crystallization.

In the following articles, the material functions A_0 to A_2 and C_0 to C_2 will be fit to known experimental results. Invariants I_1^* and I_4^* were used intentionally, as opposed to I_1 and I_4, since deformation histories which are restricted to equal triaxial extensions (pure volumetric deformations only) produce for all processes $I_1^* - 3 = 0$ and $I_4^* - 3 = 0$, which automatically decouples material functions. Most thermodynamic parameters, such as heat capacity, are assumed to measure response under equal triaxial extensions. This is used in the next article to concentrate on evaluating A_0 and C_0 from the elementary thermodynamic parameters of heat capacity, heat of fusion, melting temperature, and equilibrium crystallinity.

The third article concentrates on evaluating A_1, A_2, C_1 and C_2 from information on the mechanical effects of crystallization. To evaluate these material functions, experimental results on the instantaneous elastic response of the amorphous rubber are combined with results on the increase of elastic modulus with crystallinity and stress relaxation due to crystallization.

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