PERGAMON

International Journal of Solids and Structures 37 (2000) 2811–2824

INTERNATIONAL JOURNAL OF SOLIDS and STRUCTURES

www.elsevier.com/locate/ijsolstr

Modeling the thermomechanical effects of crystallization in natural rubber: III. Mechanical properties

Mehrdad Negahban*

Department of Engineering Mechanics and The Center for Materials Research and Analysis, W311 Nebraska Hall, University of Nebraska, Lincoln, NE 68588-0526, USA

Received 23 May 1998; received in revised form 24 March 1999

Abstract

The model proposed in part I of this series of articles for characterizing the thermomechanical response of natural rubber during crystallization is used in this article to model the mechanical effects of crystallization in natural rubber. Material functions are evaluated such that the model can reproduce existing experimental results on instantaneous rubbery elastic response of fully amorphous natural rubber (22°C), increase in elastic modulus of unconstrained natural rubber as a function of crystallinity (0°C), and stress relaxation associated with crystallization at constant stretch (−26°C). The continuum thermodynamic roots of the modeling process have made it possible to use experimental results at different temperatures to fairly accurately capture, in a single model, the temperature dependence of the mechanical response of natural rubber. Initial comparison to existing data, not used in the development of the model, indicates good agreement between the model and experiment. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Natural rubber, Crystallization; Continuum modeling; Non-isothermal, Stress relaxation; Elastic modulus; Thermodynamics of crystallization; Kinetics of crystallization; Phase transition; Nonlinear mechanical response

1. Introduction

In the first part of this series (Negahban, 2000a), a general theoretical structure was laid out for modeling the thermomechanical effects of crystallization in natural rubber. In the second part (Negahban, 2000b), elementary thermodynamic properties such as heat capacity and melting temperature were used to evaluate some of the material parameters for this model. In this part, existing

---

* Tel.: +001-402-472-2397; Fax: 402 472-8292.
E-mail address: mnegahban@unl.edu (M. Negahban).

PII: S0020-7683(99)00123-7

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 ($\mathbf{FF}^T$)
E	Elastic modulus
$\mathbf{F}(t)$	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
$\mathbf{F}^*(t)$	$=1/J^{1/3}(t)\mathbf{F}(t)$
$\mathbf{F}_s^*(t)$	$=\frac{J^{1/3}(s)}{J^{1/3}(t)}\mathbf{F}_s(t)$
J	Volume ratio ($=\det[\mathbf{F}]$)
J_{A}	Volume ratio of the amorphous polymer
J_{C}	Volume ratio of the fully crystalline polymer
t	Current time
t_{s}	Starting time of crystallization
$\mathbf{T}$	Cauchy stress tensor (true stress)
θ	Temperature
θ_0	Reference temperature
θ_{m}	Melting temperature
λ	Stretch ratio
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"

experimental results will be used to evaluate material parameters in the model associated with the mechanical effects of crystallization. Included in the experimental results used to model the material parameters are the instantaneous rubbery elastic response of the amorphous rubber, the gradual increase in the elastic modulus occurring in unconstrained isothermal crystallization, and stress relaxation accompanying isothermal crystallization under stretch.

As described in the first part of this series, a general constitutive equation for the description of thermomechanical effects of crystallization in polymers was developed in Negahban (1997a). This general formulation was based on an expression for the current free energy, $\psi(t)$, of the form

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

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 $\psi_C(t,s)$ is the effective current free energy per unit mass in the crystal created at time s. The relation between the fraction of amorphous material and the rate of crystallization is given by

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

For the purposes of modeling the behavior of natural rubber, the general expressions for the effective free energies of the two phases are selected as

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

and

$$\psi_C(t,s) = \sum_{i=0}^{2} C_i\left(I_4^* - 3\right)^i. \tag{4}$$

In these relations, the coefficients are functions described as

$$A_i[b(t),\theta(t)]$$

and

$$C_i[b(t),\theta(t),b(s),\theta(s)], \tag{5}$$

where θ denotes temperature. The invariants I_1^* and I_4^* are given in terms of the traditional invariants by extracting volumetric changes. These relations are given by

$$I_1^* = \frac{1}{J^{2/3}(t)} I_1$$

and

$$I_4^* = \frac{J^{2/3}(s)}{J^{2/3}(t)} I_4, \tag{6}$$

where $J = \det[\mathbf{F}]$ is the volume ratio, "s" denotes time s, and "t" denotes the current time t. The traditional invariants are given by $I_1 = \mathrm{tr}[\mathbf{B}(t)]$ and $I_4 = \mathrm{tr}[\mathbf{B}_s(t)]$, where $\mathbf{B}(t) = \mathbf{F}(t)\mathbf{F}^T(t)$ and $\mathbf{B}_s(t) = \mathbf{F}_s(t)\mathbf{F}_s^T(t)$. As shown in Fig. 1, $\mathbf{F}(t)$ denotes the deformation gradient comparing the current configuration to the reference configuration, and $\mathbf{F}_s(t)$ denotes the deformation gradient comparing the current configuration to the configuration at time s.

The result of the development presented in the first article was an expression for Cauchy stress, $\mathbf{T}$, given as

$$\mathbf{T} = \sigma_{\mathrm{ave}}(t)\mathbf{I} + 2\rho(t)b(t)\left[A_1 + 2A_2\left(I_1^* - 3\right)\right]\left[\mathbf{B}^*(t) - \frac{I_1^*}{3}\mathbf{I}\right] + 2\rho(t)\int_{t_s}^{t}\left[C_1 + 2C_2\left(I_4^* - 3\right)\right] \left[\mathbf{B}_s^*(t) - \frac{I_4^*}{3}\mathbf{I}\right] a(s)\mathrm{d}s, \tag{7}$$

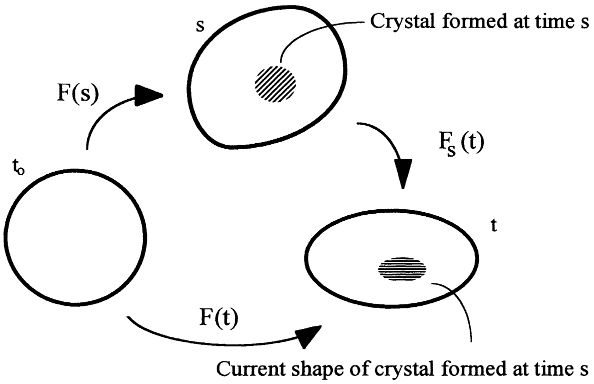

Fig. 1. Reference, intermediate, and current configuration of the macroscopic body and the deformation gradients.

where σ_{ave} is the average principal stress (negative the hydrostatic pressure), **I** is the second order tensor identity and $\rho(t)$ is the current value of density, given by

$$\frac{1}{\rho(\theta,b)} = \frac{J_{\mathrm{A}}(\theta)}{\rho_{A_0}}b + \frac{J_{\mathrm{C}}(\theta)}{\rho_{C_0}}(1-b), \tag{8}$$

where $\rho_{A_0} = 910\,\mathrm{kg/m^3}$ and $\rho_{C_0} = 1000\,\mathrm{kg/m^3}$ are, respectively, the density of the amorphous and crystalline phases of natural rubber at the reference temperature,

$$J_{\mathrm{A}}(\theta) = 1 + \frac{\mathrm{d}J_{\mathrm{A}}}{\mathrm{d}\theta}(\theta - \theta_0),$$

$$J_{\mathrm{C}}(\theta) = 1 + \frac{\mathrm{d}J_{\mathrm{C}}}{\mathrm{d}\theta}(\theta - \theta_0), \tag{9}$$

and where, for natural rubber, the reference temperature will be taken as $\theta_0 = 298°\mathrm{K}$ and

$$\frac{\mathrm{d}J_{\mathrm{A}}}{\mathrm{d}\theta} = 6.249 \times 10^{-4},$$

$$\frac{\mathrm{d}J_{\mathrm{C}}}{\mathrm{d}\theta} = 3.132 \times 10^{-4}. \tag{10}$$

In what follows, the expression given in Eq. (7) for Cauchy stress will be used in combination with existing experimental results to evaluate the material functions A_1, A_2, C_1 and C_2. The material functions A_0 and C_0 were evaluated in Negahban (2000b) based on using the elementary thermodynamic properties of natural rubber. The form selected to model the functions A_1 and A_2 can be written as

$$A_i = [A_{i1} + A_{i2}(1-b)]\theta, \tag{11}$$

which are linear functions of crystallinity and have a primarily linear dependence on temperature, as is suggested by the statistical theory of rubber elasticity (See Treloar, 1975). Other than A_{11}, which must depend on temperature to accommodate effects associated with thermal expansion, the other three material parameters A_{ij} will be taken as constant. The form of the material functions used to model C_1

and C_2 is

$$C_i = \{C_{i1} + C_{i2}[1 - b(s)]\}f[\theta(t)], \tag{12}$$

where the material parameters C_{ij} are selected as constants and the function $f[\theta(t)]$ is appropriately selected to characterize the temperature dependence of the modulus of crystalline natural rubber.

Section 2 will show how to evaluate A_{11} and A_{21} from experimental data obtained by Min (1976) for the instantaneous response of amorphous natural rubber. This is done using the tensile stress right after loading. It will be shown that a modified neo-Hookean model for fully amorphous natural rubber captures the instantaneous response accurately, even though it might be a poor model for the equilibrium response.

In Section 3, the material parameters C_{ij} are evaluated from experimental results given by Leitner (1955) on the isothermal increase in elastic modulus of unconstrained natural rubber, and the function $f[\theta(t)]$ is taken to capture the known dependence of the elastic modulus on temperature, as described by Van Krevelen and Hoftyzer (1976). This is done by assuming the amorphous rubber does not contribute significantly to the change in modulus. This assumption is later verified by comparing the model to experimental results, after including all the material parameters.

In Section 4, the material parameters A_{12} and A_{22} are evaluated based on isothermal experimental results done by Gent (1954), giving the relation between stress relaxation and crystallinity in stretched natural rubber.The experiments of Min (1976) were conducted at 22°C, the experiments of Leitner (1955) were conducted at 0°C and the experiments of Gent (1954) were conducted at −26°C. It is important to recognize that in what follows, three distinctly different experiments which were conducted at three different temperatures are used to evaluate the material functions for a single continuum model. Combined with the material functions evaluated in Negahban (2000b), these material functions fully describe the proposed free energy of natural rubber. The only missing element will be a model for the rate of crystallization.

2. Modeling fully amorphous natural rubber

Natural rubber before crystallization is an amorphous polymer. In the rubbery range, amorphous natural rubber will respond as any other rubbery elastic material. As will be shown in the following, the response of fully amorphous natural rubber is well represented by a modified neo-Hookean model. The constant for this model will be obtained using the experimental results of Min (1976). To minimize the contribution of crystallization, stress evaluated by Min immediately after loading will be used as representative of the amorphous response.

The experimental results of Min (1976) are for uniaxial extension of natural rubber. Since there is no need to keep track of intermediate configuration for the elastic response of the fully amorphous material, in this section it will be implied that all variables are evaluated at current time, avoiding unnecessary complication in the notation. Uniaxial extension along the 1-1 coordinate axis is given by the stress

$$\mathbf{T} = T_{11}\mathbf{e}_1 \otimes \mathbf{e}_1 \tag{13}$$

and is characterized by the deformation gradient

$$\mathbf{F} = \lambda\mathbf{e}_1 \otimes \mathbf{e}_1 + \sqrt{\frac{J}{\lambda}}(\mathbf{e}_2 \otimes \mathbf{e}_2 + \mathbf{e}_3 \otimes \mathbf{e}_3), \tag{14}$$

where $\mathbf{e}_1$, $\mathbf{e}_2$ and $\mathbf{e}_3$ are the base vectors for a rectangular coordinate system, as shown in Fig. 2, T_{ij} are the components of stress, λ is the stretch along the 1-1 direction, and "$\otimes$" denotes the tensor product.

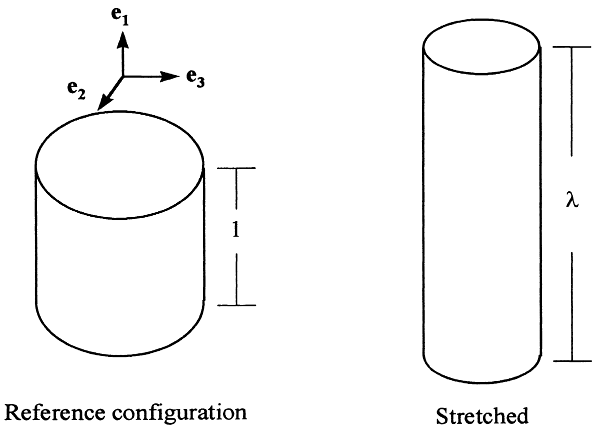

Fig. 2. Uniaxial extension, coordinate directions, and stretch ratio.

In the absence of crystallinity, the expression for the Cauchy stress given in Eq. (7) becomes

$$\mathbf{T} = \sigma_{\text{ave}}\mathbf{I} + 2\rho\left[A_1|_{b=1} + 2A_2|_{b=1}\left(I_1^* - 3\right)\right]\left[\mathbf{B}^*(t) - \frac{I_1^*}{3}\mathbf{I}\right]. \tag{15}$$

Substitution of Eqs. (11), (13) and (14) into this equation results in two independent equations. Elimination of the average stress between these equations results in the expression for axial stress T_{11} given by

$$T_{11} = 2\rho\theta\left[A_{11} + 2A_{21}\left(\lambda^{*2} + \frac{2}{\lambda^*} - 3\right)\right]\left[\lambda^{*2} - \frac{1}{\lambda^*}\right], \tag{16}$$

where $\lambda^* = \lambda/J^{1/3}$ is the axial stretch relative to the stress free state of natural rubber at the current temperature, as opposed to λ which is the stretch relative to the reference configuration. For fully amorphous natural rubber

$$\rho = \frac{\rho_0}{1 + \mathrm{d}J_A/\mathrm{d}\theta(\theta - \theta_0)}. \tag{17}$$

In the first part of this series (Negahban, 2000a), it was shown that for natural rubber, $\rho_0 = 910\ \mathrm{kg/m^3}$ and $\mathrm{d}J_A/\mathrm{d}\theta$ and θ_0 are given above.

Fig. 3 shows the data of Min (1976) for axial stress at room temperature (22°C) taken one second after loading and plotted versus strain. The solid curve shows the fit of the proposed model for the following values of the material parameters

$$A_{11} = \frac{Q}{2\rho_0}\left[1 + \frac{\mathrm{d}J_A}{\mathrm{d}\theta}(\theta - \theta_0)\right]$$

and

$$A_{21} = 0, \tag{18}$$

where $Q = 1.373 \times 10^{-3}$ MPa/K. As can be seen, this modified neo-Hookean model captures the instantaneous response of natural rubber very well.

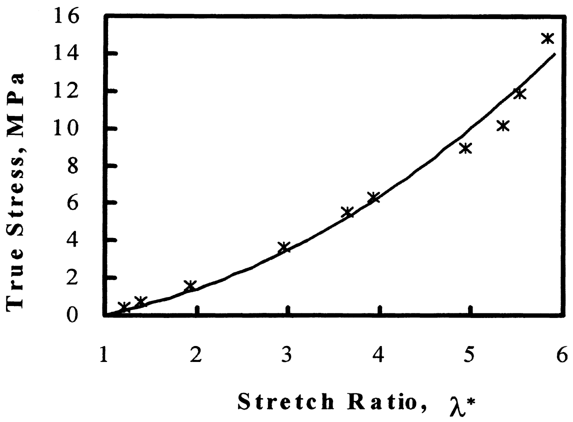

Fig. 3. Uniaxial stress–stretch diagram of amorphous natural rubber at 22°C. Data points are from Min (1976) for stress one second after loading. The continuous line is the fit by the model.

3. The increase in rigidity with crystallization

There is a noticeable increase of elastic modulus with the crystallization of natural rubber. Even small amounts of crystallization induce very large changes in the elastic modulus of natural rubber. The experimental results of Leitner (1955), shown in Fig. 4, indicate an approximately 100 fold increase in the elastic modulus as a result of about 25% crystallization. As can also be seen from this same figure, the relation between the increase in modulus and crystallinity is nonlinear, even at these low fractions of crystallized material. This effect is primarily captured by material parameters associated with the crystalline phase, since the amorphous phase is so much softer and, as a result, has a much smaller contribution to the change in modulus.

Leitner (1955) evaluated the elastic modulus of unconstrained natural rubber at 0°C as a function of the increase of its density. This was done by allowing natural rubber to undergo unconstrained isothermal crystallization, while monitoring the change in its density, and slightly extending it from time to time to calculate its modulus. The basic assumption is that the small extensions needed to evaluate

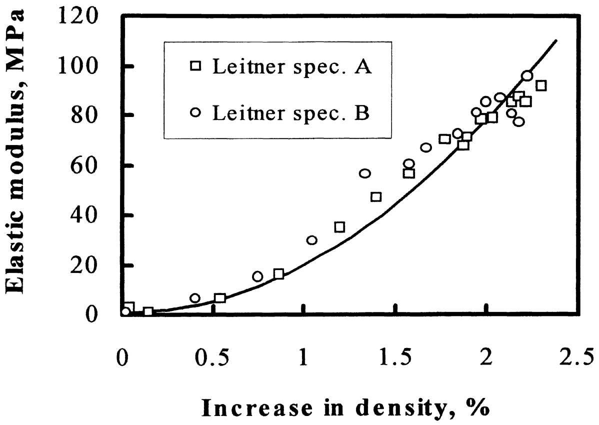

Fig. 4. Elastic modulus as a function of the increase of density for unconstrained natural rubber at 0°C. The data is from Leitner (1955). The curve is the model using all the material parameters.

the modulus have no noticeable effect on the crystallization process. This same assumption will be made to obtain expressions to fit the model to the experimental data. Since it is assumed that during the crystallization process the rubber is unconstrained, it will be assumed that only pure volumetric deformations will occur during crystallization. This can be represented by the deformation gradient

$$\mathbf{F}(s) = J^{1/3}(s)\mathbf{I}, \tag{19}$$

where s represents any time between the start of crystallization and the current time, but not the current time. At the current time, the sample is stretched to obtain the modulus, assuming no crystallization in the stretching process. Stretching along the 1-1 direction at the current time is represented by a deformation gradient

$$\mathbf{F}(t) = \lambda(t)\mathbf{e}_1 \otimes \mathbf{e}_1 + \sqrt{\frac{J(t)}{\lambda(t)}}(\mathbf{e}_2 \otimes \mathbf{e}_2 + \mathbf{e}_3 \otimes \mathbf{e}_3). \tag{20}$$

The result of extracting volumetric changes is to yield

$$\mathbf{F}^*(t) = \mathbf{F}^*_s(t) = \lambda^*(t)\mathbf{e}_1 \otimes \mathbf{e}_1 + \sqrt{\frac{1}{\lambda^*(t)}}(\mathbf{e}_2 \otimes \mathbf{e}_2 + \mathbf{e}_3 \otimes \mathbf{e}_3). \tag{21}$$

where $\lambda^*(t) = \lambda(t)/J^{1/3}(t)$ is stretch relative to the stress free configuration at the current temperature and crystallinity. In the process of stretching, it is assumed that material has zero stress on the lateral surfaces such that

$$\mathbf{T}(t) = T_{11}(t)\mathbf{e}_1 \otimes \mathbf{e}_1. \tag{22}$$

Substitution of Eqs. (21) and (22) into the expression for the Cauchy stress given in Eq. (7) and elimination of the average principal stress results in

$$T_{11}(t) = G\left[\lambda^{*2}(t) - \frac{1}{\lambda^*(t)}\right], \tag{23}$$

where

$$G = 2\rho(t)\left\{b(t)\left[A_1 + 2A_2\left(I_1^* - 3\right)\right] + \int_{t_s}^{t}\left[C_1 + 2C_2\left(I_4^* - 3\right)\right]a(s)\mathrm{d}s\right\} \tag{24}$$

and

$$I_1^* = I_4^* = \lambda^{*2}(t) + \frac{2}{\lambda^*(t)}. \tag{25}$$

The elastic modulus, E, as measured by Leitner is the change in stress as a result of a change in stretch evaluated at the stress free configuration. Due to the small changes in cross sectional area due to crystallization and due to the infinitesimal strains involved in evaluating the modulus, one need not distinguish between true and engineering stress. Using this definition to obtain the elastic modulus, one finds

$$E = \left.\frac{\partial T_{11}(t)}{\partial \lambda^*}\right|_{\lambda^*=1} = 3G|_{\lambda^*=1}, \tag{26}$$

where

$$G|_{\lambda^*=1} = 2\rho(t)\left[b(t)A_1 + \int_{t_s}^{t} C_1 a(s)\mathrm{d}s\right], \tag{27}$$

which, after integration, yields

$$E = 6\rho\left\{b\theta[A_{11} + A_{12}(1-b)] + \left[C_{11}(1-b) + C_{12}\frac{(1-b)^2}{2}\right]f(\theta)\right\}. \tag{28}$$

One can use several different methods to obtain the material parameters. Several points must be taken into account when fitting the parameters. First, the crystalline "modulus" represented by the material parameters C_{11} and C_{12} is much larger than the amorphous modulus represented by the material parameters A_{11} and A_{12}. Since the terms containing A_{12} and C_{11} are to the first approximation both functions of (1-b), it is impossible to accurately distinguish the contribution of either to the elastic modulus. As observed by Van Krevelen and Hoftyzer (1976), the dependence of the elastic modulus on crystallinity is quadratic with the linear term absent. This suggests that one can set $C_{11}=0$. Also, Van Krevelen and Hoftyzer suggest that the dependence of the modulus on temperature can be represented by the function

$$f(\theta) = \exp\left[k\frac{\theta_m/\bar{\theta}_0 - \theta_m/\theta}{\theta_m/\bar{\theta}_0 - 1}\right], \tag{29}$$

where, for natural rubber, $\theta_\mathrm{m}=309$°K, $k=$-1.15 and $\bar{\theta}_0$ is set equal to 273°K to yield $f(273)=1$. One can also assume that the contribution of all the amorphous parameters are negligible if one concentrates on fitting the modulus at sufficiently large values of crystallinity (sufficiently large so that the modulus is more than an order of magnitude larger than the modulus of the fully amorphous natural rubber). Therefore, a good approximation of the elastic modulus can be obtained from the relation

$$E \approx 3\rho(t)C_{12}\frac{(1-b)^2}{2}f(\theta), \tag{30}$$

as long as the modulus of the semi-crystalline polymer is much larger than the purely amorphous polymer. This approximate equation can be used to obtain C_{12} using one point from the data provided by Leitner (1955). The data of Leitner is in terms of elastic modulus as a function of percent change in density. To obtain the fraction of amorphous material, b, from the percent change in density one needs to solve for the fraction of amorphous material using Eq. (8) to obtain

$$b = \frac{1/\rho - J_\mathrm{C}/\rho_{C_0}}{J_\mathrm{A}/\rho_{A_0} - J_\mathrm{C}/\rho_{C_0}}, \tag{31}$$

and one also needs to know the density of fully amorphous rubber at the experiment temperature of 273°K, which is obtained from the relation

$$\rho|_{b=1} = \frac{\rho_{A_0}}{J_\mathrm{A}}. \tag{32}$$

A representative point obtained from the data of Leitner (1955), with sufficiently large E so that one can use equation Eq. (30), is E = 71 MPa at a change in density of 1.9%. Using the testing temperature of 273°K to obtain J_A and J_C from equation Eq. (9), one can show that a 1.9% change in density at this temperature is equivalent to $b = 0.775$ (22.5% crystallinity). Substituting into equation Eq. (30), one obtains

$$C_{12} = 0.5\,\frac{\text{MPa}}{\text{kg/m}^3}. \tag{33}$$

In addition to the data of Leitner, Fig. 4 shows how well the model, after incorporation of all the material constants (including the ones obtained in the next section), reproduces the response observed by Leitner.

4. Stress relaxation as a result of crystallization

Crystallization in stretched natural rubber is accompanied by stress relaxation. Experimental results from Gent (1954) conducted at −26°C and reproduced in Fig. 5 show this stress relaxation as a function of time. What is not apparent in this figure, but observed by Gent, is that there is a linear relation between stress relaxation and the decrease in the volume of natural rubber. Fig. 6, also reproduced from Gent's paper, shows that stress relaxation can be superimposed on the volume reduction data by linear superposition. Figs. 5 and 6 can be used to extract the linear relation observed by Gent. This is shown in Fig. 7. Even though the relation between stress and crystallinity is linear for a given stretch, from Fig. 7 one can see that the dependence on stretch is highly nonlinear.

To incorporate the experiment of Gent into the proposed model, we do the following. In the experiment, the sample is stretched and held at constant stretch as it crystallizes. This implies that the deformation gradient can be written as

$$\mathbf{F}(s) = \lambda \mathbf{e}_1 \otimes \mathbf{e}_1 + \sqrt{\frac{J(s)}{\lambda}}(\mathbf{e}_2 \otimes \mathbf{e}_2 + \mathbf{e}_3 \otimes \mathbf{e}_3) \tag{34}$$

for all times s from the start of crystallization up to and including the current time t, where λ is the constant stretch imposed on the sample along the 1-1 direction. This results in the expressions

$$\mathbf{F}^*(t) = \frac{\lambda}{J^{1/3}(t)}\mathbf{e}_1 \otimes \mathbf{e}_1 + \sqrt{\frac{J^{1/3}(t)}{\lambda}}(\mathbf{e}_2 \otimes \mathbf{e}_2 + \mathbf{e}_3 \otimes \mathbf{e}_3) \tag{35}$$

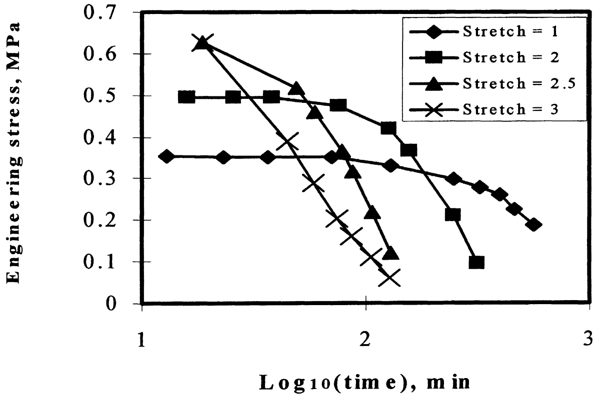

Fig. 5. Stress relaxation of natural rubber at −26°C as a function of time for four different stretches (reproduced from Gent, 1954).

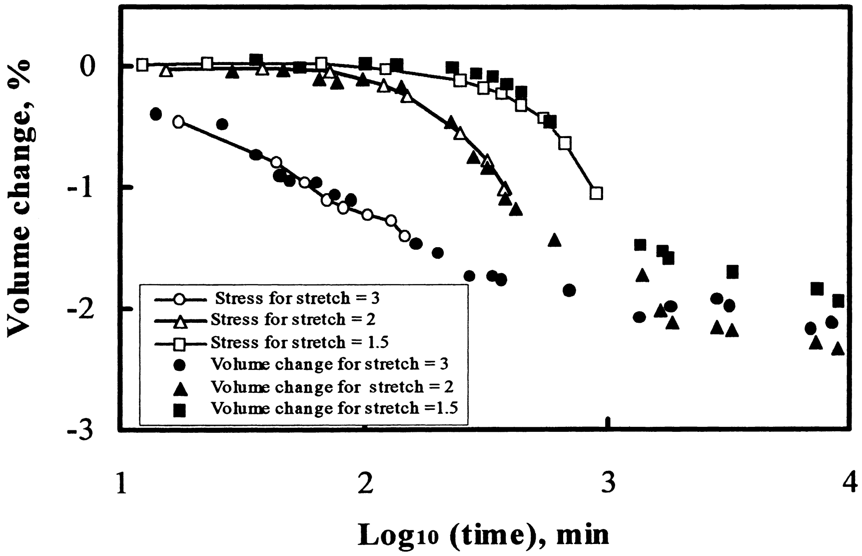

Fig. 6. Volume reduction of natural rubber at −26°C as a function of time for three different stretches (reproduced from Gent, 1954). Gent, using linear scaling, superimposed on the volume reductions the stress relaxation as shown. The data for stress stops when the sample fully relaxes, while the crystallization continues long after full stress relaxation and is accompanied by the stretching of the samples.

and

$$\mathbf{F}_s^*(t) = \frac{J^{1/3}(s)}{J^{1/3}(t)}\mathbf{e}_1 \otimes \mathbf{e}_1 + \sqrt{\frac{J^{1/3}(t)}{J^{1/3}(s)}}(\mathbf{e}_2 \otimes \mathbf{e}_2 + \mathbf{e}_3 \otimes \mathbf{e}_3). \tag{36}$$

Introduction of Eqs. (35) and (36) into Eq. (7) and assuming a stress field compatible with uniaxial extension with stress-free lateral surfaces, as given in Eq. (22), results in two independent equations. Eliminating the average principal stress from these two equations results in an expression for the axial

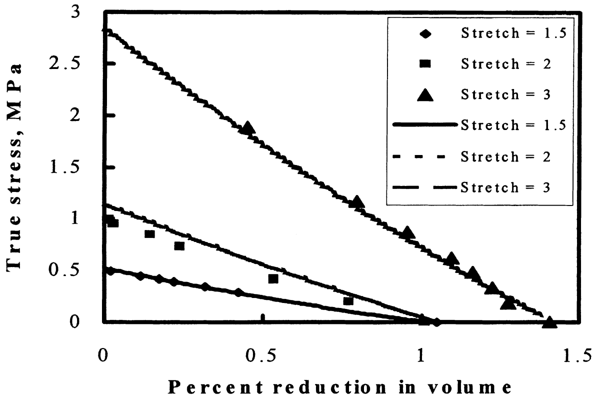

Fig. 7. Stress relaxation of natural rubber at −26°C as a function of percent reduction in volume for three different stretches (extracted from Fig. 5 and 6). The solid lines indicate the prediction of the model.

stress given by

$$T_{11}(t) = 2\rho(t)\left\{ b(t)\left[A_1 + 2A_2\left(I_1^* - 3\right)\right]\left[\frac{\lambda^2}{J^{2/3}(t)} - \frac{J^{1/3}(t)}{\lambda}\right] + \int_{t_s}^{t}\left[C_1 + 2C_2\left(I_4^* - 3\right)\right]\right.$$

$$\left.\left[\frac{J^{2/3}(s)}{J^{2/3}(t)} - \frac{J^{1/3}(t)}{J^{1/3}(s)}\right]a(s)\mathrm{d}s\right\}, \tag{37}$$

where

$$I_1^* = \frac{\lambda^2}{J^{2/3}(t)} + \frac{2J^{1/3}(t)}{\lambda}$$

and

$$I_4^* = \frac{J^{2/3}(s)}{J^{2/3}(t)} + \frac{2J^{1/3}(t)}{J^{1/3}(s)}. \tag{38}$$

The first thing to notice in the expression for stress is that the term with the integral, which represents the contribution of the crystals to the process of stress relaxation, is not a function of stretch. Therefore, the part of the model which represents the contribution of the crystals will result in a stretch independent shift of the stress. In other words, consistent with the work of Flory (1947) and others, the mechanism of stress relaxation is simply derived from the replacement of stretched amorphous rubber by unstressed crystals. Up to now, there is no evidence that C_2 is needed to model any aspect of the response of natural rubber. As you may have noticed, the terms associated with A_2 and C_2 naturally vanished from the expression for the modulus, as was shown in the last section. Any other higher order terms which we would introduce into the model for the free energy given in equations Eqs. (3) and (4) would also vanish from the expression for the elastic modulus. Keeping these in mind, it will be assumed that C_2 can be set to zero. The primary reason for introducing C_2 into the model was to show that higher order terms such as A_2 and C_2 do not appear in the expression for modulus (see Eq. (27)) during unconstrained crystallization.

Introducing expressions (11) and (12) into Eq. (37) and taking $C_2 = 0$ results in

$$T_{11}(t) = 2\rho(t)\left\{ b(t)\theta(t)\left[A_{11} + A_{12}(1 - b(t)) + 2[A_{21} + A_{22}(1 - b(t))](I*_1 - 3)\right]\right.$$

$$\left.\left[\frac{\lambda^2}{J^{2/3}(t)} - \frac{J^{1/3}(t)}{\lambda}\right] + f[\theta(t)]\int_{t_s}^{t}[C_{11} + C_{12}(1 - b(s))]\left[\frac{J^{2/3}(s)}{J^{2/3}(t)} - \frac{J^{1/3}(t)}{J^{1/3}(s)}\right]a(s)\mathrm{d}s\right\}. \tag{39}$$

Material parameters A_{11}, A_{21}, C_{11} and C_{12} were evaluated in the previous sections. It remains to evaluate A_{12} and A_{22} using the data of Gent as presented in Fig. 7. Gent's data shows that stress goes to zero at 1% volume reduction (b = 0.867) for a stretch of $\lambda = 1.5$ and the stress goes to zero at 1.4% volume reduction (b = 0.813) for a stretch of $\lambda = 3$. These two points are used to evaluate A_{12} and A_{22} as

$$A_{12} = -6.57 \times 10^{-6}\ \frac{\text{MPa}}{\text{kg/m}^3}$$

and

$$A_{22} = 1.70 \times 10^{-7}\ \frac{\text{MPa}}{\text{kg/m}^3}. \tag{40}$$

To obtain the two equations to solve for these material constants, one needs to integrate the integral in Eq. (39), noting that the volume is given by the expression

$$J(\theta,b) = \frac{\rho_0}{\rho_{A_0}} J_{\text{A}}(\theta)b + \frac{\rho_0}{\rho_{C_0}} J_{\text{C}}(\theta)(1-b). \tag{41}$$

Also, the temperature at both time s and t is set to the experiment temperature of 247°K for the evaluation of ρ, J and f.

Fig. 7 also shows how well the model fits the response observed by Gent (1954). The first thing to note is that where the theoretical graphs intersect the vertical axis represents the elastic response of the fully amorphous natural rubber at -26°C, which directly results from the modified neo-Hookean model fit to the experimental results of Min (1976) at 22°C. These points are not fit to the data of Gent, and are an indication that the rubbers are similar and that the modified neo-Hookean model is appropriate for modeling fully amorphous natural rubber over this approximately 50° range. Second, the reader will note that even though the model does not actually result in a linear relation between stress relaxation and the degree of crystallization, it is sufficiently linear that the variation of the model from linearity is within the uncertainty of the experimental data. Comparison using a straight edge shows that the response for the stretch of 2 and 3 shows noticeable nonlinear behavior, yet the behavior seems to be consistent with the data. Third, even though the model was only fit to one point on the stress relaxation at a stretch of 1.5 and one point on the stress relaxation at a stretch of 3, the model predicts the stress relax at a stretch of 2 with sufficient accuracy. No points were fit to the stress relaxation at a stretch of 2, yet the model accurately predicts the slope of the relaxation and captures the very nonlinear dependence of the stress relaxation on stretch. The reader will also note that the volume reduction at zero stress is practically identical for both a stretch of 1.5 and 2, a feature accurately captured by the model, and substantially different for the stretch of 3.

5. Summary and conclusion

In this paper, material parameters for the model proposed in Negahban (2000b) were selected so the proposed model would reproduce three distinctly different mechanical tests. These tests were the instantaneous tensile response at 22°C, the increase in elastic modulus due to crystallization of unconstrained natural rubber at 0°C, and the stress relaxation associated with crystallization under constant stretch at −26°C. The selected parameters accurately reproduce the above experimental results, yet many assumptions were made in the process of evaluating the material parameters. Like any other semi-phenomenological model, the validity of these assumptions can only be verified by comparison to additional experiments. Initial comparisons done using the data of Gent (1954) indicate that the assumptions are justified.

Since the model is all inclusive, one can use the above parameters to predict the response under different conditions. For example, based on Eq. (28), Fig. 8 shows the elastic modulus of natural rubber

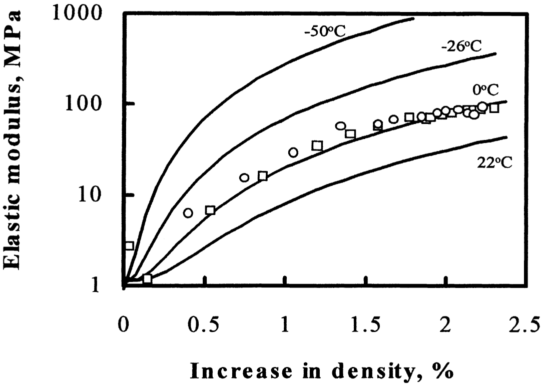

Fig. 8. Elastic modulus as a function of percent change in density for unconstrained isothermal crystallization at the indicated temperatures. The solid lines are as predicted by the model, the data is from Leitner (1955).

at four different temperatures as a function of the percent increase in density for unconstrained isothermal crystallization.

The constants evaluated in this paper and those evaluated in Negahban (2000b) fully determine the free energy of natural rubber, only leaving a model for the rate of crystallization to be developed. Even without a model for the rate of crystallization, one can now use the model to study some combined thermomechanical responses of natural rubber. Examples are: the evaluation of the anisotropic thermal expansion of samples which have crystallized under a constant stretch, or the effect of crystallization under stretch on the melting temperature and on equilibrium crystallinity. The equilibrium response under constant stretch and during slow extension has been evaluated for this model and is presented in Negahban (1997b).

References

Flory, P.J., 1947. Thermodynamics of crystallization in high polymers. I. Crystallization induced by stretching. Journal of Chemical Physics 15, 397–408.

Gent, A.N., 1954. Crystallization and the relaxation of stress in stretched natural rubber vulcanizates. Trans. Faraday Soc. 50, 51.

Leitner, M., 1955. Young's modulus of crystalline, unstretched rubber. Trans. Faraday Soc. 51, 1015.

Min, B.K., 1976. Dynamic behavior of some solids and liquids, Ph.D. thesis, Brown University, Providence, RI.

Negahban, M., 1997a. Thermodynamic modeling of the thermomechanical effects of polymer crystalliation: A general theoretical structure. International Journal of Engineering Science 35, 277–298.

Negahban, M., 1997b. Thermomechanical effects associated with crystallization of rubber under stretch and during slow extension. Journal of Engineering Materials and Technology 119, 298–304.

Negahban, M., 2000a. Modeling the thermomechanical effects of crystallization in natural rubber: I. The theoretical structure. International Journal of Solids and Structures 37, 2777–2789.

Negahban, M., 2000b. Modeling the thermomechanical effects of crystallization in natural rubber: II. Elementary thermodynamic properties. International Journal of Solids and Structures 37, 2791–2809.

Treloar, L.R.G., 1975. The Physics of Rubber Elasticity. Clarendon Press, Oxford.

Van Krevelen, D.W., Hoftyzer, P., 1976. Properties of Polymers: Their Estimation and Correlation with Chemical Structure. Elsevier Scientific Publishing Company, Amsterdam.