PERGAMON

International Journal of Solids and Structures 37 (2000) 2791–2809

INTERNATIONAL JOURNAL OF SOLIDS and STRUCTURES

www.elsevier.com/locate/ijsolstr

Modeling the thermomechanical effects of crystallization in natural rubber: II. Elementary thermodynamic properties

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

Abstract

The model proposed in the first part of this series for characterizing the thermomechanical response of natural rubber during crystallization is used in this article to model the elementary thermodynamic properties of natural rubber. In particular, known experimental results for the heat capacity, heat of fusion, fundamental melting temperature, and equilibrium crystallinity are used to calculate specific material functions associated with the proposed model. Based on these material parameters the model is used to evaluate the dependence of equilibrium crystallinity on pressure and temperature. The dependence of the melting temperature on pressure is also evaluated. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Natural rubber; Crystallization; Thermodynamics; Continuum modeling; Non-isothermal; Heat capacity; Crystallinity; Phase transition; Kinetics of crystallization

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1. Introduction

In the first part of this series (Negahban, 2000), the general theoretical structure was laid out for modeling the thermomechanical effects of crystallization in natural rubber. In this part, the elementary thermodynamic parameters are related to the model parameters and evaluated for natural rubber based on existing experimental results. The elementary thermodynamics parameters refer to quantities such as heat capacity, heat of crystallization, melting temperature, and equilibrium crystallinity. The term 'elementary' in describing the thermodynamic parameters will refer to the assumption that the parameters are evaluated under hydrostatic pressure and that only pure volumetric changes (equal

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PII: S0020-7683(99)00122-5

Nomenclature

a	Rate of crystallization in mass per unit time
b	Mass fraction of amorphous material $(= 1 - \int_{t_s}^{t} a(s)\mathrm{d}s)$
b_∞	Equilibrium mass fraction of amorphous material
$\mathbf{B}$	Left Cauchy stretch tensor $(=\mathbf{F}\mathbf{F}^T)$
c_p	Heat capacity per unit mass at constant pressure
c_v	Heat capacity per unit mass at constant volume
c_p^l	Heat capacity per unit mass of the liquid (amorphous) polymer
c_p^s	Heat capacity per unit mass of the solid (fully crystallized) polymer
e	Internal energy per unit mass
$\mathbf{F}(t)$	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
$\mathbf{F}^*(t)$	$=\frac{1}{J^{1/3}(t)}\mathbf{F}(t)$
$\mathbf{F}_s^*(t)$	$=\frac{J^{1/3}(s)}{J^{1/3}(t)}\mathbf{F}_s(t)$
h	Heat content per unit mass
h_A	Heat content per unit mass of the amorphous polymer
h_C	Heat content per unit mass of the fully crystalline polymer
Δh_m	Heat of fusion per unit mass at the melting temperature
H	Heat content
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
θ_m	Melting 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

triaxial extensions) occur during the crystallization process. This will be in contrast to, for example, the heat capacity during crystallization under stretch, which will be studied in a following article.

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

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

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. The relation between the fraction of amorphous material and the rate of crystallization is given by

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

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

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

and

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

In these relations, the coefficients are functions described as

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

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

$$I_1^* = \frac{1}{J^{2/3}(t)} I_1,\ I_4^* = \frac{J^{2/3}(s)}{J^{2/3}(t)} I_4, \tag{6}$$

where $J = \det[\mathbf{F}]$ is the volume ratio, 's' denotes time s and 't' denotes the current time t. The invariant $I_1 = \mathrm{tr}[\mathbf{B}(\mathrm{t})]$ and $I_4 = \mathrm{tr}[\mathbf{B}_s(t)]$, where $\mathbf{B}(t) = \mathbf{F}(t)\mathbf{F}^T(t)$ and $\mathbf{B}_s(t) = \mathbf{F}_s(t)\mathbf{F}_s^T(t)$. $\mathbf{F}(t)$ 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 part were expressions for Cauchy stress, $\mathbf{T}$, entropy, η, and thermodynamic force of crystallization, ξ, given, respectively, as

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

$$\eta(t) = -b(t)\sum_{i=0}^{2}\frac{\partial A_i}{\partial\theta(t)}\left(I_1^* - 3\right)^i - \sum_{i=0}^{2}\int_{t_s}^{t}\frac{\partial C_i}{\partial\theta(t)}\left(I_4^* - 3\right)^i a(s)\mathrm{d}s -$$
$$\sigma_{\text{ave}}\left[\frac{b(t)}{\rho_{\text{A}}^2(t)}\frac{\mathrm{d}\rho_{\text{A}}}{\mathrm{d}\theta}(t) + \frac{1 - b(t)}{\rho_{\text{C}}^2(t)}\frac{\mathrm{d}\rho_{\text{C}}}{\mathrm{d}\theta}(t)\right], \tag{8}$$

and

$$\xi(t) = \sum_{i=0}^{2}A_i\left(I_1^* - 3\right)^i - C_0\Bigg|_{s=t} + b(t)\sum_{i=0}^{2}\frac{\partial A_i}{\partial b(t)}\left(I_1^* - 3\right)^i + \sum_{i=0}^{2}\int_{t_s}^{t}\frac{\partial C_i}{\partial b(t)}\left(I_4^* - 3\right)^i a(s)\mathrm{d}s -$$
$$\sigma_{\text{ave}}\left[\frac{1}{\rho_{\text{A}}(t)} - \frac{1}{\rho_{\text{C}}(t)}\right], \tag{9}$$

where σ_{ave} is the average principal stress (negative of the hydrostatic pressure), $\mathbf{I}$ is the second order tensor identity, $\rho(t)$ is the current value of density, ρ_{A} and ρ_{C} are, respectively, the density of the amorphous and crystalline phases as a function of temperature.

Before we proceed, we must make explicit how we extract the thermodynamic parameters from the continuum theory. This will be done in several steps. In Section 2, we define heat flow and heat content. In Section 3, we define heat capacity, heat capacity at constant pressure, heat capacity at constant volume, heat capacity at constant pressure and crystallinity. In Section 4, we define the heat of crystallization and heat of fusion and, in Section 5, we define the melting temperature and equilibrium crystallinity.

The next stage is to define the elementary thermodynamic parameters. We consider the elementary heat capacities and heat of fusion to describe the response of the rubber under hydrostatic pressure, which is assumed to be accompanied by deformations which are described by equal triaxial extensions. The form of these parameters are calculated based on this assumption in Section 6, and each variable is fit to the known experimental results in Section 7.

Finally, in Section 8, the thermodynamic force of crystallization is used to impose the fundamental melting temperature, and the extent of crystallinity as a function of temperature, under conditions consistent with those assumed to exist for the evaluation of the elementary thermodynamic parameters.

Using the material parameters evaluated, the dependence of heat content and equilibrium crystallinity on temperature and pressure are described. In addition, the dependence of the melting temperature on pressure is evaluated and shown to be about a 9°C increase in melting temperature for every 50 MPa of hydrostatic pressure.

2. Heat flow under homogeneous conditions

Of particular concern in studying thermomechanical response is the connection between heat flow and mechanical loading. By developing a general continuum thermodynamic model for the phase transition

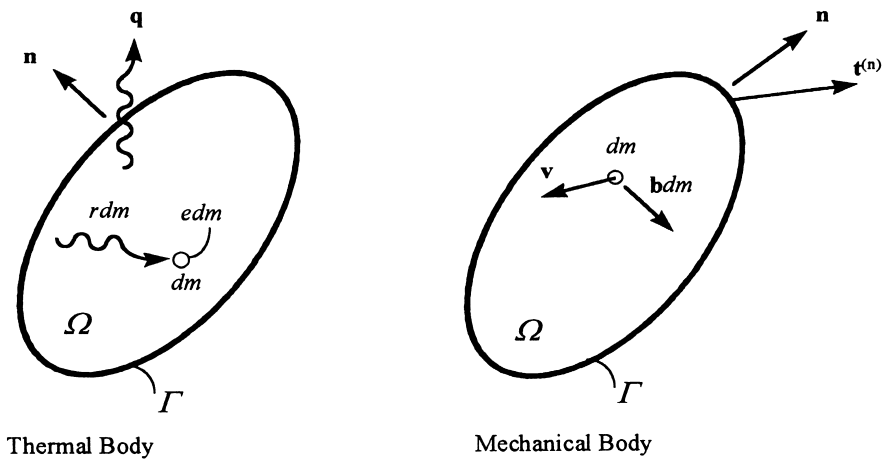

Fig. 1. The thermomechanical loading of a body.

of natural rubber, one has a natural way of evaluating both the mechanical and thermal response directly from the same model. We will proceed to evaluate the heat flow, and as a result, the heat capacities of the crystallizing polymer.

Let H denote the heat content of a material body (a control mass). The rate at which H is increasing is given by the rate at which heat is being added to the body. As shown in Fig. 1, heat may be added to a continuum body either by heat conduction through the boundaries or through radiation (or generation). The rate at which the heat content of the body is increasing is given by

$$\dot{H} = -\int_{\Gamma} \mathbf{q} \cdot \mathbf{n} \, \mathrm{d}\Gamma + \int_{\Omega} \rho r \, \mathrm{d}\Omega, \tag{10}$$

where Ω is the domain of the body with boundary Γ, $\mathbf{q}$ is the heat flux, $\mathbf{n}$ is the unit normal to Γ, and r is the heat generation or radiation. The balance of work and energy for the body requires that the rate of change of internal plus kinetic energy be equal to the rate at which the forces do work on the body and the rate at which heat is added to the body. This yields the relation

$$\dot{H} = \frac{D}{Dt}\left[\int_{\Omega} \rho\left(e + \frac{1}{2}\mathbf{v} \cdot \mathbf{v}\right)\mathrm{d}\Omega\right] - \int_{\Gamma} \mathbf{t}^{(n)} \cdot \mathbf{v} \, \mathrm{d}\Gamma - \int_{\Omega} \rho \mathbf{b} \cdot \mathbf{v} \, \mathrm{d}\Omega, \tag{11}$$

where D/Dt denotes the material time derivative, e denotes the internal energy per unit mass, $\mathbf{v}$ denotes velocity, $\mathbf{t}^{(n)}$ denotes the traction vector on the surface with normal $\mathbf{n}$, $\mathbf{n}$ denotes the unit normal vector to the boundary surface Γ and $\mathbf{b}$ denotes the body force per unit mass. Substituting into Eq. (11) using the well-known relation

$$\frac{D}{Dt}\left[\int_{\Omega} \rho\left(e + \frac{1}{2}\mathbf{v} \cdot \mathbf{v}\right)\mathrm{d}\Omega\right] = \int_{\Omega} \rho(\dot{e} + \mathbf{v} \cdot \dot{\mathbf{v}})\mathrm{d}\Omega, \tag{12}$$

the law of balance of linear momentum given by

$$\frac{D}{Dt}\left[\int_{\Omega} \rho \mathbf{v} \, \mathrm{d}\Omega\right] = \int_{\Gamma} \mathbf{t}^{(\mathbf{n})} \, \mathrm{d}\Gamma + \int_{\Omega} \rho \mathbf{b} \, \mathrm{d}\Omega, \tag{13}$$

Cauchy's relation $\mathbf{t}^{(n)} = \mathbf{T}^T\mathbf{n}$ and the divergence theorem, results in

$$\dot{H} = \int_{\Omega} [\rho\dot{e} - \mathrm{tr}(\mathbf{TL})]\mathrm{d}\Omega, \tag{14}$$

where $\mathbf{L} = \dot{\mathbf{F}}\mathbf{F}^{-1}$ is the velocity gradient.

Next, we restrict our attention to the homogeneous process. It is assumed that all the measured quantities are to reflect the homogeneous response of the rubber. It can be shown that, after the application of the conservation of mass, one obtains an expression for the rate of change of heat content per unit mass, $\dot{h}$, given by

$$\dot{h} = \dot{e} - \frac{1}{\rho}\,\mathrm{tr}(\mathbf{TL}). \tag{15}$$

Using the standard relation $e = \psi + \theta\eta$ and the general expression for ψ given in Negahban (1998), one arrives at the general expression

$$\dot{h}(t) = -\xi(t)a(t) + \theta(t)\dot{\eta}(t), \tag{16}$$

where

$$\xi(t) = \psi_{\mathrm{A}}(t) - \psi_{\mathrm{C}}(t, t) + b(t)\partial_{b(t)}\psi_{\mathrm{A}}(t) + \int_{t_s}^{t} \partial_{b(t)}\psi_{\mathrm{C}}(t, s)a(s)\mathrm{d}s - p(t)\left[\frac{1}{\rho_{\mathrm{A}}(t)} - \frac{1}{\rho_{\mathrm{C}}(t)}\right], \tag{17}$$

$$\begin{aligned}\dot{\eta} = {} & a(t)\partial_{\theta(t)}\psi_{\mathrm{A}}(t) - b(t)\dot{\overline{\partial_{\theta(t)}\psi_{\mathrm{A}}(t)}} - a(t)\partial_{\theta(t)}\psi_{\mathrm{C}}(t, t) \\ & - \int_{t_s}^{t} \dot{\overline{\partial_{\theta(t)}\psi_{\mathrm{C}}(t, s)}}a(s)\mathrm{d}s - \dot{p}(t)\left[\frac{b(t)}{\rho_{\mathrm{A}}^2(t)}\frac{\mathrm{d}\rho_{\mathrm{A}}(t)}{\mathrm{d}\theta(t)} + \frac{1 - b(t)}{\rho_c^2(t)}\frac{\mathrm{d}\rho_{\mathrm{C}}(t)}{\mathrm{d}\theta(t)}\right] \\ & - p(t)\left[\dot{\overline{\frac{b(t)}{\rho_{\mathrm{A}}^2(t)}\frac{\mathrm{d}\rho_{\mathrm{A}}(t)}{\mathrm{d}\theta(t)} + \frac{1 - b(t)}{\rho_c^2(t)}\frac{\mathrm{d}\rho_{\mathrm{C}}(t)}{\mathrm{d}\theta(t)}}}\right],\end{aligned} \tag{18}$$

and '$\dot{\overline{\ }}$' denotes a material time derivative with respect to the current time of the overlined quantity. For example, for a typical function $\mathbf{A}$ of variables $\mathbf{F}(t)$, $\theta(t)$ and $b(t)$, one will have

$$\dot{\bar{\mathbf{A}}} = [\partial_{\mathbf{F}(t)}\mathbf{A}]\mathbin{:}\dot{\mathbf{F}}(t) + [\partial_{\theta(t)}\mathbf{A}]\dot{\theta}(t) - [\partial_{b(t)}\mathbf{A}]a(t). \tag{19}$$

In the above expression, p is given by

$$p(t) = \sigma_{\mathrm{ave}}(t) - \frac{2}{3}\rho(t)b(t)\left[A_1 + 2A_2\left(I_1^* - 3\right)\right]I_1^* + \frac{2}{3}\rho(t)\int_{t_s}^{t} \left[C_1 + 2C_2\left(I_4^* - 3\right)\right]I_4^* a(s)\mathrm{d}s. \tag{20}$$

One can also integrate Eq. (15) to obtain

$$h = \psi + \eta\theta - \int \frac{1}{\rho}\,\mathrm{tr}(\mathbf{TL})\mathrm{d}s, \tag{21}$$

where the constant of integration must be fit to capture the initial heat content.

3. Heat capacity

Once the expression for the rate of change of heat content is obtained, as given in Eq. (16), one can use the expressions given in Eqs. (8) and (9) for entropy and the thermodynamic force of crystallization, respectively, to evaluate the rate of change of heat content from the expression for the free energy, the average principal stress, and the expressions for the densities of the two phases.

At least four heat capacities can be defined. First, the heat capacity at constant pressure, which represents the heat needed to change the temperature one degree under constant pressure. This is not a unique quantity since the heat needed to take the polymer through this temperature change is also dependent on the amount of crystallization which occurs during this process. As a result, the heat capacity at constant pressure is a rate dependent quantity. One can calculate the heat capacity per unit mass at constant pressure, c_p, from the rate of change of heat content by the relation

$$c_\mathrm{p} = \left(\frac{\dot{h}}{\dot{\theta}}\right)_{\sigma_\mathrm{ave}}, \tag{22}$$

where the subscript 'σ_ave' refers to the fact that the quantity is calculated at a constant average principal stress. The second heat capacity one can define is the heat capacity per unit mass at constant volume, c_v. Again, as in the case of the heat capacity at constant pressure, the heat capacity at constant volume is equal to the heat required to increase the temperature of the polymer one degree, keeping the volume of the polymer constant. In the proposed model an assumption is made that the density of each phase of the polymer is only dependent on the temperature, and the macroscopic density is controlled by the temperature and the extent of crystallinity. This relation requires that the volume must change in accordance with the thermal expansion of the two phases if the crystallinity is kept constant. As a result, one is forced to have a given change in the degree of crystallinity to accommodate the constancy of volume as the temperature is changed. From Negahban (1998), we note that

$$\dot{J} = \left[\frac{\rho_0 b}{\rho_{A_0}}\frac{\mathrm{d}J_\mathrm{A}}{\mathrm{d}\theta} + \frac{\rho_0(1-b)}{\rho_{C_0}}\frac{\mathrm{d}J_\mathrm{C}}{\mathrm{d}\theta}\right]\dot{\theta} - \left[\frac{\rho_0}{\rho_{A_0}}J_\mathrm{A} - \frac{\rho_0}{\rho_{C_0}}J_\mathrm{C}\right]a. \tag{23}$$

Constancy of volume requires that $\dot{J} = 0$, which therefore requires that the rate of crystallization be given in terms of the rate of change of temperature by

$$a = \frac{\dfrac{\rho_0 b}{\rho_{A_0}}\dfrac{\mathrm{d}J_\mathrm{A}}{\mathrm{d}\theta} + \dfrac{\rho_0(1-b)}{\rho_{C_0}}\dfrac{\mathrm{d}J_\mathrm{C}}{\mathrm{d}\theta}}{\dfrac{\rho_0}{\rho_{A_0}}J_\mathrm{A} - \dfrac{\rho_0}{\rho_{C_0}}J_\mathrm{C}}\dot{\theta}. \tag{24}$$

Substitution of this rate of crystallization into the expression for the rate of change of the heat content results in an expression for the rate of change of heat content, which is a linear function of the rate of change of temperature, and also a linear function of the average principal stress. Yet the rate of crystallization is not independent of the average principal stress (see the expression for the thermodynamic force of crystallization) and, as a result, it is theoretically possible to evaluate the average principal stress needed to obtain the given rate of crystallization, assuming one has a model for the rate of crystallization. Therefore, in principal, the rate of change of heat content will be a function of the rate of change of temperature and one can potentially obtain the heat capacity per unit mass at constant volume from the expression

$$c_{\mathrm{v}} = \left(\frac{\dot{h}}{\dot{\theta}}\right)_{\mathrm{v}}, \tag{25}$$

after making the above replacements for the rate of crystallization and average principal stress. The uniqueness of this heat capacity is, in part, dependent on the linearity of the relation between the rate of crystallization and the average principal stress.

The last two heat capacities that need to be defined are heat capacities at constant crystallinity. In real experiments crystallinity is an internal parameter and can not be directly controlled independent of how the material reacts to changes of average principal stress, strain, and temperature. Yet it is informative to know how the heat capacity is affected if one could hold crystallinity constant. One can define c_{pc} as the heat capacity per unit mass at constant pressure and crystallinity, and one can define c_{vc} as the heat capacity per unit mass at constant volume and crystallinity. The two are given by

$$c_{\mathrm{pc}} = \left(\frac{\dot{h}}{\dot{\theta}}\right)_{\sigma_{\mathrm{ave}},\, b} \tag{26}$$

and

$$c_{\mathrm{vc}} = \infty. \tag{27}$$

The fact that c_{vc} is infinite is a result of the fact that in the proposed model the volume must change due to thermal expansion if the crystallinity is held constant. The infinite value of c_{vc} is the price that must be paid to gain the many other simplifications resulting from the assumption of incompressibility of each phase during isothermal processes.

4. Heat of crystallization or fusion

One can now define the isothermal heat of crystallization. Let this be denoted by $(k_{\mathrm{c}})_\theta$ and defined as heat flow per unit mass into the body per unit change in crystallization under isothermal conditions, so that

$$(k_{\mathrm{c}})_\theta = -\left(\frac{\mathrm{d}h}{\mathrm{d}b}\right)_\theta = \left(\frac{\dot{h}}{a}\right)_\theta. \tag{28}$$

This can be obtained by setting $\dot{\theta}$ equal to zero in the equation for the rate of change of heat content and division by $a(t)$. One should note that not only the current degree of crystallization and temperature, but also the conditions of loading contribute to this heat through the average principal stress and the strain dependence of the free-energy. This heat of crystallization will continuously change as the process of crystallization proceeds.

An alternate measure of the heat of crystallization is the difference in the heat content between the heat content per unit mass in the fully crystalline phase, h_{C}, and the heat content per unit mass in the fully amorphous phase, h_{A}. The heat of crystallization, Δh, will therefore be defined as

$$\Delta h = h_{\mathrm{C}} - h_{\mathrm{A}}. \tag{29}$$

5. Fundamental melting temperature and equilibrium crystallinity

In the context of the current theory, one can define a fundamental melting temperature. This temperature represents the lowest temperature at which an unconstrained amorphous material will not show a tendency to crystallize. The fundamental melting temperature will, therefore, be the temperature for which zero average principal stress combined with equal triaxial extensions will give a thermodynamic force of crystallization equal to zero for a fully amorphous material.

This same idea can also be used to describe a variety of different melting temperatures, each characterized by different loading conditions. For example, a stretched amorphous material will have a different temperature at which the thermodynamic force of crystallinity goes to zero, and will, therefore, have a different melting temperature.

An alternate problem is to keep the temperature constant and to search for the degree of crystallinity which makes the thermodynamic force of crystallization go to zero. This would define the equilibrium degree of crystallinity. Since the thermodynamic force of crystallization is loading dependent, the equilibrium crystallinity will be loading dependent. One can define, as was done above, a fundamental equilibrium degree of crystallinity by defining a unique set of conditions to be used to arrive at this quantity. Since the elementary thermodynamic quantities are evaluated under equal triaxial extension, a fundamental equilibrium degree of crystallinity will be defined by the process of super cooling of an amorphous material to a given temperature and then isothermal crystallization subject to equal triaxial extensions and under zero average principal stress until the thermodynamic force of crystallization goes to zero.

6. Imposing equal triaxial extension

As described in the introduction, the elementary thermodynamic parameters are assumed to describe the response under homogeneous equal triaxial extension. Therefore, as the material is changing its shape, either due to thermal expansion or crystallization, its deformation is described by the deformation gradients

$$\mathbf{F}(t) = J^{1/3}(t)\mathbf{I},\ \mathbf{F}_s(t) = \frac{J^{1/3}(t)}{J^{1/3}(s)}\mathbf{I}. \tag{30}$$

As a result, one will have the volume extracted deformation gradients

$$\mathbf{F}^*(t) = \mathbf{I},\ \mathbf{F}_s^*(t) = \mathbf{I}. \tag{31}$$

Therefore,

$$\mathbf{B}^*(t) = \mathbf{I},\ \mathbf{B}_s^*(t) = \mathbf{I}, \tag{32}$$

which results in

$$I^{*1} = 3,\ I^{*4} = 3. \tag{33}$$

The velocity gradient can also be evaluated as

$$\mathbf{L} = \frac{\dot{J}(t)}{3J(t)}\mathbf{I}. \tag{34}$$

Substitution of the above into Eqs. (3) and (4) results in

$$\psi_{\mathrm{A}}(t) = A_0,\ \psi_{\mathrm{C}}(t, s) = C_0 \tag{35}$$

and, as a result, one has the expression for free energy given by

$$\psi(t) = b(t)A_0 + \int_{t_{\mathrm{s}}}^{t} C_0 a(s)\mathrm{d}s. \tag{36}$$

Substitution of the above kinematical assumptions into Eqs. (7)–(9) results in expressions for the Cauchy stress, entropy and thermodynamic force of crystallization, respectively, given as

$$\mathbf{T}(t) = \sigma_{\mathrm{ave}}(t)\mathbf{I}, \tag{37}$$

$$\eta(t) = -b(t)\frac{\partial A_0}{\partial \theta(t)} - \int_{t_{\mathrm{s}}}^{t} \frac{\partial C_0}{\partial \theta(t)} a(s)\mathrm{d}s - \sigma_{\mathrm{ave}}\left[\frac{b(t)}{\rho_{\mathrm{A}}^2(t)}\frac{\mathrm{d}\rho_{\mathrm{A}}}{\mathrm{d}\theta}(t) + \frac{1-b(t)}{\rho_{\mathrm{C}}^2(t)}\frac{\mathrm{d}\rho_{\mathrm{C}}}{\mathrm{d}\theta}(t)\right] \tag{38}$$

and

$$\xi(t) = A_0 - C_0|_{s=t} + b(t)\frac{\partial A_0}{\partial b(t)} + \int_{t_{\mathrm{s}}}^{t} \frac{\partial C_0}{\partial b(t)} a(s)\mathrm{d}s - \sigma_{\mathrm{ave}}\left[\frac{1}{\rho_{\mathrm{A}}(t)} - \frac{1}{\rho_{\mathrm{C}}(t)}\right]. \tag{39}$$

The rate of change of entropy is given by

$$\begin{aligned}
\dot{\eta}(t) = {} & a(t)\frac{\partial A_0}{\partial \theta(t)} + b(t)\left[\frac{\partial^2 A_0}{\partial \theta(t)\partial b(t)} a(t) - \frac{\partial^2 A_0}{\partial^2 \theta(t)}\dot{\theta}(t)\right] - \left.\frac{\partial C_0}{\partial \theta(t)}\right|_{s=t} a(t) + \int_{t_{\mathrm{s}}}^{t} \\
& \left[\frac{\partial^2 C_0}{\partial \theta(t)\partial b(t)} a(t) - \frac{\partial^2 C_0}{\partial^2 \theta(t)}\dot{\theta}(t)\right] a(s)\mathrm{d}s - \dot{\sigma}_{\mathrm{ave}}\left[\frac{b(t)}{\rho_{\mathrm{A}}^2(t)}\frac{\mathrm{d}\rho_{\mathrm{A}}}{\mathrm{d}\theta}(t) + \frac{1-b(t)}{\rho_{\mathrm{C}}^2(t)}\frac{\mathrm{d}\rho_{\mathrm{C}}}{\mathrm{d}\theta}(t)\right] - \sigma_{\mathrm{ave}} \\
& \left\{ -\left[\frac{1}{\rho_{\mathrm{A}}^2(t)}\frac{\mathrm{d}\rho_{\mathrm{A}}}{\mathrm{d}\theta}(t) - \frac{1}{\rho_{\mathrm{C}}^2(t)}\frac{\mathrm{d}\rho_{\mathrm{C}}}{\mathrm{d}\theta}(t)\right] a(t) - 2\left[\frac{b(t)}{\rho_{\mathrm{A}}^3(t)}\left(\frac{\mathrm{d}\rho_{\mathrm{A}}}{\mathrm{d}\theta}(t)\right)^2 + \frac{1-b(t)}{\rho_{\mathrm{C}}^3(t)}\left(\frac{\mathrm{d}\rho_{\mathrm{C}}}{\mathrm{d}\theta}(t)\right)^2\right]\dot{\theta}(t) \right. \\
& \left. + \left[\frac{b(t)}{\rho_{\mathrm{A}}^2(t)}\frac{\mathrm{d}^2\rho_{\mathrm{A}}}{\mathrm{d}\theta^2}(t) + \frac{1-b(t)}{\rho_{\mathrm{C}}^2(t)}\frac{\mathrm{d}^2\rho_{\mathrm{C}}}{\mathrm{d}\theta^2}(t)\right]\dot{\theta}(t)\right\}.
\end{aligned} \tag{40}$$

The heat capacity at constant pressure and crystallinity is evaluated from Eq. (26) by setting $a(t)$ equal to zero in the expression for the rate of change of heat content Eq. (16) and in the expression for the rate of change of entropy Eq. (40). The result of this operation is

$$\begin{aligned}
c_{\mathrm{pc}} = \frac{\theta(t)\dot{\eta}}{\dot{\theta}} = \theta(t) & \left\{ - b(t)\frac{\partial^2 A_0}{\partial \theta^2(t)} - \int_{t_{\mathrm{s}}}^{t} \frac{\partial^2 C_0}{\partial^2 \theta(t)} a(s) - \sigma_{\mathrm{ave}}\left\{ -2\left[\frac{b(t)}{\rho_{\mathrm{A}}^3(t)}\left(\frac{\mathrm{d}\rho_{\mathrm{A}}}{\mathrm{d}\theta}(t)\right)^2 + \frac{1-b(t)}{\rho_{\mathrm{C}}^3(t)}\right.\right.\right. \\
& \left.\left.\left. \left(\frac{\mathrm{d}\rho_{\mathrm{C}}}{\mathrm{d}\theta}(t)\right)^2\right] + \left[\frac{b(t)}{\rho_{\mathrm{A}}^2(t)}\frac{\mathrm{d}^2\rho_{\mathrm{A}}}{\mathrm{d}\theta^2}(t) + \frac{1-b(t)}{\rho_{\mathrm{C}}^2(t)}\frac{\mathrm{d}^2\rho_{\mathrm{C}}}{\mathrm{d}\theta^2}(t)\right]\right\}\right\}.
\end{aligned} \tag{41}$$

The heat content can be directly evaluated from Eq. (21) after using the relation

$$\frac{1}{\rho(t)}\mathrm{tr}[\mathbf{T}(t)\mathbf{L}(t)] = \frac{\sigma_{\mathrm{ave}}\dot{J}(t)}{\rho_0}, \tag{42}$$

which results after the substitution of Eqs. (34) and (37) and the expression for the law of conservation of mass given by $\rho(t)J(t)=\rho_0$. In general, under equal triaxial extensions and constant average principal stress, the expression for the heat content is given by

$$h = \psi + \eta\theta - \frac{\sigma_{\mathrm{ave}}J}{\rho_0} + D, \tag{43}$$

where D is a constant of integration. For the fully amorphous material one has

$$h_{\mathrm{A}}(t) = A_0 - \theta(t)\left[\frac{\partial A_0}{\partial\theta(t)} - \frac{\sigma_{\mathrm{ave}}}{\rho_0}\frac{\mathrm{d}J_{\mathrm{A}}}{\mathrm{d}\theta}(t)\right] - \frac{\sigma_{\mathrm{ave}}}{\rho_0}J_{\mathrm{A}}(t) + D, \tag{44}$$

where, for the fully amorphous material, $\rho_0 = J_{\mathrm{A}}(t)\rho_{\mathrm{A}}(t)$. For a fully crystalline polymer ($b = 0$), one has the heat content

$$h_{\mathrm{C}}(t) = \int_{t_s}^{t} C_0 a(s)\mathrm{d}s - \theta(t)\left[\int_{t_s}^{t}\frac{\partial C_0}{\partial\theta(t)}a(s)\mathrm{d}s - \frac{\sigma_{\mathrm{ave}}}{\rho_{C_0}}\frac{\mathrm{d}J_{\mathrm{C}}}{\mathrm{d}\theta}(t)\right] - \frac{\sigma_{\mathrm{ave}}}{\rho_{C_0}}J_{\mathrm{C}}(t) + D, \tag{45}$$

where use has been made of the relation $J(t)\rho_{C_0} = J_{\mathrm{C}}(t)\rho_{A_0}$.

Considering an isothermal process under constant average principal stress which starts with an amorphous polymer and ends with a fully crystalline polymer, one can obtain the isothermal heat of crystallization as

$$\begin{aligned}\varDelta h = h_{\mathrm{C}} - h_{\mathrm{A}} = -A_0 + \int_{t_s}^{t} C_0 a(s)\mathrm{d}s + \theta\left[\frac{\partial A_0}{\partial\theta(t)} - \int_{t_s}^{t}\frac{\partial C_0}{\partial\theta(t)}a(s)\mathrm{d}s\right] - \theta\sigma_{\mathrm{ave}}\left[\frac{1}{\rho_0}\frac{\mathrm{d}J_{\mathrm{A}}}{\mathrm{d}\theta} - \frac{1}{\rho_{C_0}}\frac{\mathrm{d}J_{\mathrm{C}}}{\mathrm{d}\theta}\right] \\ + \sigma_{\mathrm{ave}}\left[\frac{J_{\mathrm{A}}}{\rho_0} - \frac{J_{\mathrm{C}}}{\rho_{C_0}}\right].\end{aligned} \tag{46}$$

7. Heat capacity and heat content of natural rubber

Van Krevelen and Hoftyzer (1976) provide expressions for heat capacity of the ‘liquid’, $c_{\mathrm{p}}^{\mathrm{l}}$ and ‘solid’, $c_{\mathrm{p}}^{\mathrm{s}}$, phases of polymers. These will be interpreted to represent, respectively, the heat capacity for the fully amorphous and the fully crystalline phases of our natural rubber. Since either heat capacity is given for a constant degree of crystallinity, the heat capacities provided by Van Krevelen and Hoftyzer will be interpreted as equivalent to c_{pc} as defined above, evaluated, respectively, for $b = 1$ and $b = 0$. The average principal stress will be assumed to be equal to zero for the purposes of this comparison.

Van Krevelen and Hoftyzer (1976) provide expressions for the heat capacity of many polymers, each put in the form

$$c_{\mathrm{p}}^{\mathrm{l}} = c_{\mathrm{p}}^{\mathrm{l}}(298\mathrm{K}) + \frac{\mathrm{d}c_{\mathrm{p}}^{\mathrm{l}}}{\mathrm{d}\theta}(\theta - 298),\ c_{\mathrm{p}}^{\mathrm{s}} = c_{\mathrm{p}}^{\mathrm{s}}(298\mathrm{K}) + \frac{\mathrm{d}c_{\mathrm{p}}^{\mathrm{s}}}{\mathrm{d}\theta}(\theta - 298), \tag{47}$$

where temperature is in degrees Kelvin, and $c_{\mathrm{p}}^{\mathrm{l}}(298\mathrm{K})$ and $c_{\mathrm{p}}^{\mathrm{s}}(298\mathrm{K})$ are, respectively, the heat capacities

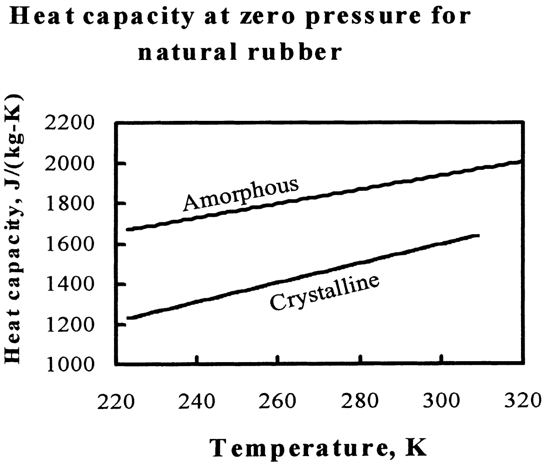

Fig. 2. Heat capacity as a function of temperature for fully crystalline and fully amorphous natural rubber at zero average principal stress.

of the fully amorphous and fully crystalline polymer at 298°K. For natural rubber, the constants are given as

$$c_{\mathrm{p}}^{\mathrm{l}}(298\mathrm{K}) = 1930\,\frac{\mathrm{J}}{\mathrm{kg}-\mathrm{K}},\ \frac{\mathrm{d}c_{\mathrm{p}}^{\mathrm{s}}}{\mathrm{d}\theta} = 3.474\,\frac{\mathrm{J}}{\mathrm{kg}-\mathrm{K}^2}, \tag{48}$$

$$c_{\mathrm{p}}^{\mathrm{s}}(298\mathrm{K}) = 1590\,\frac{\mathrm{J}}{\mathrm{kg}-\mathrm{K}},\ \frac{\mathrm{d}c_{\mathrm{p}}^{\mathrm{s}}}{\mathrm{d}\theta} = 4.77\,\frac{\mathrm{J}}{\mathrm{kg}-\mathrm{K}^2}, \tag{49}$$

where J in the units refers to Joules (not the volume ratio). Fig. 2 shows the heat capacity as a function of temperature for the fully amorphous and fully crystalline natural rubber based on the above material parameters.

At zero average principal stress and zero percent crystallinity ($b = 1$), the heat capacity at constant pressure and crystallinity is obtained from Eq. (41) as

$$c_{\mathrm{pc}}|_{b=1} = -\theta(t)\frac{\partial^2 A_0}{\partial\theta^2(t)}|_{b=1}. \tag{50}$$

Equating Eq. (50) and the expression for $c_{\mathrm{p}}^{\mathrm{l}}$ in Eq. (47), reorganization and integrating to obtain A_0 results in

$$A_0|_{b=1} = -\left[c_{\mathrm{p}}^{\mathrm{l}}(298\mathrm{K}) - 298\frac{\mathrm{d}c_{\mathrm{p}}^{\mathrm{l}}}{\mathrm{d}\theta}\right](\theta\ln(\theta) - \theta) - \frac{1}{2}\frac{\mathrm{d}c_{\mathrm{p}}^{\mathrm{l}}}{\mathrm{d}\theta}\theta^2 + \beta_{\mathrm{A}}\theta + \gamma_{\mathrm{A}}, \tag{51}$$

where since it is assumed that $A_0[\theta(t), b(t)]$, each one of the material parameters $c_{\mathrm{p}}^{\mathrm{l}}(298\mathrm{K})$, $\frac{\mathrm{d}c_{\mathrm{p}}^{\mathrm{l}}}{\mathrm{d}\theta}$, β_{A} and γ_{A} may be considered as the values evaluated at $b = 1$ of more general material functions (material parameters which are functions of b).

At zero average principal stress and 100 percent crystallinity ($b = 0$), the heat capacity at constant pressure and crystallinity is obtained from Eq. (41) as

$$c_{\mathrm{pc}}|_{b=0} = \theta(t)\int_1^0 \frac{\partial^2 C_0}{\partial\theta^2(t)}|_{b(t)=0}\,\mathrm{d}b(s). \tag{52}$$

For the sake of simplicity, it will be assumed that C_0 is only a function of $\theta(t)$ and $b(t)$. This will allow completion of the integration without the need for further information about the material response. The result of this integration is

$$c_{\mathrm{pc}}|_{b=0} = -\theta(t)\frac{\partial^2 C_0}{\partial\theta^2(t)}|_{b=0}. \tag{53}$$

Equating Eq. (53) and the expression for $c_{\mathrm{p}}^{\mathrm{s}}$ in Eq. (47), reorganization and integrating to obtain C_0 results in

$$C_0|_{b=0} = -\left[c_{\mathrm{p}}^{\mathrm{s}}(298\mathrm{K}) - 298\frac{\mathrm{d}c_{\mathrm{p}}^{\mathrm{s}}}{\mathrm{d}\theta}\right](\theta\ln(\theta)-\theta) - \frac{1}{2}\frac{\mathrm{d}c_{\mathrm{p}}^{\mathrm{s}}}{\mathrm{d}\theta}\theta^2 + \beta_{\mathrm{C}}\theta + \gamma_{\mathrm{C}}. \tag{54}$$

Again, $c_{\mathrm{p}}^{\mathrm{s}}(298\mathrm{K})$, $\frac{\mathrm{d}c_{\mathrm{p}}^{\mathrm{s}}}{\mathrm{d}\theta}$, β_{C} and γ_{C} are the values at $b = 0$ of more general material parameters which are each a function of $b(t)$.

From Eq. (44), one can evaluate the heat content of the fully amorphous polymer using the expression for A_0 given in Eq. (51). This results in

$$h_{\mathrm{A}} = \left[c_{\mathrm{p}}^{\mathrm{l}}(298\mathrm{K}) - 298\frac{\mathrm{d}c_{\mathrm{p}}^{\mathrm{l}}}{\mathrm{d}\theta}\right]\theta + \frac{1}{2}\frac{\mathrm{d}c_{\mathrm{p}}^{\mathrm{l}}}{\mathrm{d}\theta}\theta^2 + \gamma_{\mathrm{A}} + \frac{\sigma_{\mathrm{ave}}}{\rho_0}\left[\theta\frac{\mathrm{d}J_{\mathrm{A}}}{\mathrm{d}\theta} - J_{\mathrm{A}}\right] + D. \tag{55}$$

Using Eq. (45) and substituting for C_0 from Eq. (54) results in an expression for the heat content of the fully crystallized polymer to be given by

$$h_{\mathrm{C}} = \left[c_{\mathrm{p}}^{\mathrm{s}}(298\mathrm{K}) - 298\frac{\mathrm{d}c_{\mathrm{p}}^{\mathrm{s}}}{\mathrm{d}\theta}\right]\theta + \frac{1}{2}\frac{\mathrm{d}c_{\mathrm{p}}^{\mathrm{s}}}{\mathrm{d}\theta}\theta^2 + \gamma_{\mathrm{C}} + \frac{\sigma_{\mathrm{ave}}}{\rho_{C_0}}\left[\theta\frac{\mathrm{d}J_{\mathrm{C}}}{\mathrm{d}\theta} - J_{\mathrm{C}}\right] + D. \tag{56}$$

A common assumption is to set the heat content of the fully crystalline material equal to zero at the temperature equal to absolute zero. To this is added the condition that the average principal stress be zero, and one gets

$$\gamma_{\mathrm{C}} + D = 0, \tag{57}$$

which yields an expression for the heat content of the fully crystalline material as

$$h_{\mathrm{C}} = \left[c_{\mathrm{p}}^{\mathrm{s}}(298\mathrm{K}) - 298\frac{\mathrm{d}c_{\mathrm{p}}^{\mathrm{s}}}{\mathrm{d}\theta}\right]\theta + \frac{1}{2}\frac{\mathrm{d}c_{\mathrm{p}}^{\mathrm{s}}}{\mathrm{d}\theta}\theta^2 + \frac{\sigma_{\mathrm{ave}}}{\rho_{C_0}}\left[\theta\frac{\mathrm{d}J_{\mathrm{C}}}{\mathrm{d}\theta} - J_{\mathrm{C}}\right]. \tag{58}$$

The reader will note that at this point, h_{C} is fully determined by the constants given in Eq. (49) and in Negahban (2000).

At the melting temperature, θ_{m}, the heat of fusion, Δh_{m}, is given by the relation

$$h_{\mathrm{A}} = h_{\mathrm{C}} + \Delta h_{\mathrm{m}}. \tag{59}$$

Van Krevelen and Hoftyzer (1976) provide information on the heat of fusion for a variety of polymers at their melting temperature, including that for natural rubber. If the data they provide is interpreted to represent response at zero average principal stress, one can use Eq. (59) to obtain the unknown constants in the expression for h_{A}. This results in

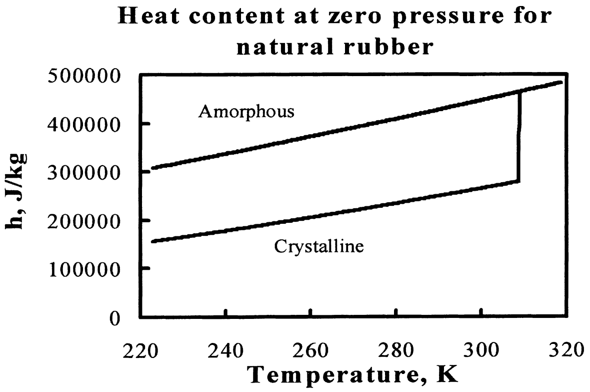

Fig. 3. Heat content as a function of temperature at zero average principal stress for a fully crystalline and fully amorphous natural rubber.

$$\gamma_{\mathrm{A}} + D = \left[c_{\mathrm{p}}^{\mathrm{s}}(298\mathrm{K}) - c_{\mathrm{p}}^{\mathrm{l}}(298\mathrm{K}) - 298\left(\frac{\mathrm{d}c_{\mathrm{p}}^{\mathrm{s}}}{\mathrm{d}\theta} - \frac{\mathrm{d}c_{\mathrm{p}}^{\mathrm{l}}}{\mathrm{d}\theta}\right)\right]\theta_{\mathrm{m}} + \frac{1}{2}\left[\frac{\mathrm{d}c_{\mathrm{p}}^{\mathrm{s}}}{\mathrm{d}\theta} - \frac{\mathrm{d}c_{\mathrm{p}}^{\mathrm{l}}}{\mathrm{d}\theta}\right]\theta_{\mathrm{m}}^{2} + \Delta h_{\mathrm{m}}, \tag{60}$$

which gives

$$\begin{aligned} h_{\mathrm{A}} = {} & \left[c_{\mathrm{p}}^{\mathrm{l}}(298\mathrm{K}) - 298\frac{\mathrm{d}c_{\mathrm{p}}^{\mathrm{l}}}{\mathrm{d}\theta}\right]\theta + \frac{1}{2}\frac{\mathrm{d}c_{\mathrm{p}}^{\mathrm{l}}}{\mathrm{d}\theta}\theta^{2} + \frac{\sigma_{\mathrm{ave}}}{\rho_0}\left[\theta\frac{\mathrm{d}J_{\mathrm{A}}}{\mathrm{d}\theta} - J_{\mathrm{A}}\right] + \left[c_{\mathrm{p}}^{\mathrm{s}}(298\mathrm{K}) - c_{\mathrm{p}}^{\mathrm{l}}(298\mathrm{K})\right. \\ & \left. - 298\left(\frac{\mathrm{d}c_{\mathrm{p}}^{\mathrm{s}}}{\mathrm{d}\theta} - \frac{\mathrm{d}c_{\mathrm{p}}^{\mathrm{l}}}{\mathrm{d}\theta}\right)\right]\theta_{\mathrm{m}} + \frac{1}{2}\left[\frac{\mathrm{d}c_{\mathrm{p}}^{\mathrm{s}}}{\mathrm{d}\theta} - \frac{\mathrm{d}c_{\mathrm{p}}^{\mathrm{l}}}{\mathrm{d}\theta}\right]\theta_{\mathrm{m}}^{2} + \Delta h_{\mathrm{m}}. \end{aligned} \tag{61}$$

As reported by Van Krevelen and Hoftyzer (1976), the heat of fusion for natural rubber at its melting temperature $\theta_{\mathrm{m}} = 309^{\circ}\mathrm{K}$ is

$$\Delta h_{\mathrm{m}} = 184338 \text{ J/kg}. \tag{62}$$

At this point, the expression for the heat content of the fully amorphous material is also completely defined by the material parameters given in Eqs. (48) and (62) and the expressions given in Negahban (2000).

Fig. 3 shows the heat content for both amorphous natural rubber and for fully crystalline natural rubber as a function of temperature based on using the above equations and the stated material parameters. Figs. 4 and 5 show, respectively, the pressure dependence of the heat content of amorphous and fully crystalline natural rubber.

8. Melting temperature and equilibrium crystallinity for natural rubber

The next step is to impose upon the model a fundamental melting temperature and existing information on the equilibrium degree of crystallinity. Both are imposed through the expression for the thermodynamic force of crystallinity.

At this point, it will further be assumed that the expression for A_0 is identical to that given for $A_0|_{b\,=\,1}$ in Eq. (51), with the exception of the fact that β_{A} is replaced by a linear function of $b(t)$ such that

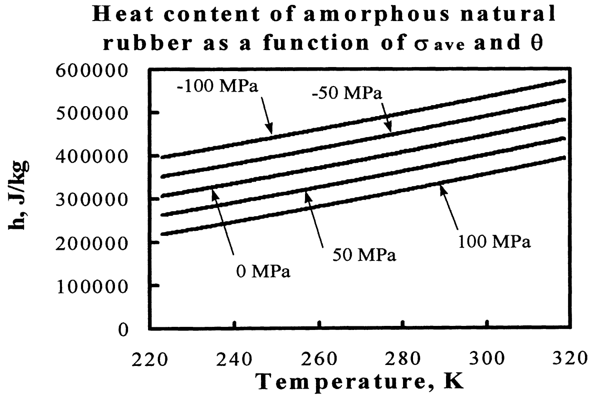

Fig. 4. Heat content as a function of temperature and average principal stress for fully amorphous natural rubber.

$$\beta_{\mathrm{A}} = \beta_{\mathrm{A}}|_{b=0} + \frac{\mathrm{d}\beta_{\mathrm{A}}}{\mathrm{d}b} b \tag{63}$$

and

$$A_0 = -\left[c_{\mathrm{p}}^{\mathrm{l}}(298\mathrm{K}) - 298\frac{\mathrm{d}c_{\mathrm{p}}^{\mathrm{l}}}{\mathrm{d}\theta}\right]\left[\theta\ln(\theta) - \theta\right] - \frac{1}{2}\frac{\mathrm{d}c_{\mathrm{p}}^{\mathrm{l}}}{\mathrm{d}\theta}\theta^2 + \left[\beta_{\mathrm{A}}|_{b=0} + \frac{\mathrm{d}\beta_{\mathrm{A}}}{\mathrm{d}b} b\right]\theta + \gamma_{\mathrm{A}}. \tag{64}$$

In a similar way it will be assumed that

$$\beta_{\mathrm{C}} = \beta_{\mathrm{C}}|_{b=0} + \frac{\mathrm{d}\beta_{\mathrm{C}}}{\mathrm{d}b} b \tag{65}$$

and

$$C_0 = -\left[c_{\mathrm{p}}^{\mathrm{s}}(298\mathrm{K}) - 298\frac{\mathrm{d}c_{\mathrm{p}}^{\mathrm{s}}}{\mathrm{d}\theta}\right]\left[\theta\ln(\theta) - \theta\right] - \frac{1}{2}\frac{\mathrm{d}c_{\mathrm{p}}^{\mathrm{s}}}{\mathrm{d}\theta}\theta^2 + \left[\beta_{\mathrm{C}}|_{b=0} + \frac{\mathrm{d}\beta_{\mathrm{C}}}{\mathrm{d}b} b\right]\theta + \gamma_{\mathrm{C}}. \tag{66}$$

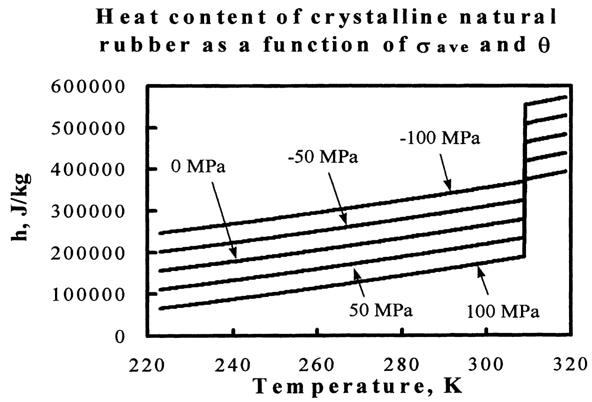

Fig. 5. Heat content as a function of temperature and average principal stress for a fully crystalline natural rubber.

This results in the thermodynamic force of crystallization in Eq. (39) to become

$$\xi = \left[c_{\mathrm{p}}^{\mathrm{s}}(298\mathrm{K}) - c_{\mathrm{p}}^{\mathrm{l}}(298\mathrm{K}) - 298\left(\frac{\mathrm{d}c_{\mathrm{p}}^{\mathrm{s}}}{\mathrm{d}\theta} - \frac{\mathrm{d}c_{\mathrm{p}}^{\mathrm{l}}}{\mathrm{d}\theta}\right)\right]\left[\theta \ln(\theta) - \theta + \theta_{\mathrm{m}}\right] + \frac{1}{2}\left(\frac{\mathrm{d}c_{\mathrm{p}}^{\mathrm{s}}}{\mathrm{d}\theta} - \frac{\mathrm{d}c_{\mathrm{p}}^{\mathrm{l}}}{\mathrm{d}\theta}\right)\left(\theta^2 + \theta_{\mathrm{m}}^2\right)$$
$$+ (\beta_{\mathrm{A}} - \beta_{\mathrm{C}})\theta + \Delta h_{\mathrm{m}} + \left[b\frac{\mathrm{d}\beta_{\mathrm{A}}}{\mathrm{d}b} + (1-b)\frac{\mathrm{d}\beta_{\mathrm{C}}}{\mathrm{d}b}\right]\theta - \sigma_{\mathrm{ave}}\left[\frac{1}{\rho_{\mathrm{A}}} - \frac{1}{\rho_{\mathrm{C}}}\right], \tag{67}$$

where $\gamma_{\mathrm{A}}-\gamma_{\mathrm{C}}$ has been eliminated using Eqs. (57) and (60).

The melting temperature is defined above as the lowest temperature at which the material has no tendency to crystallize. This condition is forced upon the model by requiring the thermodynamic force of crystallization for the fully amorphous material to be zero at the melting temperature. Using the expression for the thermodynamic force of crystallization given in Eq. (67), setting $\xi=0$, $b = 1$, $\sigma_{\mathrm{ave}}=0$ and $\theta=\theta_{\mathrm{m}}$, one obtains the following equation

$$\left(\beta_{\mathrm{A}} + \frac{\mathrm{d}\beta_{\mathrm{A}}}{\mathrm{d}b} - \beta_{\mathrm{C}}\right)_{b=1} = -\frac{1}{\theta_{\mathrm{m}}}\left\{\left[c_{\mathrm{p}}^{\mathrm{s}}(298\mathrm{K}) - c_{\mathrm{p}}^{\mathrm{l}}(298\mathrm{K}) - 298\left(\frac{\mathrm{d}c_{\mathrm{p}}^{\mathrm{s}}}{\mathrm{d}\theta} - \frac{\mathrm{d}c_{\mathrm{p}}^{\mathrm{l}}}{\mathrm{d}\theta}\right)\right]\theta_{\mathrm{m}} \ln(\theta_{\mathrm{m}})\right.$$
$$\left. + \left(\frac{\mathrm{d}c_{\mathrm{p}}^{\mathrm{s}}}{\mathrm{d}\theta} - \frac{\mathrm{d}c_{\mathrm{p}}^{\mathrm{l}}}{\mathrm{d}\theta}\right)\theta_{\mathrm{m}}^2 + \Delta h_{\mathrm{m}}\right\}. \tag{68}$$

For natural rubber this requires that

$$\left(\beta_{\mathrm{A}} + \frac{\mathrm{d}\beta_{\mathrm{A}}}{\mathrm{d}b} - \beta_{\mathrm{C}}\right)_{b=1} = 3166\,\frac{\mathrm{J}}{\mathrm{kg-K}}. \tag{69}$$

The equilibrium fraction of amorphous polymer can be obtained from Eq. (67) by setting the force of crystallization equal to zero and solving for the mass fraction of amorphous material. Letting b_∞ denote the equilibrium fraction of amorphous material, one obtains

$$b_\infty(\theta, \sigma_{\mathrm{ave}}) =$$
$$-\frac{1}{2\left(\dfrac{\mathrm{d}\beta_{\mathrm{A}}}{\mathrm{d}b} - \dfrac{\mathrm{d}\beta_{\mathrm{C}}}{\mathrm{d}b}\right)}\left\{\left[c_{\mathrm{p}}^{\mathrm{s}}(298\mathrm{K}) - c_{\mathrm{p}}^{\mathrm{l}}(298\mathrm{K}) - 298\left(\frac{\mathrm{d}c_{\mathrm{p}}^{\mathrm{s}}}{\mathrm{d}\theta} - \frac{\mathrm{d}c_{\mathrm{p}}^{\mathrm{l}}}{\mathrm{d}\theta}\right)\right]\left[\ln(\theta) + \frac{\theta_{\mathrm{m}} - \theta}{\theta}\right]\right.$$
$$\left. + \frac{1}{2}\left(\frac{\mathrm{d}c_{\mathrm{p}}^{\mathrm{s}}}{\mathrm{d}\theta} - \frac{\mathrm{d}c_{\mathrm{p}}^{\mathrm{l}}}{\mathrm{d}\theta}\right)\frac{\theta^2 + \theta_{\mathrm{m}}^2}{\theta} + \left(\beta_{\mathrm{A}} - \beta_{\mathrm{C}} + \frac{\mathrm{d}\beta_{\mathrm{C}}}{\mathrm{d}b}\right)_{b=0} + \frac{\Delta h_{\mathrm{m}}}{\theta} - \frac{\sigma_{\mathrm{ave}}}{\theta}\left[\frac{1}{\rho_{\mathrm{A}}} - \frac{1}{\rho_{\mathrm{C}}}\right]\right\}. \tag{70}$$

This can be reorganized using Eq. (68) to obtain

$$b_\infty(\theta, \sigma_{\mathrm{ave}}) = 1 - \frac{1}{2\left(\dfrac{\mathrm{d}\beta_{\mathrm{A}}}{\mathrm{d}b} - \dfrac{\mathrm{d}\beta_{\mathrm{C}}}{\mathrm{d}b}\right)}\left\{\left[c_{\mathrm{p}}^{\mathrm{s}}(298\mathrm{K}) - c_{\mathrm{p}}^{\mathrm{l}}(298\mathrm{K}) - 298\left(\frac{\mathrm{d}c_{\mathrm{p}}^{\mathrm{s}}}{\mathrm{d}\theta} - \frac{\mathrm{d}c_{\mathrm{p}}^{\mathrm{l}}}{\mathrm{d}\theta}\right)\right]\right.$$
$$\left.\left[\ln\left(\frac{\theta}{\theta_{\mathrm{m}}}\right) + \frac{\theta_{\mathrm{m}} - \theta}{\theta}\right] + \frac{1}{2}\left(\frac{\mathrm{d}c_{\mathrm{p}}^{\mathrm{s}}}{\mathrm{d}\theta} - \frac{\mathrm{d}c_{\mathrm{p}}^{\mathrm{l}}}{\mathrm{d}\theta}\right)\frac{(\theta - \theta_{\mathrm{m}})^2}{\theta} + \Delta h_{\mathrm{m}}\left(\frac{1}{\theta} - \frac{1}{\theta_{\mathrm{m}}}\right) - \frac{\sigma_{\mathrm{ave}}}{\theta}\left[\frac{1}{\rho_{\mathrm{A}}} - \frac{1}{\rho_{\mathrm{C}}}\right]\right\}. \tag{71}$$

Using the data of Leitner (1955) to fit the equilibrium crystallinity to 20% at zero average principal

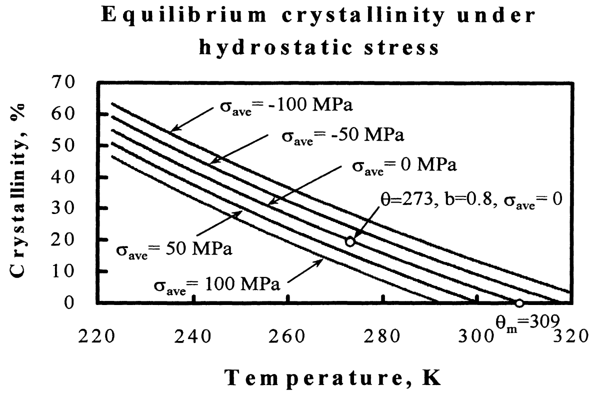

Fig. 6. Equilibrium crystallinity as a function of temperature for five different values of average principal stress.

stress and at zero degrees centigrade, one obtains

$$\frac{\mathrm{d}\beta_{\mathrm{A}}}{\mathrm{d}b}-\frac{\mathrm{d}\beta_{\mathrm{C}}}{\mathrm{d}b}=190\,\frac{\mathrm{J}}{\mathrm{kg}-\mathrm{K}}. \tag{72}$$

Fig. 6 shows the equilibrium crystallinity of natural rubber as a function of average principal stress and temperature using Eq. (71). The figure is based on forcing the model to fit the fundamental melting temperature of 309°K and to have an equilibrium crystallinity of 20% at zero degrees centigrade. Otherwise, the remainder represents predictions of the proposed model, which suggests about a 9°K rise in the melting temperature for every 50 MPa of hydrostatic pressure, which compares favorably with the Clausius–Clapeyron equation that gives an 8.3°K change in melting temperature per 50 MPa rise in pressure (see Mandelkern, 1964: Eq. 5-1, p. 120) and is consistent with published experimental results (Magill, 1995). Also, Fig. 6 shows that 100% crystallinity will be obtained at equilibrium if the material is crystallized at 175°K. At 175°K, rubber is in its glassy state and will not crystallize due to restrictions on the mobility of the molecules and, as a result, the later statement simply reflects the potential for obtaining full crystallinity if the rubber could arrive at thermodynamic equilibrium.

Entropy of the rubber can be evaluated from Eq. (38) using the expressions for A_0 and C_0 given in Eqs. (64) and (66). This results in

$$\begin{aligned}\eta={}&-b\left[c_{\mathrm{p}}^{\mathrm{s}}(298\mathrm{K})-c_{\mathrm{p}}^{\mathrm{l}}(298\mathrm{K})-298\left(\frac{\mathrm{d}c_{\mathrm{p}}^{\mathrm{s}}}{\mathrm{d}\theta}-\frac{\mathrm{d}c_{\mathrm{p}}^{\mathrm{l}}}{\mathrm{d}\theta}\right)\right]\ln(\theta)-b\left(\frac{\mathrm{d}c_{\mathrm{p}}^{\mathrm{s}}}{\mathrm{d}\theta}-\frac{\mathrm{d}c_{\mathrm{p}}^{\mathrm{l}}}{\mathrm{d}\theta}\right)\theta-b(\beta_{\mathrm{A}}-\beta_{\mathrm{C}})_{b=0}+\\&b^2\left(\frac{\mathrm{d}\beta_{\mathrm{C}}}{\mathrm{d}b}-\frac{\mathrm{d}\beta_{\mathrm{A}}}{\mathrm{d}b}\right)+\left[c_{\mathrm{p}}^{\mathrm{s}}(298\mathrm{K})-298\frac{\mathrm{d}c_{\mathrm{p}}^{\mathrm{s}}}{\mathrm{d}\theta}\right]\ln(\theta)+\frac{\mathrm{d}c_{\mathrm{p}}^{\mathrm{s}}}{\mathrm{d}\theta}\theta-\beta_{\mathrm{C}}|_{b=0}-\frac{\mathrm{d}\beta_{\mathrm{C}}}{\mathrm{d}b}b-\\&\sigma_{\mathrm{ave}}\left[\frac{b}{\rho_{\mathrm{A}_0}}\frac{\mathrm{d}J_{\mathrm{A}}}{\mathrm{d}\theta}-\frac{1-b}{\rho_{\mathrm{C}_0}}\frac{\mathrm{d}J_{\mathrm{C}}}{\mathrm{d}\theta}\right].\end{aligned} \tag{73}$$

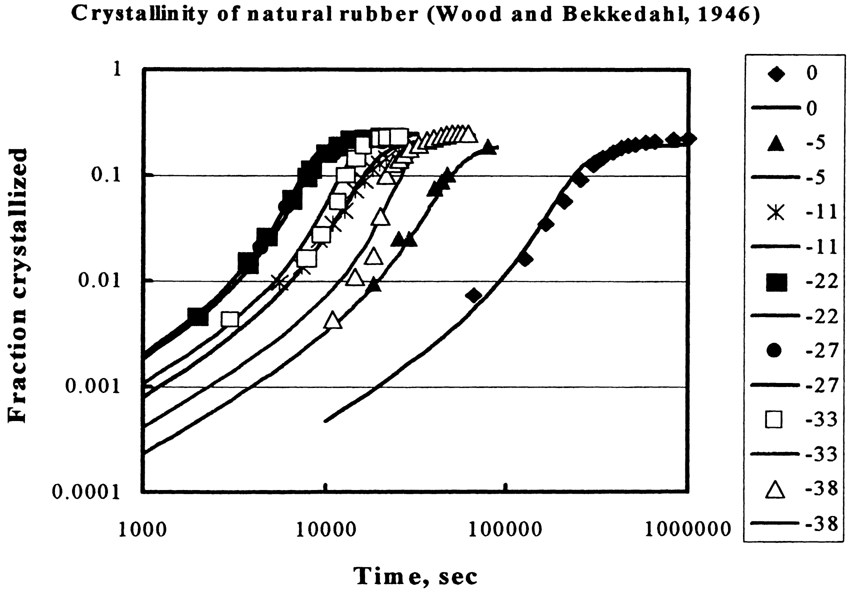

Fig. 7. Crystallinity during isothermal crystallization as a function of time for seven different temperatures. Comparison between model and the data of Wood and Bekkedahl (1946).

9. Summary and conclusion

Using elementary thermodynamic material parameters which can be obtained for most polymers, the material functions A_0 and C_0 have been evaluated for natural rubber. In the process, it is shown how the elementary material properties such as heat capacity, heat content, and melting temperature can be defined in the context of a general thermodynamic model, as is used for this study. Byproducts of this operation are explicit expressions providing the dependence of all parameters on hydrostatic pressure. For example, it is shown that the model predicts about a nine degree rise in melting temperature for each 50 MPa rise in hydrostatic pressure. Also, as shown in Fig. 7, a kinetic model can be developed that fits the experimental results of Wood and Bekkedahl (1946). Even though the experiments of Wood and Bekkedahl (1946) were conducted on unvulcanized natural rubber, the ability of the current model to fit the data is an indication of the general strength of this modeling technique.

In the process of evaluating the material functions many assumption were made. Many of these assumptions can be changed provided one has additional information about the material response. In this sense, the current article represents an example of how to use the model developed in Negahban (1997) and its simplification presented in Negahban (2000) to characterize polymer response.

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