

## SIMULATION OF MECHANICAL RESPONSE IN POLYMER CRYSTALLIZATION

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**Abstract**—The problem of following the mechanical response of a polymer during crystallization is studied using a theory developed by Negahban and Wineman [1]. Elastic modulus, shear modulus, and Poisson's ratio are defined in the context of polymer crystallization. For unconstrained crystallization and crystallization under constant uniaxial stretching, the values of elastic modulus, shear modulus, Poisson's ratio, and residual stretch are evaluated. The proposed model is fit to data available for natural rubber and the predictions of the model are discussed.

### 1. INTRODUCTION

In a recent article Negahban and Wineman [1] introduced a theory for modeling the mechanical response during polymer crystallization. The focus of the current article is to use this theory to develop example solutions to problems of experimental significance, and to show the close correlation of these predictions to experimental results.

Not all polymers crystallize, but many polymers do. For example, polyethylene, polycarbonate, polypropylene, and natural rubber all crystallize. Polymers in the amorphous (uncrystallized) form are considered to be an unorganized array of long-chain molecules. Order is introduced into the arrangement of these molecules when a polymer crystallizes. For polymers this is a gradual process and, depending on the crystallization conditions, might take up to several years to be completed. The mechanical properties of polymers change dramatically with crystallization. For example, with crystallization one can get up to five orders of magnitude increase in the elastic modulus for some polymers. Crystallization is one of the important factors in the strength of drawn polymer fibers. The purpose of this article is to show how a model proposed by Negahban and Wineman [1] can capture the changes commonly observed in polymers as they crystallize.

The theory developed by Negahban and Wineman [1] is a microstructurally motivated one. This theory produces a full multidimensional constitutive equation for the Cauchy stress. The theory incorporates the observation that crystallization in polymers is a gradual and continuous process. It is assumed that crystals are continuously being generated and that the response of these crystals will change as the conditions of crystallization change. The mechanism for including this effect is the assumption that the macroscopic value of the Cauchy stress is the mass weighted average of the effective stress in the amorphous (uncrystallized) material and the stresses in the different crystals. This results in a constitutive equation for the Cauchy stress  $\mathbf{T}$  at the current time  $t$  of the form

$$\mathbf{T}(t) = b(t)\mathbf{T}^A(t) + \int_{t_s}^t a(s)\mathbf{T}^C(t, s) ds, \quad (1)$$

where  $b(t)$  is the current ratio of amorphous matter to total matter at the particular material point,  $a(s)$  is the normalized rate of mass transfer from amorphous matter to crystalline matter at time  $s$ ,  $\mathbf{T}^A(t)$  is the current value of the effective stress in the amorphous portion of the material,  $\mathbf{T}^C(t, s)$  is the current value of the effective stress in the crystal created at time  $s$ , and  $t_s$  is the starting time of crystallization. In this expression time  $s$  is used as a marker to distinguish between crystals formed at different times, under different conditions, and which have different mechanical properties.

The rate of crystallization  $a(s)$  is the rate of mass transfer per unit total mass (amorphous plus crystallized mass) at any particular material point. Conservation of mass requires a balance between the reduction in amorphous matter and the increase in crystalline matter at any material point. This results in the following relation

$$b(t) = 1 - \int_{t_s}^t a(s) ds. \quad (2)$$

After introducing the kinematical variables in Section 2, the specific model used for this article will be developed in Section 3. In Section 4 this model will be used to simulate the gradual change in the elastic modulus, shear modulus and Poisson's ratio for unconstrained crystallization. In Section 5 this model will be used to evaluate the stress relaxation and the gradual change in the different material moduli for crystallization under a fixed uniaxial strain. In Section 6 the limit values at 100% crystallization will be calculated.

The model will be fit to specific experimental results for natural rubber in Section 7. The predictions of this model for the case of natural rubber will be discussed in Section 8.

## 2. KINEMATICS

$\kappa_0$  will denote the reference configuration of the body which will be selected as its initial stress-free configuration.  $\kappa(s)$  will denote the configuration of the body at time  $s$ . The location of a particle  $X$  in the initial configuration will be denoted by  $\mathbf{X}$ , and its location in the configuration  $\kappa(s)$  will be denoted by  $\mathbf{x}(s)$ . The motion of the body will be given by a function  $\chi$  so that

$$\mathbf{x}(t) = \chi(\mathbf{X}, t) \quad (3)$$

for any current time  $t$ .

The deformation gradient  $\mathbf{F}$  at particle  $X$  and at time  $s$  will be given by

$$\mathbf{F}(s) = \left. \frac{\partial \chi(\mathbf{r}, s)}{\partial \mathbf{r}} \right|_{\mathbf{r}=\mathbf{x}}. \quad (4)$$

The deformation gradient comparing the current configuration  $\kappa(t)$  to the configuration at time  $s$ ,  $\kappa(s)$ , will be denoted by  $\mathbf{F}_s(t)$  and defined as

$$\mathbf{F}_s(t) = \mathbf{F}(t)\mathbf{F}^{-1}(s). \quad (5)$$

The two left Cauchy strain tensors created by  $\mathbf{F}(t)$  and  $\mathbf{F}_s(t)$  will be given by

$$\mathbf{B}(t) = \mathbf{F}(t)\mathbf{F}^T(t), \quad \text{and} \quad \mathbf{B}_s(t) = \mathbf{F}_s(t)\mathbf{F}_s^T(t). \quad (6)$$

The volume ratio, the ratio of current volume to initial volume at any material point, will be denoted by  $J(t)$  and is given by

$$J(t) = \det(\mathbf{F}(t)), \quad (7)$$

where  $\det(\cdot)$  denotes the determinant operation.

### 3. DESCRIPTION OF THE GENERAL MODEL

Motivated by the assumptions of Gent [3] and others, we will assume: (a) that the material is incompressible in either state (i.e. the amorphous matter is incompressible and the crystallized matter is incompressible), (b) that the macroscopic volume at each material point is the sum of the volume of the amorphous and crystalline parts, (c) that the crystals have the same density irrespective of the conditions under which they are created. These assumptions require that any change in the macroscopic volume be only a result of transfer of matter from the amorphous to crystalline state. Under these assumptions we can write

$$\frac{1}{\rho(t)} = \frac{b(t)}{\rho_A} + \frac{(1-b(t))}{\rho_C}, \quad (8)$$

where  $\rho(t)$  is the macroscopic density of the material (total mass divided by total volume),  $\rho_A$  is the density of the amorphous material (mass of amorphous material divided by volume of amorphous material), and  $\rho_C$  is the density of the crystalline material (mass of crystals divided by volume of crystals). By the above assumptions  $\rho_A$  and  $\rho_C$  are constant. Denoting by  $J(t)$  the ratio of the current macroscopic volume to its initial value, and assuming that all the material is amorphous at the initial time, one can get the relation

$$\frac{J(t)}{\rho_A} = \frac{b(t)}{\rho_A} + \frac{(1-b(t))}{\rho_C}. \quad (9)$$

Letting  $m = \rho_C/\rho_A$  and reorganization gives

$$b(t) = \frac{mJ(t) - 1}{m - 1}. \quad (10)$$

From this relation and equation (2) it follows that

$$a(s) = -\frac{m}{m-1} \frac{dJ(s)}{ds} \quad (11)$$

In the absence of recrystallization, under these assumptions, the volume ratio  $J(s)$  is a monotonic function of  $s$ . For such situations, we can rewrite the constitutive equation for the Cauchy stress as

$$\mathbf{T}(t) = p\mathbf{I} + \frac{mJ(t) - 1}{m - 1} \mathbf{T}^A(t) + \frac{m}{m - 1} \int_{J(t)}^1 \mathbf{T}^C(t, s) dJ(s), \quad (12)$$

where the integration over time has been replaced by integration over volume ratio and an indeterminate constant  $p$  is introduced due to incompressibility. The introduction of  $p$  is required due to the fact that the volume is totally determined from the percent of crystallization and not the current value of stress.

Since the polymers are assumed to start from an amorphous state which is described by an unordered distribution of long-chain molecules, it seems reasonable to assume that the material is initially isotropic. Negahban and Wineman [1] have produced a general model for an initially isotropic material. A modification of this model which accounts for the ‘‘incompressibility’’ is given by

$$\begin{aligned} \mathbf{T}(t) = & p\mathbf{I} + b(t)[p_1\mathbf{B}(t) + p_2\mathbf{B}(t)^2] + \int_{t_0}^t a(s)\{w_2\mathbf{B}(t) + w_3\mathbf{B}^2(t) + w_4\mathbf{B}_s(t) + w_5\mathbf{B}_s^2(t) \\ & + w_6[\mathbf{B}(t)\mathbf{B}_s(t) + \mathbf{B}_s(t)\mathbf{B}(t)] + w_7[\mathbf{B}^2(t)\mathbf{B}_s(t) + \mathbf{B}_s(t)\mathbf{B}^2(t)] \\ & + w_8[\mathbf{B}(t)\mathbf{B}_s^2(t) + \mathbf{B}_s^2(t)\mathbf{B}(t)] + w_9[\mathbf{B}^2(t)\mathbf{B}_s^2(t) + \mathbf{B}_s^2(t)\mathbf{B}^2(t)]\} ds, \end{aligned} \quad (13)$$

where  $p_1, p_2$  can be scalar functions of the three isotropic invariants of  $\mathbf{B}(t)$ , and where  $w_2, \dots, w_9$  can be scalar valued functions of the three isotropic invariants of  $\mathbf{B}(t)$ ,

$$I_1 = \text{tr}(\mathbf{B}(t)), \quad I_2 = \frac{1}{2}[I_1^2 - \text{tr}(\mathbf{B}^2(t))], \quad I_3 = \det(\mathbf{B}(t)), \quad (14)$$

the three isotropic invariants of  $\mathbf{B}_s(t)$ ,

$$I_4 = \text{tr} \mathbf{B}_s(t), \quad I_5 = \frac{1}{2}[I_4^2 - \text{tr}(\mathbf{B}_s^2(t))], \quad I_6 = \det(\mathbf{B}_s(t)), \quad (15)$$

and the four joint invariants of  $\mathbf{B}(t)$  and  $\mathbf{B}_s(t)$ ,

$$I_7 = \text{tr}(\mathbf{B}(t)\mathbf{B}_s(t)), \quad I_8 = \text{tr}(\mathbf{B}^2(t)\mathbf{B}_s(t)), \quad I_9 = \text{tr}(\mathbf{B}(t)\mathbf{B}_s^2(t)), \quad I_{10} = \text{tr}(\mathbf{B}^2(t)\mathbf{B}_s^2(t)). \quad (16)$$

For the purpose of illustrating the predictions of this model and for the purpose of reproducing the behavior of natural rubber, we will assume the following special form

$$\mathbf{T}(t) = p\mathbf{I} + \frac{mJ(t) - 1}{m - 1} q(t)\mathbf{B}(t) + \frac{m}{m - 1} \int_{J(t)}^1 w(s)\mathbf{B}_s(t) dJ(s), \quad (17)$$

where  $q(t)$  can be a function of the volume ratio  $J(t)$ , and  $w(s)$  can be a function of the three isotropic invariants of  $\mathbf{B}(s)$ . In essence, we are assuming the equation for the effective stress in the amorphous part to be given by  $\mathbf{T}^A(t) = q(t)\mathbf{B}(t)$  and in the crystals to be given by  $\mathbf{T}^C(t, s) = w(s)\mathbf{B}_s(t)$ .

We will later select the particular form of  $q(t) = Q_1 + Q_2(1 - J(t))$  and  $w(s) = W_1 + W_2(1 - J(s))$  to fit experimental results for natural rubber.  $Q_1, Q_2, W_1$  and  $W_2$  are taken to be constants.

#### 4. UNCONSTRAINED CRYSTALLIZATION

We will consider unconstrained crystallization to be crystallization under the condition of equal triaxial extension with zero stress. Let us consider a material which is undergoing unconstrained crystallization from time  $t_s$  to time  $t_1$ . During the crystallization the deformation of the material is given by the deformation gradient

$$\mathbf{F}(s) = \begin{pmatrix} J^{1/3}(s) & 0 & 0 \\ 0 & J^{1/3}(s) & 0 \\ 0 & 0 & J^{1/3}(s) \end{pmatrix} \quad \text{for } s \in (t_s, t_1]. \quad (18)$$

##### 4.1. Change in elastic modulus

At time  $t_1$  the polymer is extended to facilitate the calculation of the incremental elastic modulus. This is similar to the experiments done by Leitner [2] on natural rubber. It will be assumed that this extension will not alter the crystal structure. This will be the case if the extension is small and if it is done in a time interval much smaller than the time scale for the crystallization. To capture this condition mathematically, we assume the rate of crystallization to be non-zero up to time  $t_1$  and zero after this time.

For the axial extension after time  $t_1$  it is assumed that the material undergoes no further crystallization. If the extension is along the third coordinate direction, and for the current time

$t$  greater than  $t_1$ , the deformation gradient at time  $t$  is given by

$$\mathbf{F}(t) = \begin{pmatrix} \left(\frac{J(t_1)}{\lambda(t)}\right)^{1/2} & 0 & 0 \\ 0 & \left(\frac{J(t_1)}{\lambda(t)}\right)^{1/2} & 0 \\ 0 & 0 & \lambda(t) \end{pmatrix} \text{ for } t > t_1, \quad (19)$$

where  $\lambda(t)$  is the stretch ratio along the direction of extension. This results in the expressions

$$\mathbf{B}(t) = \begin{pmatrix} \frac{J(t_1)}{\lambda(t)} & 0 & 0 \\ 0 & \frac{J(t_1)}{\lambda(t)} & 0 \\ 0 & 0 & \lambda^2(t) \end{pmatrix} \text{ for } t > t_1, \quad (20)$$

and

$$\mathbf{B}_s(t) = \begin{pmatrix} \frac{J(t_1)}{\lambda(t)J^{2/3}(s)} & 0 & 0 \\ 0 & \frac{J(t_1)}{\lambda(t)J^{2/3}(s)} & 0 \\ 0 & 0 & \frac{\lambda^2(t)}{J^{2/3}(s)} \end{pmatrix} \text{ for } t > t_1 \text{ and } s \in (t_s, t_1]. \quad (21)$$

Assuming that the deformations are homogeneous and the stress is given by

$$\mathbf{T}(t) = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & T_{33}(t) \end{pmatrix} \text{ for } t > t_1, \quad (22)$$

the following two independent equations result from the substitution of this stress into the constitutive equation (17).

$$0 = p + \frac{mJ(t_1) - 1}{m - 1} q(t_1) \frac{J(t_1)}{\lambda(t)} + \frac{m}{m - 1} \int_{J(t_1)}^1 w(s) \frac{J(t_1)}{\lambda(t)J^{2/3}(s)} dJ(s), \quad (23)$$

$$T_{33}(t) = p + \frac{mJ(t_1) - 1}{m - 1} q(t_1) \lambda^2(t) + \frac{m}{m - 1} \int_{J(t_1)}^1 w(s) \frac{\lambda^2(t)}{J^{2/3}(s)} dJ(s). \quad (24)$$

It is noted that the limit of the integral is set from  $J(t_1)$  to 1 since the rate of crystallization (and, therefore, the rate of change of  $J$ ) will be zero after  $t_1$ . Elimination of  $p$  from these equations yields

$$T_{33}(t) = \left[ \frac{mJ(t_1) - 1}{m - 1} q(t_1) + \frac{m}{m - 1} \int_{J(t_1)}^1 \frac{w(s)}{J^{2/3}(s)} dJ(s) \right] \left[ \lambda^2(t) - \frac{J(t_1)}{\lambda(t)} \right]. \quad (25)$$

This equation would represent the one dimensional stress-stretch ratio relation of the polymer if it would undergo no further crystallization.

The incremental elastic modulus  $E$  will be defined as

$$E = \frac{dT_{33}(t)}{d\lambda(t)} = \left[ \frac{mJ(t_1) - 1}{m - 1} q(t_1) + \frac{m}{m - 1} \int_{J(t_1)}^1 \frac{w(s)}{J^{2/3}(s)} dJ(s) \right] \left[ 2\lambda(t) + \frac{J(t_1)}{\lambda^2(t)} \right]. \quad (26)$$

That is,  $E$  is the ratio of the change in stress to change in stretch ratio at any particular stretch ratio.

The elastic modulus at zero stress will be denoted by  $E^0$ . The stretch ratio at zero stress will be denoted by  $\lambda^0$ , and in this case is given by  $\lambda^0 = J^{1/3}(t_1)$ . Therefore,  $E^0$  is given by

$$E^0 = \left. \frac{dT_{33}(t)}{d\lambda(t)} \right|_{\lambda(t)=\lambda^0} = \left[ \frac{mJ(t_1) - 1}{m - 1} q(t_1) + \frac{m}{m - 1} \int_{J(t_1)}^1 \frac{w(s)}{J^{2/3}(s)} dJ(s) \right] [3J^{1/3}(t_1)]. \quad (27)$$

There is the relation

$$\frac{d\varepsilon(t)}{d\lambda(t)} = \frac{1}{\lambda(t)}, \quad (28)$$

where  $\varepsilon(t)$  is strain measured using change in length per unit current length. Using this relation, one can define a incremental elastic modulus  $\hat{E}$  which is the change in stress per unit change of  $\varepsilon(t)$ . This would result relation

$$\hat{E} = \frac{dT_{33}(t)}{d\varepsilon(t)} = \lambda(t)E = \left[ \frac{mJ(t_1) - 1}{m - 1} q(t_1) + \frac{m}{m - 1} \int_{J(t_1)}^1 \frac{w(s)}{J^{2/3}(s)} dJ(s) \right] \left[ 2\lambda^2(t) + \frac{J(t_1)}{\lambda(t)} \right]. \quad (29)$$

For this definition of elastic modulus one obtains the relation

$$\hat{E}^0 = J^{1/3}(t_1)E^0. \quad (30)$$

In most cases there will be little difference between  $\hat{E}^0$  and  $E^0$  since  $J(t_1)$  is very close to unity.

#### 4.2. Poisson's ratio

One can define a Poisson's ratio as the ratio of the change in the transverse stretch ratio to change in the axial stretch ratio in a simple extension process. After the crystallization has stopped at time  $t_1$ , a Poisson's ratio can be defined as

$$\nu = - \frac{d\lambda_t(t)}{d\lambda_a(t)}, \quad (31)$$

where  $\lambda_t(t)$  is the transverse stretch ratio and  $\lambda_a(t)$  is the axial stretch ratio. Using the relation  $\lambda_t^2(t)\lambda_a(t) = J(t_1)$ , one can get

$$\nu = \frac{1}{2} \left( \frac{J(t_1)}{\lambda_a^3(t)} \right)^{1/2}. \quad (32)$$

It is noted that this Poisson's ratio is not equal to  $\frac{1}{2}$  in general. The Poisson's ratio at zero stress can be obtained by replacing  $\lambda_a(t)$  by its value at zero stress given by  $\lambda^0 = J^{1/3}(t_1)$ . This gives the Poisson's ratio at zero stress,  $\nu^0$ , as

$$\nu^0 = \frac{1}{2}. \quad (33)$$

An alternate definition of Poisson's ratio can be given in terms of the axial and transverse strains measured relative to the current lengths,  $\varepsilon_a(t)$  and  $\varepsilon_t(t)$ , respectively. There are the following relations

$$\frac{d\varepsilon_a(t)}{d\lambda_a(t)} = \frac{1}{\lambda_a(t)}, \quad \text{and} \quad \frac{d\varepsilon_t(t)}{d\lambda_t(t)} = \frac{1}{\lambda_t(t)}. \quad (34)$$

We denote the Poisson's ratio relative to this measure of strain as  $\hat{\nu}$  and it is given by

$$\hat{\nu} = - \frac{d\varepsilon_t(t)}{d\varepsilon_a(t)} = - \frac{\lambda_a(t) d\lambda_t(t)}{\lambda_t(t) d\lambda_a(t)}. \quad (35)$$

The value of this Poisson's ratio at zero stress will be given by the substitution  $\lambda_a^0(t) = \lambda_t^0(t) = J^{1/3}(t_1)$ . This yields

$$\hat{\nu}^0 = \nu^0 = \frac{1}{2}. \quad (36)$$

### 4.3. Shear modulus

Consider subjecting the material to a triaxial extension and shear after the completion of crystallization at time  $t_1$ . For a shear in the 1–2 plane and of the magnitude  $\gamma(t)$ , the deformation gradient can be written as

$$\mathbf{F}(t) = \begin{pmatrix} \lambda_1(t) & \gamma(t)\lambda_2(t) & 0 \\ 0 & \lambda_2(t) & 0 \\ 0 & 0 & \lambda_3(t) \end{pmatrix} \text{ for } t > t_1, \quad (37)$$

where  $\lambda_1(t)$ ,  $\lambda_2(t)$ , and  $\lambda_3(t)$  are stretch ratios in the three coordinate directions. This results in the relative deformation gradient  $\mathbf{F}_s(t)$  for this case to be

$$\mathbf{F}_s(t) = \begin{pmatrix} \frac{\lambda_1(t)}{J^{1/3}(s)} & \frac{\gamma(t)\lambda_2(t)}{J^{1/3}(s)} & 0 \\ 0 & \frac{\lambda_2(t)}{J^{1/3}(s)} & 0 \\ 0 & 0 & \frac{\lambda_3(t)}{J^{1/3}(s)} \end{pmatrix} \text{ for } t > t_1 \text{ and } s \in (t_s, t_1]. \quad (38)$$

This results in the expressions

$$\mathbf{B}(t) = \begin{pmatrix} \lambda_1^2(t) + \gamma^2(t)\lambda_2^2(t) & \gamma(t)\lambda_2^2(t) & 0 \\ \gamma(t)\lambda_2^2(t) & \lambda_2^2(t) & 0 \\ 0 & 0 & \lambda_3^2(t) \end{pmatrix} \text{ for } t > t_1, \quad (39)$$

and

$$\mathbf{B}_s(t) = \begin{pmatrix} \frac{\lambda_1^2(t)}{J^{2/3}(s)} + \frac{\gamma^2(t)\lambda_2^2(t)}{J^{2/3}(s)} & \frac{\gamma(t)\lambda_2^2(t)}{J^{2/3}(s)} & 0 \\ \frac{\gamma(t)\lambda_2^2(t)}{J^{2/3}(s)} & \frac{\lambda_2^2(t)}{J^{2/3}(s)} & 0 \\ 0 & 0 & \frac{\lambda_3^2(t)}{J^{2/3}(s)} \end{pmatrix} \text{ for } t > t_1 \text{ and } s \in (t_s, t_1]. \quad (40)$$

Assuming a homogeneous stress field of the form

$$\mathbf{T}(t) = \begin{pmatrix} T_{11}(t) & T_{12}(t) & 0 \\ T_{12}(t) & T_{22}(t) & 0 \\ 0 & 0 & T_{33}(t) \end{pmatrix} \text{ for } t > t_1, \quad (41)$$

and substituting into the constitutive equation (17) yields the expression for shear stress  $T_{12}(t)$  as

$$T_{12}(t) = \left[ \frac{mJ(t_1) - 1}{m - 1} q(t_1) + \frac{m}{m - 1} \int_{J(t_1)}^1 \frac{w(s)}{J^{2/3}(s)} dJ(s) \right] \gamma(t)\lambda_2^2(t). \quad (42)$$

The incremental shear modulus  $G$  will be given by

$$G = G_{12} = \frac{\partial T_{12}(t)}{\partial \gamma(t)} = \left[ \frac{mJ(t_1) - 1}{m - 1} q(t_1) + \frac{m}{m - 1} \int_{J(t_1)}^1 \frac{w(s)}{J^{2/3}(s)} dJ(s) \right] \lambda_2^2(t). \quad (43)$$

It is noted that, even though this shear modulus is independent of the magnitude of  $\gamma(t)$ , the shear modulus is a function of the stretch ratio  $\lambda_2(t)$ . The shear modulus in the stress-free configuration will be denoted by  $G^0$  and is obtained from  $G$  by the substitution of  $\lambda^0 = J^{1/3}(t_1)$

for  $\lambda_2(t)$ . This operation yields

$$G^0 = \left[ \frac{mJ(t_1) - 1}{m - 1} q(t_1) + \frac{m}{m - 1} \int_{J(t_1)}^1 \frac{w(s)}{J^{2/3}(s)} dJ(s) \right] J^{2/3}(t_1). \quad (44)$$

This yields the relation

$$G^0 = \frac{\hat{E}^0}{3}. \quad (45)$$

## 5. CRYSTALLIZATION UNDER A FIXED UNIAXIAL STRAIN

Consider a process in which a polymer is held with constant strain along the third material axis and allowed to crystallize. During the crystallization process the deformation gradient is given by

$$\mathbf{F}(s) = \begin{pmatrix} \left(\frac{J(s)}{\bar{\lambda}}\right)^{1/2} & 0 & 0 \\ 0 & \left(\frac{J(s)}{\bar{\lambda}}\right)^{1/2} & 0 \\ 0 & 0 & \bar{\lambda} \end{pmatrix}, \quad (46)$$

where  $s$  denotes any time during the crystallization process and  $\bar{\lambda}$  denotes the constant stretch ratio. As can be seen, even though the stretch is constant along one direction, it will vary along the other two directions due to the change in volume of the material during crystallization.

### 5.1. Stress relaxation

The decrease in stress as a sample crystallizes can be evaluated from (17). The stress field is taken to be homogeneous and given by

$$\mathbf{T}(t) = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & T_{33}(t) \end{pmatrix}. \quad (47)$$

Noting that the deformation gradient at time  $t$  is similar to that given in (46), the expression for  $\mathbf{B}(t)$  will be given as

$$\mathbf{B}(t) = \begin{pmatrix} \frac{J(t)}{\bar{\lambda}} & 0 & 0 \\ 0 & \frac{J(t)}{\bar{\lambda}} & 0 \\ 0 & 0 & \bar{\lambda}^2 \end{pmatrix}, \quad (48)$$

and the expression for  $\mathbf{B}_s(t)$  will be given by

$$\mathbf{B}_s(t) = \begin{pmatrix} \frac{J(t)}{J(s)} & 0 & 0 \\ 0 & \frac{J(t)}{J(s)} & 0 \\ 0 & 0 & 1 \end{pmatrix}. \quad (49)$$



Substitution of these expressions into the constitutive expression for the stress given in (17), yields the two independent equations

$$0 = p + \frac{mJ(t) - 1}{m - 1} q(t) \frac{J(t)}{\bar{\lambda}} + \frac{m}{m - 1} \int_{J(t)}^1 w(s) \frac{J(t)}{J(s)} dJ(s), \quad (50)$$

$$T_{33}(t) = p + \frac{mJ(t) - 1}{m - 1} q(t) \bar{\lambda}^2 + \frac{m}{m - 1} \int_{J(t)}^1 w(s) dJ(s). \quad (51)$$

Elimination of  $p$  yields the equation for the stress relaxation as

$$T_{33}(t) = \frac{mJ(t) - 1}{m - 1} q(t) \left[ \bar{\lambda}^2 - \frac{J(t)}{\bar{\lambda}} \right] + \frac{m}{m - 1} \left[ \int_{J(t)}^1 w(s) dJ(s) - J(t) \int_{J(t)}^1 \frac{w(s)}{J(s)} dJ(s) \right]. \quad (52)$$

### 5.2. Change in the axial incremental elastic modulus

Consider an experiment in which a sample is stretched and held along the third material axis at a stretch ratio  $\bar{\lambda}$  from time  $t_s$  to time  $t_1$ . In this time interval the polymer is assumed to crystallize by some amount. At time  $t_1$  the sample is slightly extended further and the change in stress divided by the change in stretch ratio is defined as the axial incremental elastic modulus. This is similar to tests done by Stevenson [4] on natural rubber. It is assumed that this small extension does not alter the crystal structure or the crystallization process. It is also assumed that the time it takes to do this measurement is much smaller than the time scale of crystallization and, therefore, no substantial further crystallization occurs when doing these measurements.

To reproduce this experiment mathematically, we assume that the crystallization in the time taken to do the second extension is insignificant, and, therefore, the rate of crystallization can be put at zero in this interval. The deformation gradient in this second extension will be given as

$$\mathbf{F}(t) = \begin{pmatrix} \left( \frac{J(t_1)}{\lambda(t)} \right)^{1/2} & 0 & 0 \\ 0 & \left( \frac{J(t_1)}{\lambda(t)} \right)^{1/2} & 0 \\ 0 & 0 & \lambda(t) \end{pmatrix} \text{ for } t > t_1, \quad (53)$$

where  $\lambda(t)$  is a stretch ratio along the same direction as the initial extension. This results in the expressions

$$\mathbf{B}(t) = \begin{pmatrix} \frac{J(t_1)}{\lambda(t)} & 0 & 0 \\ 0 & \frac{J(t_1)}{\lambda(t)} & 0 \\ 0 & 0 & \lambda^2(t) \end{pmatrix} \text{ for } t > t_1, \quad (54)$$

and

$$\mathbf{B}_s(t) = \begin{pmatrix} \frac{J(t_1) \bar{\lambda}}{\lambda(t) J(s)} & 0 & 0 \\ 0 & \frac{J(t_1) \bar{\lambda}}{\lambda(t) J(s)} & 0 \\ 0 & 0 & \frac{\lambda^2(t)}{\bar{\lambda}^2} \end{pmatrix} \text{ for } t > t_1 \text{ and } s \in (t_s, t_1]. \quad (55)$$

Assuming a homogeneous stress distribution of the form

$$\mathbf{T}(t) = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & T_{33}(t) \end{pmatrix}, \quad (56)$$

and substitution into (17) yields the two equations

$$0 = p + \frac{mJ(t_1) - 1}{m - 1} q(t_1) \frac{J(t_1)}{\lambda(t)} + \frac{m}{m - 1} \int_{J(t_1)}^1 w(s) \frac{J(t_1)\bar{\lambda}}{\lambda(t)J(s)} dJ(s), \quad (57)$$

$$T_{33}(t) = p + \frac{mJ(t_1) - 1}{m - 1} q(t_1)\lambda(t)^2 + \frac{m}{m - 1} \int_{J(t_1)}^1 w(s) \frac{\lambda^2(t)}{\bar{\lambda}^2} dJ(s). \quad (58)$$

Elimination of  $p$  yields

$$T_{33}(t) = \frac{mJ(t_1) - 1}{m - 1} q(t_1) \left[ \lambda^2(t) - \frac{J(t_1)}{\lambda(t)} \right] + \frac{m}{m - 1} \left[ \frac{\lambda^2(t)}{\bar{\lambda}^2} \int_{J(t_1)}^1 w(s) dJ(s) - \frac{J(t_1)\bar{\lambda}}{\lambda(t)} \int_{J(t_1)}^1 \frac{w(s)}{J(s)} dJ(s) \right]. \quad (59)$$

This equation is the post crystallization axial stress-stretch ratio relation for a material which has stopped crystallizing at time  $t_1$ .

The axial incremental elastic modulus  $E_a$  will be given by

$$E_a = \frac{dT_{33}(t)}{d\lambda(t)} = \frac{mJ(t_1) - 1}{m - 1} q(t_1) \left[ 2\lambda(t) + \frac{J(t_1)}{\lambda^2(t)} \right] + \frac{m}{m - 1} \left[ \frac{2\lambda(t)}{\bar{\lambda}^2} \int_{J(t_1)}^1 w(s) dJ(s) + \frac{J(t_1)\bar{\lambda}}{\lambda^2(t)} \int_{J(t_1)}^1 \frac{w(s)}{J(s)} dJ(s) \right]. \quad (60)$$

The value of  $E_a$  at  $\lambda(t) = \bar{\lambda}$  will be denoted by  $\bar{E}_a$  and is given by

$$\bar{E}_a = \frac{mJ(t_1) - 1}{m - 1} q(t_1) \left[ 2\bar{\lambda} + \frac{J(t_1)}{\bar{\lambda}^2} \right] + \frac{m}{\bar{\lambda}(m - 1)} \left[ 2 \int_{J(t_1)}^1 w(s) dJ(s) + J(t_1) \int_{J(t_1)}^1 \frac{w(s)}{J(s)} dJ(s) \right]. \quad (61)$$

Even though equation (61) yields the incremental elastic modulus as defined by Stevenson [4], it is sometimes more informative to work in terms of a strain defined in terms of change in length divided by current length,  $\varepsilon(t)$ . Using the relation given in (28), one can obtain

$$\hat{E}_a = \frac{dT_{33}(t)}{d\varepsilon(t)} = \lambda(t)E_a, \quad (62)$$

and

$$\hat{E}_a = \left. \frac{dT_{33}(t)}{d\varepsilon(t)} \right|_{\varepsilon(t)=0} = \bar{\lambda}\bar{E}_a. \quad (63)$$

### 5.3. Residual strain after crystallization

After crystallization the residual strain in the sample can be evaluated by unloading it to zero stress. Mathematically this can be done by setting  $T_{33}(t) = 0$  in equation (59) and solving for the stretch ratio corresponding to this stress. Denoting the axial stretch ratio at zero stress by  $\lambda_a^0$ , it will, therefore, be the solution of

$$0 = \frac{mJ(t_1) - 1}{m - 1} q(t_1) \left[ \lambda_a^{0^2} - \frac{J(t_1)}{\lambda_a^0} \right] + \frac{m}{m - 1} \left[ \frac{\lambda_a^{0^2}}{\bar{\lambda}^2} \int_{J(t_1)}^1 w(s) dJ(s) - \frac{J(t_1)\bar{\lambda}}{\lambda_a^0} \int_{J(t_1)}^1 \frac{w(s)}{J(s)} dJ(s) \right]. \quad (64)$$

This gives the relation

$$\lambda_a^{03} = \frac{\left[ (mJ(t_1) - 1)q(t_1) + m\bar{\lambda} \int_{J(t_1)}^1 \frac{w(s)}{J(s)} dJ(s) \right] J(t_1)}{(mJ(t_1) - 1)q(t_1) + \frac{m}{\bar{\lambda}^2} \int_{J(t_1)}^1 w(s) dJ(s)}. \quad (65)$$

Using the definitions

$$K_1 = \frac{1}{m-1} \left[ (mJ(t_1) - 1)q(t_1) + m\bar{\lambda} \int_{J(t_1)}^1 \frac{w(s)}{J(s)} dJ(s) \right], \quad (66)$$

$$K_2 = \frac{1}{m-1} \left[ (mJ(t_1) - 1)q(t_1) + \frac{m}{\bar{\lambda}^2} \int_{J(t_1)}^1 w(s) dJ(s) \right], \quad (67)$$

we can write

$$\lambda_a^0 = \left( \frac{K_1 J(t_1)}{K_2} \right)^{1/3}. \quad (68)$$

The transverse stretch ratio at zero stress,  $\lambda_t^0$ , is simply given by

$$\lambda_t^0 = \left( \frac{J(t_1)}{\lambda_a^0} \right)^{1/2} = \left( \frac{K_2 J^2(t_1)}{K_1} \right)^{1/6}. \quad (69)$$

#### 5.4. Change in the moduli at zero stress

5.4.1. *Elastic moduli.* The axial elastic modulus at zero stress can be obtained by substitution

of the axial stretch ratio,  $\lambda_a^0$  given in (68), into the incremental modulus expression given in (60). Denoting the axial elastic modulus at zero stress by  $E_a^0$ , one can get

$$E_a^0 = 3(K_1 K_2^2 J(t_1))^{1/3}, \quad (70)$$

where  $K_1$  and  $K_2$  are given in (66) and (67), respectively.

The transverse elastic modulus at zero stress can be obtained by extending the polymer along any transverse direction. For such a deformation, the current value of the deformation gradient is given by

$$\mathbf{F}(t) = \begin{pmatrix} \lambda_1(t) & 0 & 0 \\ 0 & \lambda_2(t) & 0 \\ 0 & 0 & \lambda_3(t) \end{pmatrix}. \quad (71)$$

This results in

$$\mathbf{B}(t) = \begin{pmatrix} \lambda_1^2(t) & 0 & 0 \\ 0 & \lambda_2^2(t) & 0 \\ 0 & 0 & \lambda_3^2(t) \end{pmatrix} \quad \text{for } t > t_1, \quad (72)$$

and

$$\mathbf{B}_s(t) = \begin{pmatrix} \frac{\lambda_1^2(t)\bar{\lambda}}{J(s)} & 0 & 0 \\ 0 & \frac{\lambda_2^2(t)\bar{\lambda}}{J(s)} & 0 \\ 0 & 0 & \frac{\lambda_3^2(t)}{\bar{\lambda}^2} \end{pmatrix} \quad \text{for } t > t_1 \quad \text{and } s \in (t_s, t_1]. \quad (73)$$

Assuming extension along the second axis with a homogeneous stress distribution given by

$$\mathbf{T}(t) = \begin{pmatrix} 0 & 0 & 0 \\ 0 & T_{22}(t) & 0 \\ 0 & 0 & 0 \end{pmatrix}, \quad (74)$$

by substitution into (17) one obtains the three equations

$$0 = p + \frac{mJ(t_1) - 1}{m - 1} q(t_1) \lambda_1^2(t) + \frac{m}{m - 1} \int_{J(t_1)}^1 w(s) \frac{\lambda_1^2(t) \bar{\lambda}}{J(s)} dJ(s), \quad (75)$$

$$T_{22}(t) = p + \frac{mJ(t_1) - 1}{m - 1} q(t_1) \lambda_2^2(t) + \frac{m}{m - 1} \int_{J(t_1)}^1 w(s) \frac{\lambda_2^2(t) \bar{\lambda}}{J(s)} dJ(s), \quad (76)$$

$$0 = p + \frac{mJ(t_1) - 1}{m - 1} q(t_1) \lambda_3^2(t) + \frac{m}{m - 1} \int_{J(t_1)}^1 w(s) \frac{\lambda_3^2(t)}{\bar{\lambda}^2} dJ(s). \quad (77)$$

Using the condition  $\lambda_1(t) \lambda_2(t) \lambda_3(t) = J(t_1)$  and by elimination of  $p$  from (75) and (77), one gets

$$\lambda_1^2(t) = \left( \frac{K_2}{K_1} \right)^{1/2} \frac{J(t_1)}{\lambda_2(t)}, \quad \lambda_3^2(t) = \left( \frac{K_1}{K_2} \right)^{1/2} \frac{J(t_1)}{\lambda_2(t)}, \quad \text{and} \quad p = -(K_1 K_2)^{1/2} \frac{J(t_1)}{\lambda_2(t)}, \quad (78)$$

where  $K_1$  and  $K_2$  are the same as given in (66) and (67), respectively. Substitution of  $p$  into (76) yields the expression for the stress  $T_{22}(t)$  as

$$T_{22}(t) = K_1 \lambda_2^2(t) - (K_1 K_2)^{1/2} \frac{J(t_1)}{\lambda_2(t)}. \quad (79)$$

The transverse incremental elastic modulus  $E_t$  can be evaluated from this relation by

$$E_t = \frac{dT_{22}(t)}{d\lambda_2(t)} = 2K_1 \lambda_2(t) + (K_1 K_2)^{1/2} \frac{J(t_1)}{\lambda_2^2(t)}. \quad (80)$$

Substituting the value of the stress-free stretch ratio  $\lambda_r^0$  from (69) for  $\lambda_2(t)$  yields the expression for the transverse elastic modulus at zero stress as

$$E_t^0 = 3[K_1^5 K_2 J^2(t_1)]^{1/6}. \quad (81)$$

Comparison of the zero stress axial and transverse elastic moduli given in equations (70) and (81), respectively, yields the relation

$$\frac{E_t^0}{E_a^0} = \left( \frac{K_1}{K_2} \right)^{1/2} = \left( \frac{\lambda_a^{03}}{J(t_1)} \right)^{1/2}. \quad (82)$$

One can define different elastic moduli in terms of strain  $\varepsilon(t)$  which measures the change in length per current length. The relation between this measure of strain and the stretch ratio is given in equation (34).  $\hat{E}_a$  and  $\hat{E}_t$  will denote the axial and transverse incremental elastic moduli, respectively. They will have the value

$$\hat{E}_a = \frac{dT_{33}(t)}{d\varepsilon_a(t)} = \lambda_a(t) E_a, \quad (83)$$

and

$$\hat{E}_t = \frac{dT_{22}(t)}{d\varepsilon_t(t)} = \lambda_t(t) E_t, \quad (84)$$

where  $T_{33}(t)$  is given in (59) and  $T_{22}(t)$  is given in (79). The corresponding values of the moduli at zero stress will be obtained as

$$\hat{E}_a^0 = \lambda_a^0 E_a^0 = 3(K_1^2 K_2 J^2(t_1))^{1/3}, \quad (85)$$

and

$$\hat{E}_t^0 = \lambda_t^0 E_t^0 = 3(K_1^2 K_2 J^2(t_1))^{1/3}. \quad (86)$$

It is noted that for this definition of elastic modulus  $\hat{E}_a^0 = \hat{E}_t^0$ .

5.4.2. *Poisson's ratio.* Consider an experiment in which one holds the polymer at a constant stretch ratio  $\bar{\lambda}$  along the axial direction (the third material axis) for a period of crystallization from time  $t_s$  to  $t_1$ . After the crystallization, the sample is deformed along the same axial direction and the ratio of change of the transverse stretch ratio to the axial stretch ratio is studied. We will define a Poisson's ratio for this situation as

$$\nu_{ia} = \nu_{13} = \nu_{23} = -\frac{d\lambda_i(t)}{d\lambda_a(t)}, \quad (87)$$

where  $\nu_{ij}$  denotes the Poisson's ratio obtained from stretching along the  $j$  direction and evaluating the ratio of the contraction in the  $i$  direction to the change in extension in the  $j$  direction. Using the relation  $\lambda_a(t)\lambda_i^2(t) = J(t_1)$  one can get

$$\nu_{ia} = \nu_{13} = \nu_{23} = \frac{1}{2} \left( \frac{J(t_1)}{\lambda_a^3(t)} \right)^{1/2}. \quad (88)$$

To evaluate this Poisson's ratio at zero stress,  $\nu_{ia}^0$ , one can substitute for  $\lambda_a(t)$  from (68) to get

$$\nu_{ia}^0 = \nu_{13}^0 = \nu_{23}^0 = \frac{1}{2} \left( \frac{K_2}{K_1} \right)^{1/2} = \frac{E_a^0}{2E_i^0}. \quad (89)$$

As can be seen, for this definition of Poisson's ratio, even though the material is incompressible after crystallization, the Poisson's ratio is not  $\frac{1}{2}$ .

At least two other Poisson's ratios can be defined. Consider the same crystallization process, but after the crystallization extend the sample along one of the transverse directions (first or second material axis). If one extends the material along the second material axis, one can define the Poisson's ratios for this process as

$$\nu_{32} = -\frac{d\lambda_3(t)}{d\lambda_2(t)} = \nu_{31} \quad \text{and} \quad \nu_{12} = -\frac{d\lambda_1(t)}{d\lambda_2(t)} = \nu_{21}. \quad (90)$$

Using the relations given in (78), which are derived for similar boundary conditions, one obtains

$$\nu_{32} = \nu_{31} = \frac{1}{2} \left( \frac{K_1 J^2(t_1)}{K_2 \lambda_2^6(t)} \right)^{1/4} \quad \text{and} \quad \nu_{12} = \nu_{21} = \frac{1}{2} \left( \frac{K_2 J^2(t_1)}{K_1 \lambda_2^6(t)} \right)^{1/4}. \quad (91)$$

To get these Poisson's ratios at the stress-free configuration, one can substitute  $\lambda_i^0$  for  $\lambda_2(t)$  from (69). This yields the Poisson's ratios at zero stress as

$$\nu_{32}^0 = \nu_{31}^0 = \frac{1}{2} \left( \frac{K_1}{K_2} \right)^{1/2} = \frac{E_i^0}{2E_a^0} = \frac{1}{4\nu_{13}^0}, \quad (92)$$

and

$$\nu_{12}^0 = \nu_{21}^0 = \frac{1}{2}, \quad (93)$$

where  $E_a^0$  and  $E_i^0$  are the axial and transverse elastic moduli at zero stress as given in (70) and (81), respectively.

One can define different Poisson's ratios in terms of strain  $\varepsilon(t)$  which measures the change in length per unit current length. We define  $\hat{\nu}_{ij}$  as

$$\hat{\nu}_{ij} = -\frac{d\varepsilon_i(t)}{d\varepsilon_j(t)} \quad (94)$$

in a problem where we extend a sample along direction  $j$  and allow the free contraction of the other dimensions. The relation between  $\varepsilon_i(t)$  and the stretch ratio is given in equation (34).

Using this relation one obtains

$$\hat{\nu}_{ij} = -\frac{\lambda_j(t) d\lambda_i(t)}{\lambda_i(t) d\lambda_j(t)} = -\frac{\lambda_j(t)}{\lambda_i(t)} \nu_{ij}. \quad (95)$$

It can be shown that

$$\hat{\nu}_{12}^0 = \hat{\nu}_{21}^0 = \hat{\nu}_{13}^0 = \hat{\nu}_{31}^0 = \hat{\nu}_{23}^0 = \hat{\nu}_{32}^0 = \frac{1}{2}. \quad (96)$$

**5.4.3. Shear moduli.** At least two shear moduli can be defined, one for shear in the plane perpendicular to the initial axis of extension and one for shear in the plane containing the initial axis of extension. We define  $\gamma_{ij}$  to be the shear strain in a process which takes the unit square in the  $i$ - $j$  plane to a parallelogram where the line along the  $i$  direction remains along the  $i$  direction and the line along the  $j$  direction rotates an angle equal to the inverse tangent of  $\gamma_{ij}$ . The shear modulus  $G_{ij}$  will be defined in a similar way.

For calculating the shear modulus due to shearing in a plane perpendicular to the axis of extension, after the crystallization has stopped at time  $t_1$  we subject the sample to the deformation given by

$$\mathbf{F}(t) = \begin{pmatrix} \lambda_1(t) & \gamma_{12}(t)\lambda_2(t) & 0 \\ 0 & \lambda_2(t) & 0 \\ 0 & 0 & \lambda_3(t) \end{pmatrix} \quad \text{for } t > t_1, \quad (97)$$

where  $\lambda_1(t)$ ,  $\lambda_2(t)$ , and  $\lambda_3(t)$  are stretch ratios in the three coordinate directions and  $\gamma_{12}(t)$  is the shear strain in the 1-2 plane. This results in the relative deformation gradient  $\mathbf{F}_s(t)$  for this case to be

$$\mathbf{F}_s(t) = \begin{pmatrix} \lambda_1(t) \left( \frac{\bar{\lambda}}{J(s)} \right)^{1/2} & \gamma_{12}(t)\lambda_2(t) \left( \frac{\bar{\lambda}}{J(s)} \right)^{1/2} & 0 \\ 0 & \lambda_2(t) \left( \frac{\bar{\lambda}}{J(s)} \right)^{1/2} & 0 \\ 0 & 0 & \frac{\lambda_3(t)}{\bar{\lambda}} \end{pmatrix} \quad \text{for } t > t_1 \quad \text{and } s \in (t_s, t_1]. \quad (98)$$

This, therefore, results in the expressions

$$\mathbf{B}(t) = \begin{pmatrix} \lambda_1^2(t) + \gamma_{12}^2(t)\lambda_2^2(t) & \gamma_{12}(t)\lambda_2^2(t) & 0 \\ \gamma_{12}(t)\lambda_2^2(t) & \lambda_2^2(t) & 0 \\ 0 & 0 & \lambda_3^2(t) \end{pmatrix} \quad \text{for } t > t_1, \quad (99)$$

and

$$\mathbf{B}_s(t) = \begin{pmatrix} \frac{\lambda_1^2(t)\bar{\lambda}}{J(s)} + \frac{\gamma_{12}^2(t)\lambda_2^2(t)\bar{\lambda}}{J(s)} & \frac{\gamma_{12}(t)\lambda_2^2(t)\bar{\lambda}}{J(s)} & 0 \\ \frac{\gamma_{12}(t)\lambda_2^2(t)\bar{\lambda}}{J(s)} & \frac{\lambda_2^2(t)\bar{\lambda}}{J(s)} & 0 \\ 0 & 0 & \frac{\lambda_3^2(t)}{\bar{\lambda}^2} \end{pmatrix} \quad \text{for } t > t_1 \quad \text{and } s \in (t_s, t_1]. \quad (100)$$

Assuming a homogeneous stress field of the form

$$\mathbf{T}(t) = \begin{pmatrix} T_{11}(t) & T_{12}(t) & 0 \\ T_{12}(t) & T_{22}(t) & 0 \\ 0 & 0 & T_{33}(t) \end{pmatrix} \quad \text{for } t > t_1, \quad (101)$$

and substituting into the constitutive equation (17) yields the expression for shear stress  $T_{12}(t)$  as

$$T_{12}(t) = \left[ \frac{mJ(t_1) - 1}{m - 1} q(t_1) + \frac{m\bar{\lambda}}{m - 1} \int_{J(t_1)}^1 \frac{w(s)}{J(s)} dJ(s) \right] \gamma_{12}(t) \lambda_2^2(t) = K_1 \gamma_{12}(t) \lambda_2^2(t), \quad (102)$$

where  $K_1$  is the same as given in (66). The incremental shear modulus  $G_{12}$  will be given by

$$G_{12} = \frac{\partial T_{12}(t)}{\partial \gamma_{12}(t)} = K_1 \lambda_2^2(t). \quad (103)$$

It is noted that, even though this shear modulus is independent of the magnitude of  $\gamma_{12}(t)$ , the shear modulus is a function of the stretch ratio  $\lambda_2(t)$ . The shear modulus in the stress-free configuration will be denoted by  $G_{12}^0$  and is obtained from  $G_{12}$  by the substitution of  $\lambda_i^0$  from (69) for  $\lambda_2(t)$ . This operation yields

$$G_{12}^0 = (K_1^2 K_2 J^2(t_1))^{1/3} = G_{21}^0. \quad (104)$$

Another shear modulus can be defined by shearing in the 1–3 plane where the material surfaces move parallel to the 1–2 plane. In this case, the deformation is given by

$$\mathbf{F}(t) = \begin{pmatrix} \lambda_1(t) & 0 & \gamma_{13}(t) \lambda_3(t) \\ 0 & \lambda_2(t) & 0 \\ 0 & 0 & \lambda_3(t) \end{pmatrix} \quad \text{for } t > t_1. \quad (105)$$

This results in the expressions

$$\mathbf{B}(t) = \begin{pmatrix} \lambda_1^2(t) + \gamma_{13}^2(t) \lambda_3^2(t) & 0 & \gamma_{13}(t) \lambda_3^2(t) \\ 0 & \lambda_2^2(t) & 0 \\ \gamma_{13}(t) \lambda_3^2(t) & 0 & \lambda_3^2(t) \end{pmatrix} \quad \text{for } t > t_1, \quad (106)$$

and

$$\mathbf{B}_s(t) = \begin{pmatrix} \frac{\lambda_1^2(t) \bar{\lambda}}{J(s)} + \frac{\gamma_{13}^2(t) \lambda_3^2(t)}{\bar{\lambda}^2} & 0 & \frac{\gamma_{13}(t) \lambda_3^2(t)}{\bar{\lambda}^2} \\ 0 & \frac{\lambda_2^2(t) \bar{\lambda}}{J(s)} & 0 \\ \frac{\gamma_{13}(t) \lambda_3^2(t)}{\bar{\lambda}^2} & 0 & \frac{\lambda_3^2(t)}{\bar{\lambda}^2} \end{pmatrix} \quad \text{for } t > t_1 \quad \text{and } s \in (t_s, t_1]. \quad (107)$$

We assume a homogeneous stress field of the form

$$\mathbf{T}(t) = \begin{pmatrix} T_{11}(t) & 0 & T_{13}(t) \\ 0 & T_{22}(t) & 0 \\ T_{13}(t) & 0 & T_{33}(t) \end{pmatrix} \quad \text{for } t > t_1. \quad (108)$$

Substitution into (17) yields the expression for the shear stress  $T_{13}(t)$  as

$$T_{13}(t) = \left[ \frac{mJ(t_1) - 1}{m - 1} q(t_1) + \frac{m}{\bar{\lambda}^2(m - 1)} \int_{J(t_1)}^1 w(s) dJ(s) \right] \gamma_{13}(t) \lambda_3^2(t) = K_2 \gamma_{13}(t) \lambda_3^2(t), \quad (109)$$

where  $K_2$  is the same as given in (67). The incremental shear modulus  $G_{13}$  will be given by

$$G_{13} = \frac{\partial T_{13}(t)}{\partial \gamma_{13}(t)} = K_2 \lambda_3^2(t) = G_{23}. \quad (110)$$

The shear modulus in the stress-free configuration will be denoted by  $G_{13}^0$  and is obtained from  $G_{13}$  by the substitution of  $\lambda_a^0$  from (68) for  $\lambda_3(t)$ . This operation yields

$$G_{13}^0 = (K_1^2 K_2 J^2(t_1))^{1/3} = G_{23}^0 \quad (111)$$

It is seen that  $G_{12}^0 = G_{13}^0$ . It can be shown that

$$G^0 = G_{12}^0 = G_{21}^0 = G_{13}^0 = G_{31}^0 = G_{23}^0 = G_{32}^0. \quad (112)$$

**5.4.4. Comment of material symmetry.** As can be seen from the results presented above, when one defines the different moduli with respect to strain relative to the current shape, one will see that the material is isotropic after crystallization. It is simple to show that for the particular model selected, the material will always be isotropic after crystallization. This will not be the case for other choices of the crystallization models proposed for Negahban and Wineman [1].

## 6. PROPERTIES AT 100% CRYSTALLIZATION

Even though most polymers stop crystallizing long before 100% crystallization is achieved (due to entanglement and other barriers to the motion of the chains), it is informative to see what the predictions of this model are for 100% crystallization.

At 100% crystallization  $b(t)$  (the ratio of amorphous matter) is zero and equation (9) yields

$$J = \frac{1}{m}. \quad (113)$$

### 6.1. Unconstrained crystallization

For unconstrained crystallization equation (27) gives the elastic modulus at zero stress as

$$E^0 = \frac{3m^{2/3}}{m-1} \int_{1/m}^1 \frac{w(s)}{J^{2/3}(s)} dJ(s). \quad (114)$$

The shear modulus at zero stress in this case can be obtained from equation (44) as

$$G^0 = \frac{m^{1/3}}{m-1} \int_{1/m}^1 \frac{w(s)}{J^{2/3}(s)} dJ(s) = \frac{m^{-1/3} E^0}{3}. \quad (115)$$

### 6.2. Crystallization at fixed stretch

For the case of crystallization under a fixed stretch ratio along the third coordinate axis, as given above, one will observe the following.

The stress after 100% crystallization is obtained from equation (52) as

$$T_{33} = \frac{1}{m-1} \int_{1/m}^1 w(s) \frac{mJ(s) - 1}{J(s)} dJ(s). \quad (116)$$

This states that  $T_{33}$  will always be positive since  $m$ , the ratio of the crystal's density to the density of amorphous material, is greater than unity,  $w(s)$ , the effective modulus of the crystal created at time  $s$ , is positive, and  $mJ(s)$  is greater than unity for all  $s$ . Since  $w(s)$  can depend on the stretch ratio during crystallization,  $\bar{\lambda}$ , the stress can be dependent on this value.

The axial incremental elastic modulus evaluated at  $\bar{\lambda}$  can be obtained from equation (61) as

$$\bar{E}_a = \frac{1}{\bar{\lambda}(m-1)} \int_{1/m}^1 w(s) \frac{2mJ(s) + 1}{J(s)} dJ(s), \quad (117)$$

and from equation (63)

$$\hat{E}_a = \frac{1}{(m-1)} \int_{1/m}^1 w(s) \frac{2mJ(s) + 1}{J(s)} dJ(s). \quad (118)$$

One notes that for a material which has a  $w(s)$  which is only a function of  $J(s)$ , at 100% crystallization  $\bar{E}_a$  decreases with the increase of  $\bar{\lambda}$  and that  $\hat{E}_a$  is independent of  $\bar{\lambda}$ .



For 100% crystallization the expression for  $K_1$  and  $K_2$  in (66) and (67) will become

$$K_1 = \frac{m\bar{\lambda}}{m-1} \int_{1/m}^1 \frac{w(s)}{J(s)} dJ(s), \quad (119)$$

$$K_2 = \frac{m}{\bar{\lambda}^2(m-1)} \int_{1/m}^1 w(s) dJ(s). \quad (120)$$

Using this relation, the axial stretch ratio at zero stress,  $\lambda_a^0$ , and the transverse stretch ratio at zero stress,  $\lambda_t^0$ , will be given by

$$\lambda_a^0 = \bar{\lambda} \left( \frac{\int_{1/m}^1 \frac{w(s)}{J(s)} dJ(s)}{m \int_{1/m}^1 w(s) dJ(s)} \right)^{1/3}, \quad (121)$$

and

$$\lambda_t^0 = \left( \frac{1}{m\bar{\lambda}} \right)^{1/2} \left( \frac{m \int_{1/m}^1 w(s) dJ(s)}{\int_{1/m}^1 \frac{w(s)}{J(s)} dJ(s)} \right)^{1/6}. \quad (122)$$

Since  $1/m \leq J(s) \leq 1$  for all  $s$ , and assuming  $w(s)$  is positive, it follows that  $\lambda_a^0 < \bar{\lambda}$  and  $\lambda_t^0 > (1/m\bar{\lambda})^{1/2}$  at 100% crystallization.

## 7. FITTING OF THE MODEL TO EXPERIMENTAL RESULTS FOR NATURAL RUBBER

To study the response of this model, we will select the particular forms

$$q(t) = Q_1 + Q_2(1 - J(t)) \quad (123)$$

for the effective modulus of the amorphous portion, and

$$w(s) = W_1 + W_2(1 - J(s)) \quad (124)$$

for the effective modulus of the crystal created at time  $s$ . The coefficients  $Q_1$ ,  $Q_2$ ,  $W_1$ , and  $W_2$  are constants.  $Q_1$  is the modulus of the amorphous material before crystallization.  $Q_2$  should be negative and represent the diminishing importance of the amorphous portion as more crystals get generated (the quantity  $[1 - J(t)]$  monotonically increases with the increase in crystallinity). Both  $W_1$  and  $W_2$  should be positive,  $W_1$  is the effective modulus of the first crystal generated and  $W_2$  is the rate (relative to  $J$ ) of increase of the effective modulus as crystals are generated. It is worth mentioning that at 100% crystallization the effective modulus of the last crystal created is

$$W_1 + \frac{(m-1)}{m} W_2.$$

This quantity might represent the value of the modulus of a crystal as evaluated from a microscopic analysis of the crystal's elastic modulus.

The values

$$\begin{aligned} Q_1 = 0.327 \text{ MPa}, \quad Q_2 = -31.88 \text{ MPa}, \quad W_1 = 5.19 \text{ MPa}, \\ W_2 = 11889.7 \text{ MPa}, \quad \text{and} \quad m = 1.099 \end{aligned} \quad (125)$$

were used to fit the experimental results of Leitner [2] and Gent [3].

## 8. SIMULATIONS OF THE RESPONSE OF NATURAL RUBBER

All the theoretical curves use the special form given by (123) and (124), and the material constants given in (125). In these results, the change in crystallization is represented by the percent change in density,  $\Delta$ , which can be given as

$$\Delta(t) = 100 \frac{1 - J(t)}{J(t)}. \quad (126)$$

For the typically observed values of  $J(t)$  ( $0.97 \leq J(t) \leq 1$  for natural rubber), there is a close to linear relation between  $\Delta$  and change in volume ratio. For natural rubber the percent of crystallization is typically ten times  $\Delta$ . This can be observed from the fact that  $m = 1.099$  and the relation for the percent of crystallization is given as

$$100(1 - b(t)) = 100 \frac{m(1 - J(t))}{m - 1} = \frac{mJ(t)\Delta(t)}{m - 1}, \quad (127)$$

obtained from equation (10).

### 8.1. Unconstrained crystallization

Figure 1 shows both the theoretical fit and the experimental results of Leitner [2] for the change in elastic modulus as a function of change in density for unconstrained natural rubber at 0°C. Leitner did these experiments by leaving the rubber at 0°C and slightly extending the samples at different points in the crystallization process. The theoretical curve is evaluated using equation (27). One can see the ability of the model to capture quantitatively the change in the elastic modulus. Figure 2 shows the theoretical prediction for the change in the shear modulus for the same crystallization conditions, as given by equation (44).

### 8.2. Crystallization at a constant stretch

The theoretical assumptions force the sample into compression after about 10% crystallization. Since actual samples buckle rather than go into compression, most comparisons after about 1% density change should not give quantitative agreement for most experimental setups.

Figure 3 shows the stress relaxation for crystallization under different fixed stretch ratios  $\bar{\lambda}$ , as given by equation (52). Point A on this graph represents approximately 1% volume change. The material constants given in (125) were selected so the stress relaxation plots pass through point A, as suggested by the results of Gent [3]. Otherwise, the curves are purely predicted by the theory. The fact that these curves show a close to linear relation between the volume change and stress relaxation has been observed experimentally by Gent [3] for similar conditions of crystallization, but at -26°C.

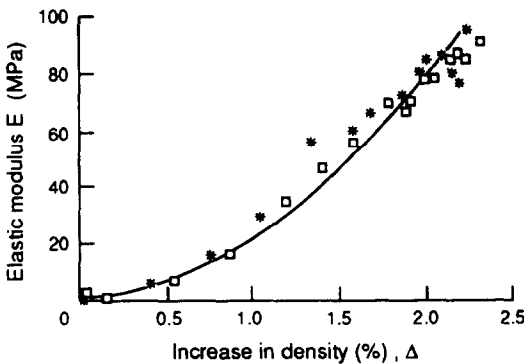


Fig. 1. Change in the elastic modulus at zero stress,  $E^0$ , for unconstrained crystallization of natural rubber; theoretical fit (—); Leitner sample A (\*) and sample B (□).

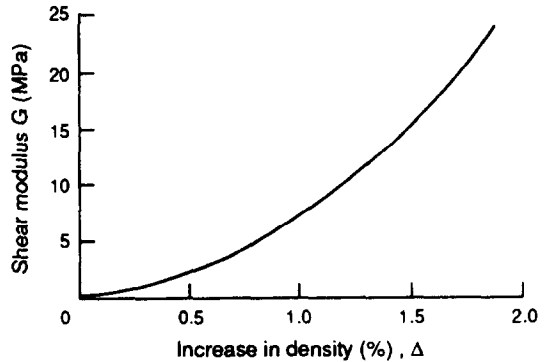


Fig. 2. Theoretical evaluation of the change in shear modulus,  $G$ , for unconstrained crystallization of natural rubber.

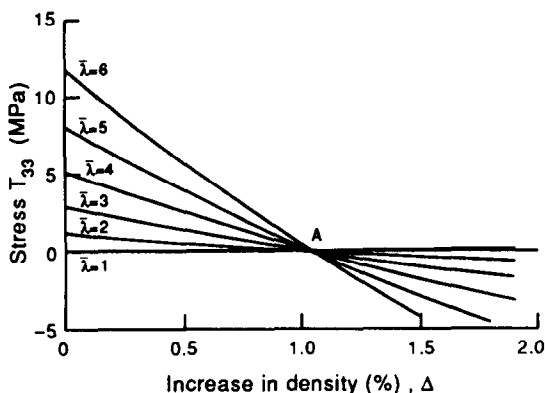


Fig. 3. Theoretical evaluation of stress relaxation for samples of natural rubber crystallizing at different constant stretch ratios,  $\bar{\lambda}$ . Material constants are fit to require total stress relaxation at approximately 1% volume change as suggested by results of Gent. This makes all stress relaxation curves pass through point A.

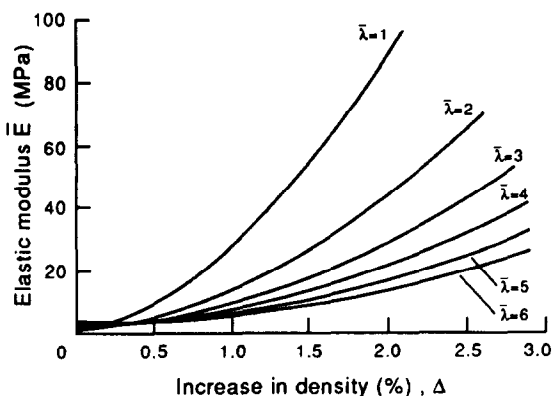


Fig. 4. Theoretical evaluation of the increase in the axial incremental elastic modulus,  $\bar{E}_a$ , for crystallization of natural rubber at different constant stretch ratios,  $\bar{\lambda}$ . These moduli are evaluated at the same stretch ratio  $\bar{\lambda}$  as the crystallization condition.

Figure 4 shows the increase in axial elastic modulus evaluated at a stretch ratio of  $\bar{\lambda}$  when the rubber is crystallizing at the same stretch ratio  $\bar{\lambda}$  (i.e.  $\bar{E}_a$ ). The curves are obtained from equation (61). This elastic modulus is similar to that experimentally obtained by Stevenson [4], where samples of natural rubber were stretched and held at different stretch ratios. In Stevenson's experiments, at different points in the crystallization process, the samples were slightly extended and the ratio of the change in stress to change in stretch was recorded as the incremental elastic modulus. It is noted that for the same change in density the modulus is smaller for samples held at higher stretch ratios, for this special version of the model. Since Stevenson observed the long term elastic modulus to be independent of the stretch ratio at crystallization, this suggests that samples held at higher stretch ratios undergo more crystallization as predicted by the model. Figure 5 shows the change in  $\bar{E}_a$  as given by equation (63). One notes that this measure of elastic modulus is much less dependent on stretch ratio  $\bar{\lambda}$ .

Figure 6 shows the change in the axial "residual stretch ratios,"  $\lambda_a^0$ , and the transverse "residual stretch ratio,"  $\lambda_t^0$ , for samples crystallizing at several different stretch ratios  $\bar{\lambda}$ . These curves are obtained from equations (68) and (69), respectively.

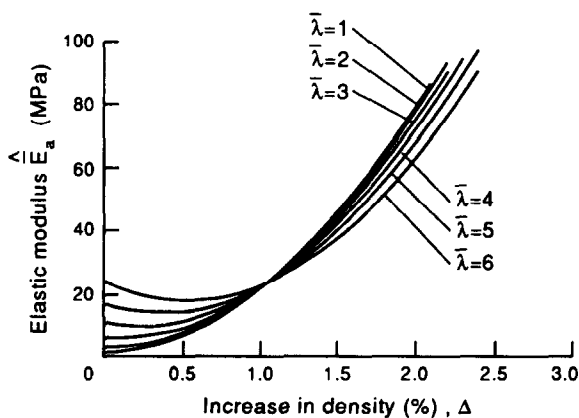


Fig. 5. Theoretical evaluation of the increase in the axial incremental elastic modulus,  $\bar{E}_a$ , for crystallization of natural rubber at different constant stretch ratios,  $\bar{\lambda}$ . This modulus is evaluated with respect to strains measured relative to the current shape of samples. These moduli are evaluated at the same stretch ratio  $\bar{\lambda}$  as the crystallization condition.

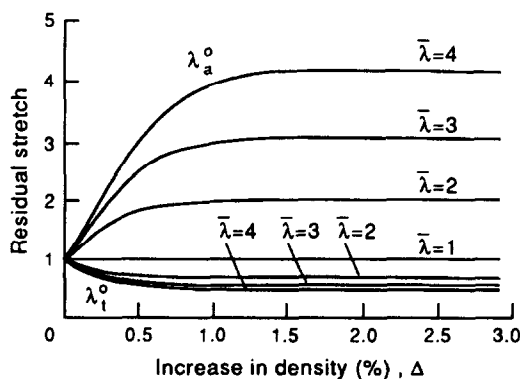


Fig. 6. Theoretical evaluation of the axial stretch ratio at zero stress,  $\lambda_a^0$ , and the transverse stretch ratio at zero stress,  $\lambda_t^0$ , for the crystallization of natural rubber at several different stretch ratios  $\bar{\lambda}$ .

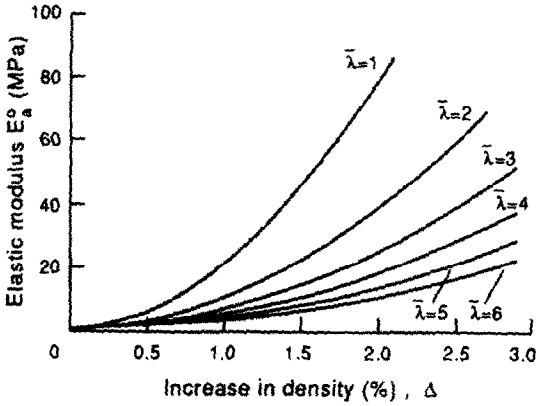


Fig. 7. Theoretical evaluation of the increase in the axial incremental elastic modulus at zero stress,  $E_a^0$ , for crystallization of natural rubber at different constant stretch ratios  $\bar{\lambda}$ .

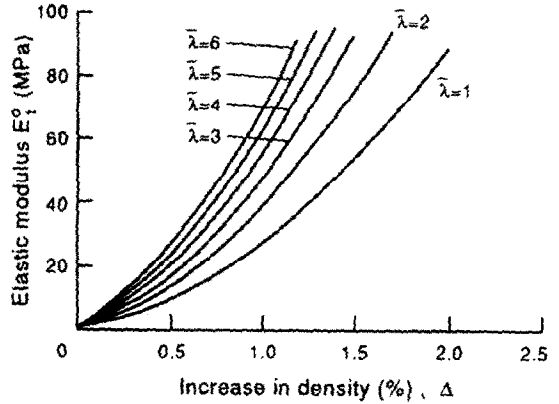


Fig. 8. Theoretical evaluation of the increase in the transverse incremental elastic modulus at zero stress,  $E_t^0$ , for crystallization of natural rubber at different constant stretch ratios  $\bar{\lambda}$ .

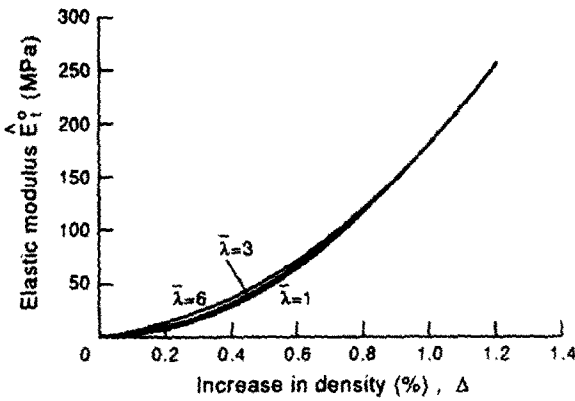


Fig. 9. Theoretical evaluation of the increase in the incremental elastic modulus at zero stress  $E_a^0 = E_t^0$ , for crystallization of natural rubber at different constant stretch ratios  $\bar{\lambda}$ .

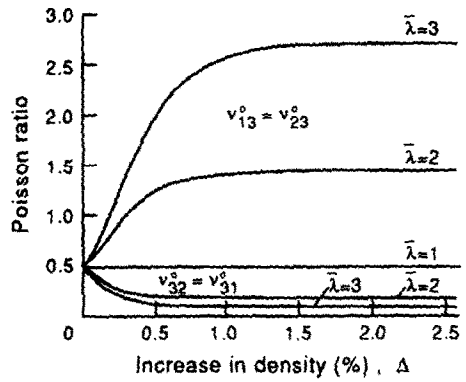


Fig. 10. Theoretical evaluation of the change in Poisson's ratio at zero stress for crystallization of natural rubber at different constant stretch ratios  $\bar{\lambda}$ .

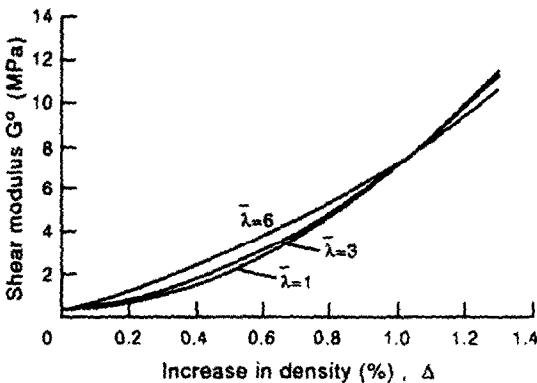


Fig. 11. Theoretical evaluation of the increase in the incremental shear modulus at zero stress,  $G^0$ , for crystallization of natural rubber at different constant stretch ratios  $\bar{\lambda}$ .

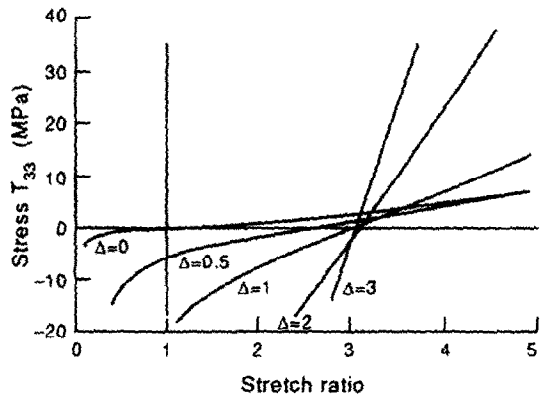


Fig. 12. Theoretical plots of the axial stress-stretch ratio relation after crystallization under a fixed stretch ratio  $\bar{\lambda} = 3$  for different values of final percent change in density  $\Delta$ .

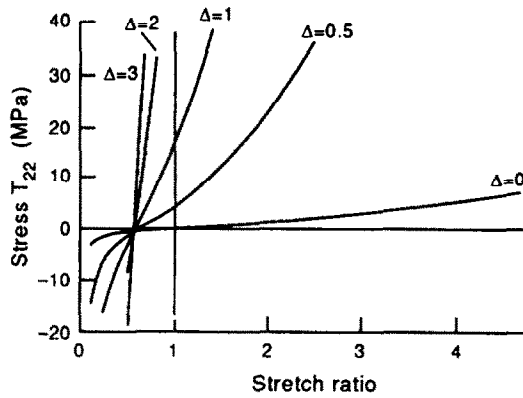


Fig. 13. Theoretical plots of the transverse stress–stretch ratio relation after crystallization under a fixed stretch ratio  $\bar{\lambda} = 3$  for different values of final percent change in density  $\Delta$ .

Figures 7 and 8 show the gradual change in the axial and transverse elastic moduli at zero stress for samples held at different stretch ratios  $\bar{\lambda}$ . These curves are obtained from equations (70) and (81), respectively. Figure 9 shows the change in  $\bar{E}_a^0 = \bar{E}_t^0$  as given by equation (86).

Figure 10 shows the gradual change in Poisson's ratios evaluated in the stress-free configuration for samples crystallizing under different stretch ratios  $\bar{\lambda}$ . These curves are obtained using equations (89) and (92). The values of Poisson's ratio larger than  $\frac{1}{2}$  are a result of assuming incompressibility and the large mismatch between the axial and transverse stretch. It is noted that the values of all the Poisson's ratios are  $\frac{1}{2}$  if one selects to measure strain relative to the current shape.

Figure 11 shows the gradual change in the shear modulus in the stress-free configuration for samples crystallizing under different stretch ratios  $\bar{\lambda}$ . All curves pass through the same point at approximately 1% change in volume, where the stress goes to zero. This observation can be shown mathematically.

Figure 12 shows the post crystallization axial stress–stretch ratio curves for a sample crystallized at a stretch ratio  $\bar{\lambda} = 3$ . The different curves are for samples having different amounts of crystallization, represented by different percent change in the density  $\Delta$ . These curves are obtained from equation (59). Figure 13 shows the post crystallization transverse stress–stretch ratio curves for crystallization under similar conditions. These curves were obtained from equation (79).

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