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A Constitutive Equation for the Elasto-Viscoplastic Deformation of Glassy Polymers

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Abstract. Constitutive equations for finite elastic-plastic deformation of polymers and metals are usually formulated by assuming an isotropic relation between the Jaumann rate of the Cauchy-stress tensor and the strain-rate tensor. However, the Jaumann-stress rate is known to display spurious non-physical behaviour in the elastic region. Replacing the Jaumann-stress rate by a Truesdell-stress rate results in an adequate description in the elastic region, but gives rise to a volume decrease during plastic flow in tensile deformation. In this paper a “compressible-Leonov model” is introduced, in which the elastic volume response is rigorously separated from the elasto-viscoplastic isochoric deformation. This has the advantage that the model can be extended in a straightforward way to include a spectrum of relaxation times. It is shown that in the limit of small elastic strains, the compressible Leonov model reduces to the Jaumann-stress rate model, but diverges from the Truesdell-stress rate model. Finally, a comparison is made of the above mentioned models in a homogeneous uniaxial tensile test and a homogeneous plane-stress shear test, using polycarbonate (PC) as a model system. All models considered in this paper are “single mode” models (i.e. one relaxation time), and, therefore, cannot describe the full (non)linear viscoelastic region, nor the strain-hardening or strain-softening response.

Key words: elasto-viscoplastic deformation, mathematical models, polymers, thermodynamics, yield-point

1. Introduction

The yield behaviour of polymer materials is classically described by using yield criteria, of which the pressure- and rate-dependent generalization of the von Mises criterion seems to be most successful. After yielding, strain hardening sets in, sometimes preceded by intrinsic strain softening (Ward, 1990).

The principle to describe yield-like behaviour of polymeric materials by use of a stress-dependent relaxation time, dates back to Tobolsky and Eyring (1943). It was later used by Haward and Thackray (1968) who added a finite-extendible spring (a so-called “Langevin” spring) to account for a maximum draw ratio during strain hardening (see Figure 1).

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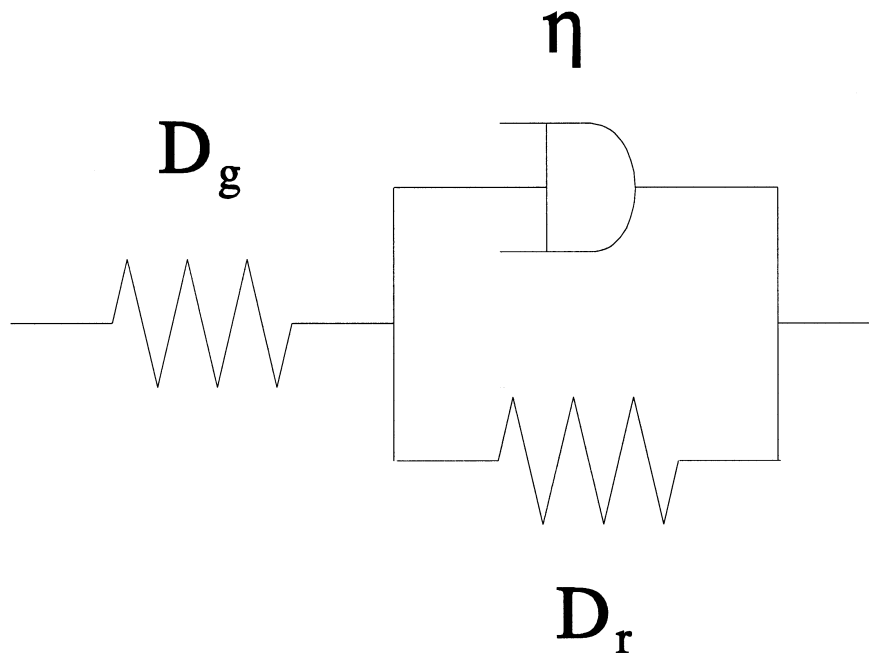


Figure 1. Mechanical analogue of the Haward–Thackray model. The initial elastic response is described by the compliance D_g , the yield point is determined by a stress-dependent viscosity η , and the strain-hardening response follows from D_r .

The stress dependence of the relaxation time in the Haward–Thackray model is incorporated using a stress shift factor $a_\sigma(\tau)$, defined as the ratio of the relaxation time at a given stress level and the linear relaxation time at zero (very low) stress, with τ a scalar measure of the stress state. The effect of a stress-dependent relaxation time is revealed most clearly in creep tests at different stress levels, see Figure 2. At very low stress levels, the relaxation time is constant, and the behaviour is linear (the creep compliance is independent of stress). At higher stress levels, the relaxation time is reduced by a factor $a_\sigma(\tau)$. Using a logarithmic time axis, this results in a horizontal shift of the compliance curve.

A set of calculated true stress-strain curves, at different strain rates, using the Haward–Thackray model, is schematically depicted in Figure 3. From this figure, it is clear that the model correctly accounts for the rate-dependence of the yield stress and the initial “glassy” modulus. However, the use of a single stress-dependent relaxation time results in an abrupt transition from elastic to plastic behaviour, similar to elasto-plastic behaviour, employing a rate-dependent yield criterion. Moreover, using only a single relaxation time, it is not possible to describe an experimental linear relaxation modulus.

More recently, Boyce et al. (1988) introduced the “BPA-model”, which is essentially an extension of the Haward–Thackray model to three-dimensional finite deformations, using the Argon theory and the three-chain model (James and Guth,

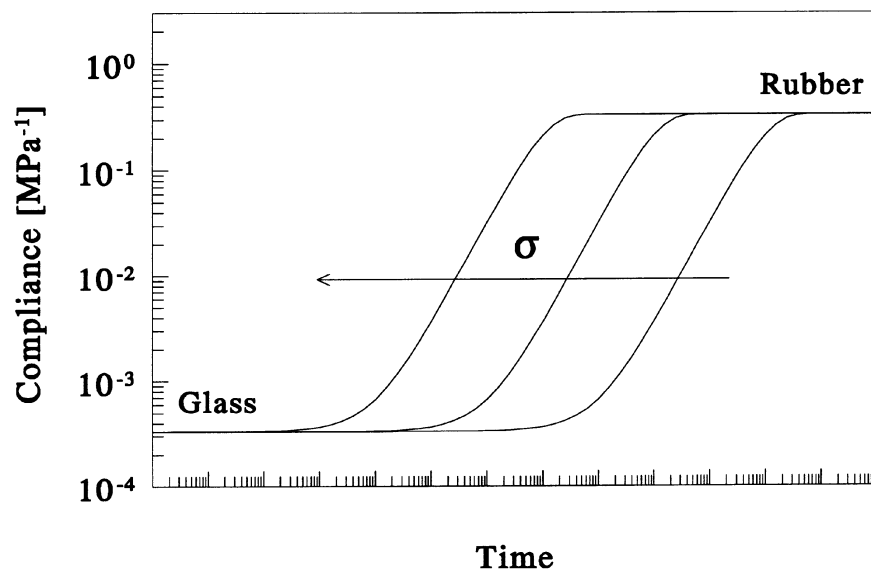


Figure 2. Schematic representation of the creep compliance of the Haward–Thackray model at different stress levels.

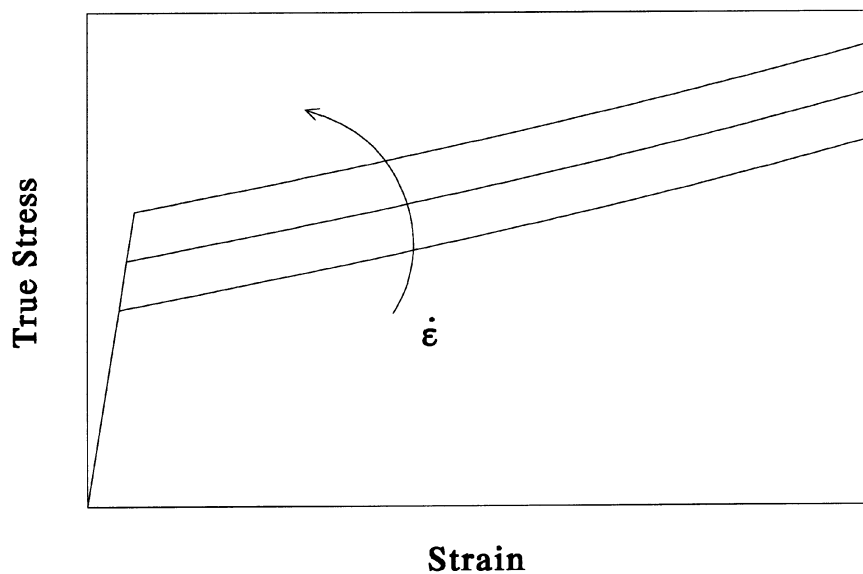


Figure 3. Schematic representation of stress-strain curves, according to the Haward–Thackray model at different strain rates.

1943) to describe, respectively, the plastic flow process and the strain-hardening response. The BPA-model was later refined by Arruda (1992) and Wu and van der Giesen (1993) with respect to the strain-hardening response and by Hasan et al. (1993) to include the effect of aging and rejuvenation. In all these models, no explicit use is made of a yield criterion. Instead, like in the Haward–Thackray model, the deformation behaviour is determined by a single relaxation time that is dependent on an equivalent stress (proportional to the von Mises stress). Consequently, these models suffer from the same drawbacks as the Haward–Thackray model, as described above.

One way to improve the Haward–Thackray model, with respect to its poor description of the linear viscoelastic deformation behaviour, would be the application of a *spectrum* of relaxation times rather than one (Tervoort et al., 1996). In case of three-dimensional behaviour this requires a splitting of the volume deformation and the deviatoric deformation, since it is well known that, to a good approximation, the compressibility of materials is not affected by plastic flow. This study is, therefore, concerned with the derivation of a three-dimensional constitutive model for the finite elasto-viscoplastic deformation of (polymeric) materials, in which the deviatoric response is determined by a stress-dependent relaxation time, and the volume response remains elastic. The model will be derived using a formalism developed to describe thermodynamically consistent constitutive equations (Jongschaap et al., 1994).

2. Theory

2.1. MATRIX REPRESENTATION OF CONSTITUTIVE EQUATIONS

In the simple fluid concept it is assumed that constitutive variables like the stress tensor are fully determined by the history of deformation (axiom of determinism). Using the concept of fading memory, the history dependence of the material is then described by functional relations (Coleman and Noll, 1963). However, using this framework it is difficult to incorporate information about the microstructure into the constitutive equation. Therefore, in recent polymer rheology as well as plasticity literature it is recognized advantageous to formulate constitutive equations using state variables, e.g., the natural reference state concept of Besseling and van der Giessen (1994) in the field of plasticity, the Poisson-bracket approach of Beris and Edwards (1990) and the matrix model by Jongschaap et al. (1994) in polymer rheology. Here, the latter will be used to derive a constitution equation for the rate-dependent yield behaviour of polymer glasses without strain hardening. To this intention, the matrix model will briefly be introduced first. For a more elaborate discussion the reader is referred to the original papers of Jongschaap (1990, 1994).

The notion of *state variables* plays a central role in the matrix model of Jongschaap. The current state of a material body is completely determined by the instantaneous values of the external rate variables, $[\mathbf{F}, \dot{\mathbf{F}}, \ddot{\mathbf{F}}, \dots, \dot{Q}]$ (\mathbf{F} is the deformation gradient tensor, Q is the radiating energy, while the dot denotes the material time

derivative). Although the body as a whole can be in a non-equilibrium state, it is assumed that there are subsystems which are in thermodynamic equilibrium. The internal (thermodynamic) state of these subsystems is described in the sense of equilibrium thermodynamics by the current value(s) of a (set of) state variable(s) $[X_1, X_2, \dots, X_n]$. These may be scalar quantities like free volume, higher order tensorial quantities like the stored elastic strain, or even distribution functions. Since state variables completely specify the state of the material body in the sense of *equilibrium* thermodynamics, it must in principle be possible to fix or control their value for an arbitrary time span by adjusting the external rate variables. Moreover, the state variables must appear in Gibb's fundamental equation, since this equation completely describes the thermodynamic equilibrium state of the material body:

$$U = U(S, X_1, X_2, \dots, X_n) \quad (1)$$

with S the entropy per unit volume. The rate of internal energy is obtained by differentiating Equation (1) with respect to time:

$$\dot{U} = T\dot{S} + F_1\dot{X}_1 + F_2\dot{X}_2 + \dots + F_n\dot{X}_n. \quad (2)$$

Here, T is the absolute temperature $T = \partial U / \partial S$ and F_i are the thermodynamic forces associated to the state variables, defined as:

$$F_i = \frac{\partial U}{\partial X_i} = F_i(S, X_1, X_2, \dots, X_n). \quad (3)$$

Since entropy is not an easy quantity to control in practice, it can be eliminated from the list of independent variables by introducing the *Helmholtz free energy* $A = U - TS$ and thus:

$$\dot{A} = -S\dot{T} + F_1\dot{X}_1 + F_2\dot{X}_2 + \dots + F_n\dot{X}_n. \quad (4)$$

From this equation it can be concluded that in an isothermal process, the rate of free energy \dot{A} equals the rate of reversible storage of energy (Astarita and Marrucci, 1974).

The rate of entropy production Σ is defined as: $\Sigma = \dot{S} - \dot{Q}/T$ and can be obtained by eliminating \dot{U} from the law of conservation of energy:

$$\dot{U} = \dot{Q} + \dot{W} = \dot{Q} + \mathbf{T} : \mathbf{L} \quad (5)$$

and Equation (2) which results in:

$$\begin{aligned} \Sigma &= \frac{\Delta}{T}, \\ \Delta &= \mathbf{T} : \mathbf{L} - \sum_{i=1}^n F_i \dot{X}_i, \end{aligned} \quad (6)$$

with \mathbf{T} the Cauchy-stress tensor and \mathbf{L} the velocity gradient tensor. The quantity Δ is the difference between the total external power supply to the material body and the rate of reversible energy storage in the body and is denoted as the *rate of dissipation*. By the second law of thermodynamics the absolute temperature is always positive and the rate of entropy production is greater than or equal to zero. Therefore, the rate of dissipation is always greater than or equal to zero.

Without loss of generality, for the moment it is assumed that the internal variable which determines the internal state of the body is a second-order tensor \mathbf{S} (sometimes called a “structure tensor”) with an associated thermodynamic force $\mathbf{M} = \partial A / \partial \mathbf{S}$. In that case, for isothermal conditions, combining Equations (4) and (6), the rate of dissipation can be written as:

$$\Delta = \mathbf{T} : \mathbf{L} - \dot{A} = \mathbf{T} : \mathbf{L} - \frac{\partial A}{\partial \mathbf{S}} : \dot{\mathbf{S}} = \mathbf{T} : \mathbf{L} - \mathbf{M} : \dot{\mathbf{S}} \geq 0. \quad (7)$$

An important concept in the matrix model of Jongschaap is that of *macroscopic time reversal*, where it is examined to what extent the rate of the state variables $\dot{\mathbf{S}}$ and the stress tensor \mathbf{T} are affected by a reversal of the macroscopic external velocity gradient \mathbf{L} . Here it should be noted that any function $f(\mathbf{L})$ can be decomposed in an even part f^+ and an odd part f^- according to:

$$f(\mathbf{L}) = f^+(\mathbf{L}) + f^-(\mathbf{L}) = \frac{1}{2} [f(\mathbf{L}) + f(-\mathbf{L})] + \frac{1}{2} [f(\mathbf{L}) - f(-\mathbf{L})]. \quad (8)$$

By definition, the parity of the velocity gradient \mathbf{L} itself is odd. Recognizing that state variables are even and assuming that the rate of dissipation is also even, it is possible to decompose Equation (7) in an even part:

$$\Delta = \Delta^+ = \mathbf{T}^- : \mathbf{L} - \mathbf{M} + \dot{\mathbf{S}}^+ \quad (9)$$

and an odd part:

$$0 = \mathbf{T}^+ : \mathbf{L} - \mathbf{M} : \dot{\mathbf{S}}^-. \quad (10)$$

Without loss of generality, the reversible part of $\dot{\mathbf{S}}$, $\dot{\mathbf{S}}^-$ can be written as:

$$\dot{\mathbf{S}}^- = \underline{\mathbf{A}} : \mathbf{L}, \quad (11)$$

where the tensor $\underline{\mathbf{A}} = \underline{\mathbf{A}}(\mathbf{M}, \mathbf{L})$ is of rank four and even with respect to \mathbf{L} . A very general expression for the reversible part of the stress tensor $\mathbf{T}^R = \mathbf{T}^+$ is obtained by substitution of Equation (11) in Equation (10):

$$\mathbf{T}^+ = \mathbf{T}^R = \mathbf{M} : \underline{\mathbf{A}} = \underline{\mathbf{A}}^T : \mathbf{M}. \quad (12)$$

A similar relation was first discussed by Grmela (1985) in his Poisson-bracket formulation of material behaviour.

To complete the matrix model, the fourth-order tensors $\underline{\boldsymbol{\eta}}$ and $\underline{\boldsymbol{\beta}}$ are introduced to describe the dissipative parts of the stress tensor \mathbf{T}^D and the time derivative of the state variable $\dot{\mathbf{S}}^D$:

$$\mathbf{T}^D = \mathbf{T}^- = \underline{\boldsymbol{\eta}}(\mathbf{M}, \mathbf{L}) : \mathbf{L} \quad \text{and} \quad \dot{\mathbf{S}}^D = \dot{\mathbf{S}}^+ = -\underline{\boldsymbol{\beta}}(\mathbf{M}, \mathbf{L}) : \mathbf{M}. \quad (13)$$

The tensors $\underline{\eta}$ and $\underline{\beta}$ are (semi-)positive definite and even with respect to \mathbf{L} . Equations (11), (12) and (13) can be written in matrix notation, which concludes the generic matrix representation of constitutive equations:

$$\begin{bmatrix} \mathbf{T} \\ \dot{\mathbf{S}} \end{bmatrix} = \begin{bmatrix} \underline{\eta} & -\underline{\Lambda}^T \\ \underline{\Lambda} & \underline{\beta} \end{bmatrix} : \begin{bmatrix} \mathbf{L} \\ -\mathbf{M} \end{bmatrix}. \quad (14)$$

2.2. VISCOELASTIC BEHAVIOUR

The matrix model of Jongschaap will now be applied to derive a general “single mode” viscoelastic relationship. To illustrate the method, the limit case of complete (isotropic) elastic behaviour will be considered first.

2.2.1. Elastic Behaviour

In case of isotropic elastic behaviour it is assumed that the state variable determining the free energy is the left Cauchy–Green strain tensor \mathbf{B} . Because of isotropy, the free energy A can be expressed in the invariants of \mathbf{B} : $A = A(I_B, II_B, III_B)$. The thermodynamic force consequently equals:

$$\begin{aligned} \mathbf{M} = \frac{dA}{d\mathbf{B}} &= \frac{\partial A}{\partial I_B} \frac{dI_B}{d\mathbf{B}} + \frac{\partial A}{\partial II_B} \frac{dII_B}{d\mathbf{B}} + \frac{\partial A}{\partial III_B} \frac{dIII_B}{d\mathbf{B}} \\ &= \alpha_1 \mathbf{I} + \alpha_2 [\text{tr}(\mathbf{B})\mathbf{I} - \mathbf{B}] + \alpha_3 \det(\mathbf{B})\mathbf{B}^{-1} \end{aligned} \quad (15)$$

with α_i the derivatives of the free energy (per unit volume) with respect to the invariants of \mathbf{B} .

From kinematics it follows that the Truesdell (upper converted) derivative $\overset{\nabla}{\mathbf{B}}$ of \mathbf{B} equals the null tensor \mathbf{O} :

$$\overset{\nabla}{\mathbf{B}} = \dot{\mathbf{B}} - \mathbf{L} \cdot \mathbf{B} - \mathbf{B} \cdot \mathbf{L}^T = \mathbf{O}. \quad (16)$$

This leads to the evolution equation for \mathbf{B} :

$$\dot{\mathbf{B}} = \mathbf{L} \cdot \mathbf{B} + \mathbf{B} \cdot \mathbf{L}^T = \underline{\Lambda} : \mathbf{L} \quad \text{with} \quad \Lambda_{ijkl} = \delta_{ik} B_{mj} + B_{im} \delta_{jk}. \quad (17)$$

Since there is no dissipation, $\underline{\eta}$ and $\underline{\beta}$ vanish and with Equations (14), (15) and (17) the constitutive equation for isotropic elastic behaviour reduces to:

$$\begin{cases} \mathbf{T} = \mathbf{M} : \underline{\Lambda} = 2[\alpha_3 \det(\mathbf{B})\mathbf{I} + (\alpha_1 + \alpha_2 \text{tr} \mathbf{B})\mathbf{B} - \alpha_2 \mathbf{B} \cdot \mathbf{B}], \\ \overset{\nabla}{\mathbf{B}} = 0, \end{cases} \quad (18)$$

which is the well-known expression for Green elastic behaviour (Hunter, 1983).

The objective of this study is to develop a three-dimensional expression for viscoelastic behaviour, where the volume response is purely elastic. Therefore, as

a second example, the case of purely elastic behaviour will be considered where the volume deformation and the change of shape are uncoupled.

Because of the independent volume deformation it is assumed that the free energy is determined by two state variables, which can be derived from \mathbf{B} : the volume deformation factor $J = \det \mathbf{F} = \sqrt{\det \mathbf{B}}$ (for convenience $J\mathbf{I}$ will be used, instead of J) and the left Cauchy–Green strain tensor at constant volume $\tilde{\mathbf{B}} = J^{-2/3}\mathbf{B}$. In case of isotropic behaviour, the free energy will be a function of J and of the invariants of $\tilde{\mathbf{B}}$:

$$A = A(J, I_{\tilde{\mathbf{B}}}, II_{\tilde{\mathbf{B}}}), \quad (III_{\tilde{\mathbf{B}}} = \det \tilde{\mathbf{B}} = 1). \quad (19)$$

Two conjugated thermodynamic forces can be distinguished now, one related to the volume deformation (\mathbf{N}) and one related to the change of shape ($\tilde{\mathbf{M}}$):

$$\mathbf{N} = \frac{\partial A}{\partial J\mathbf{I}} = \frac{1}{3} \left(\frac{\partial A}{\partial J} \right) \mathbf{I}, \quad (20a)$$

$$\tilde{\mathbf{M}} = \frac{\partial A}{\partial \tilde{\mathbf{B}}} = \tilde{\alpha}_1 \mathbf{I} + \tilde{\alpha}_2 (\text{tr}(\tilde{\mathbf{B}})\mathbf{I} - \tilde{\mathbf{B}}^T). \quad (20b)$$

From kinematics it follows that:

$$\dot{J}\mathbf{I} = J\text{tr}(\mathbf{D})\mathbf{I} = J\mathbf{II} : \mathbf{L} \quad (21a)$$

$$\dot{\tilde{\mathbf{B}}} = \mathbf{L}^d \cdot \tilde{\mathbf{B}} + \tilde{\mathbf{B}} \cdot (\mathbf{L}^d)^T = \left(\underline{\mathbf{A}} - \frac{2}{3} \tilde{\mathbf{B}}\mathbf{I} \right) : \mathbf{L} = \tilde{\underline{\mathbf{A}}} : \mathbf{L}, \quad (21b)$$

where the fourth-order tensor \mathbf{II} is the dyadic product of the second-order identity tensor with itself, and $\tilde{\mathbf{B}}\mathbf{I}$ is the dyadic product of $\tilde{\mathbf{B}}$ with \mathbf{I} .

The constitutive equation for elastic behaviour now becomes:

$$\left[\begin{array}{l} \mathbf{T} = \mathbf{N} : J\mathbf{II} + \tilde{\mathbf{M}} : \tilde{\mathbf{A}} = \mathbf{T}^h + \mathbf{T}^d \\ \quad = J \left(\frac{\partial A}{\partial J} \right) \mathbf{I} + 2\tilde{\alpha}_1 \tilde{\mathbf{B}}^d + 2\tilde{\alpha}_2 \text{tr}(\tilde{\mathbf{B}})\tilde{\mathbf{B}}^d + 2\tilde{\alpha}_2 (\tilde{\mathbf{B}} \cdot \tilde{\mathbf{B}})^d, \\ \dot{\tilde{\mathbf{B}}} = \mathbf{L}^d \cdot \tilde{\mathbf{B}} + \tilde{\mathbf{B}} \cdot (\mathbf{L}^d)^T, \\ \dot{J}\mathbf{I} = J\text{tr}(\mathbf{D})\mathbf{I}. \end{array} \right. \quad (22)$$

Following Simo et al. (1985) and Rubin (1994), a formal separation of the volume effects from the shape deformation can now be achieved by assuming that there are two uncoupled contributions to the free energy, a “volumetric” part A^v and an “isochoric” (constant volume) part A^i :

$$A = A(J, I_{\tilde{\mathbf{B}}}, II_{\tilde{\mathbf{B}}}) = A^v(J) + A^i(I_{\tilde{\mathbf{B}}}, II_{\tilde{\mathbf{B}}}), \quad (23)$$

which results in:

$$\frac{\partial A}{\partial J} = \frac{\partial A^v}{\partial J}, \quad \tilde{\alpha}_1 = \tilde{\alpha}_1(\tilde{\mathbf{B}}), \quad \tilde{\alpha}_2 = \tilde{\alpha}_2(\tilde{\mathbf{B}}). \quad (24)$$

As might be expected, the hydrostatic stress \mathbf{T}^h is determined solely by the volume deformation, whereas the deviatoric stress \mathbf{T}^d is governed by $\tilde{\mathbf{B}}$.

2.2.2. Decomposition of the Rate-of-Strain Tensor, Viscoelastic Behaviour

In order to develop a basic viscoelastic constitutive equation for glassy polymers, the expression for elastic behaviour with a separated volume response, Equation (22), will be used as a starting point. First it is noted that the evolution equation for $\tilde{\mathbf{B}}$ may also be written as:

$$\overset{\circ}{\tilde{\mathbf{B}}} = \dot{\tilde{\mathbf{B}}} - \mathbf{W} \cdot \tilde{\mathbf{B}} - \tilde{\mathbf{B}} \cdot \mathbf{W}^T = \mathbf{D}^d \cdot \tilde{\mathbf{B}} + \tilde{\mathbf{B}} \cdot \mathbf{D}^d, \quad (25)$$

where $\overset{\circ}{\tilde{\mathbf{B}}}$ is the Jaumann rate of $\tilde{\mathbf{B}}$, and \mathbf{D} and \mathbf{W} are the symmetric and skewsymmetric part of \mathbf{L} , respectively.

In case of plastic deformation it is now assumed that the accumulation of elastic strain (at constant volume) is reduced because of the existence of a (deviatoric) plastic rate-of-strain \mathbf{D}_p (Leonov, 1976). Therefore, the evolution equation for $\tilde{\mathbf{B}}$ is modified to:

$$\overset{\circ}{\tilde{\mathbf{B}}}_e = (\mathbf{D}^d - \mathbf{D}_p) \cdot \tilde{\mathbf{B}}_e + \tilde{\mathbf{B}}_e \cdot (\mathbf{D}^d - \mathbf{D}_p). \quad (26)$$

Hence, there is no direct coupling anymore between the state variable $\tilde{\mathbf{B}}_e$ and the external rate variables, as in the case of elastic deformation in the previous section. Therefore, kinematic arguments alone are not sufficient to solve the evolution equation for $\tilde{\mathbf{B}}_e$ and a constitutive description of the plastic rate-of-strain tensor \mathbf{D}_p must be provided.

For materials in general (Krausz and Eyring, 1975) and polymers in specific (Ward, 1990), it is known that the plastic shear rate is often well modelled by using an Eyring-flow process. In the Eyring-flow process it is assumed that the free energy barrier for molecular jump events becomes asymmetric upon the application of a (shear) stress.

The Eyring flow model can be depicted one-dimensionally as:

$$\dot{\gamma}_p = \frac{1}{A} \sinh \left(\frac{\tau}{\tau_0} \right). \quad (27)$$

Here, τ is the shear stress and $\dot{\gamma}_p$ is the plastic shear. The material constants (at constant temperature) A and τ_0 are related to the activation energy, ΔH , and the activation volume, V^* , respectively:

$$A = A_0 \exp \left(\frac{\Delta H}{RT} \right),$$

$$\tau_0 = \frac{RT}{V^*}, \quad (28)$$

with A_0 a pre-exponential factor involving the fundamental vibration frequency, R the universal gas constant and T the absolute temperature.

By inversion of the Eyring equation (Equation (27)), a viscosity can be defined:

$$\dot{\gamma}_p = \frac{\tau}{(\tau \operatorname{arcsinh}(A\dot{\gamma}_p)/\dot{\gamma}_p)} = \frac{\tau}{\eta(\dot{\gamma}_p)}. \quad (29)$$

The Eyring-flow equation (Equation (29)) is a special case of a one-dimensional non-Newtonian fluid relationship, which can be generalized into a three-dimensional form in a standard way (Bird et al., 1987, chapter 4):

$$\begin{aligned} \mathbf{D}_p &= \frac{\mathbf{T}^d/2}{\tau_0 \operatorname{arcsinh}(A\dot{\gamma}_{\text{eq}}/\dot{\gamma}_{\text{eq}})} = \frac{\mathbf{T}^d/2}{\eta(\dot{\gamma}_{\text{eq}})}, \\ \dot{\gamma}_{\text{eq}} &= \sqrt{2\operatorname{tr}(\mathbf{D}_p \cdot \mathbf{D}_p)}. \end{aligned} \quad (30)$$

The equivalent rate-of-strain, $\dot{\gamma}_{\text{eq}}$, is defined such that in case of a shear flow $\dot{\gamma}_{\text{eq}}$ reduces to the plastic rate of shear $\dot{\gamma}_p$ (and then Equation (30) reduces to (29)). Note that the plastic rate-of-strain tensor is parallel to the deviatoric Cauchy stress tensor, since plastic flow is assumed to be incompressible ($\operatorname{tr} \mathbf{D}_p = 0$). Complementary to the equivalent rate-of-strain, an equivalent stress (τ_{eq}) can be defined satisfying:

$$\dot{\gamma}_{\text{eq}} = \frac{1}{A} \sinh\left(\frac{\tau_{\text{eq}}}{\tau_0}\right), \quad \tau_{\text{eq}} = \sqrt{\frac{1}{2} \operatorname{tr}(\mathbf{T}^d \cdot \mathbf{T}^d)}. \quad (31)$$

Substitution of Equation (31) into (30), results in a three-dimensional Eyring equation, relating the plastic rate-of-strain tensor to the deviatoric part of the Cauchy-stress tensor:

$$\mathbf{D}_p = \frac{\mathbf{T}^d}{2\eta(\tau_{\text{eq}})}, \quad \eta(\tau_{\text{eq}}) = A\tau_0 \frac{(\tau_{\text{eq}}/\tau_0)}{\sinh(\tau_{\text{eq}}/\tau_0)} = \eta_0 a_\sigma(\tau_{\text{eq}}), \quad (32)$$

with the so-called *shift function* a_σ . The Eyring equation can be augmented in a straightforward way, to allow for pressure dependence and intrinsic softening effects, but this will not be considered here.

On a fitting level, the Eyring equation is almost indistinguishable from the Argon equation (Argon, 1973), used in the “BPA-model” (Boyce et al., 1988) and the “full chain model” (Wu and van der Giessen, 1993), but conceptually there are differences (Ward, 1990). In contrast to the Argon theory, which regards yielding as a nucleation-controlled process, the Eyring approach implies that deformation mechanisms are essentially always present and that stress merely changes the rate of deformation. This is clearly expressed by the functional dependence of the Eyring viscosity on stress (Equation (32)). There is a linear region at low (equivalent) stress ($\tau_{\text{eq}} \ll \tau_0$), where the viscosity is equal to the *zero-shear viscosity* $\eta_0 = A\tau_0$ and all the non-linear stress effects are incorporated into the shift function a_σ . Thus, according to the Eyring equation, deformation processes at very low stresses, as

observed in linear viscoelastic measurements, are accelerated by stress. This point of view has been explored in more detail by Tervoort et al. (1996).

A constitutive formulation for viscoelastic behaviour with an elastic volume response is now obtained by combining Equation (22) for elastic behaviour with the new evolution equation for $\tilde{\mathbf{B}}_e$, Equations (26) and (32), leading to:

$$\left[\begin{array}{l} \mathbf{T} = J \left(\frac{dA}{dJ} \right) \mathbf{I} + 2\tilde{\alpha}_1 \tilde{\mathbf{B}}_e^d + 2\tilde{\alpha}_2 \text{tr}(\tilde{\mathbf{B}}_e) \tilde{\mathbf{B}}_e^d + 2\tilde{\alpha}_2 (\tilde{\mathbf{B}}_e \cdot \tilde{\mathbf{B}}_e)^d, \\ \dot{\tilde{\mathbf{B}}} = (\mathbf{D}^d - \mathbf{D}_p) \cdot \tilde{\mathbf{B}}_e + \tilde{\mathbf{B}}_e \cdot (\mathbf{D}^d - \mathbf{D}_p), \\ \dot{J} \mathbf{I} = J \text{tr}(\mathbf{D}) \mathbf{I}, \\ \mathbf{D}_p = \frac{\mathbf{T}^d}{2\eta(\tau_{eq})} . \end{array} \right. \quad (33)$$

It is assumed that the volume changes remain small ($J \approx 1$). According to Hooke's law, the hydrostatic-stress term $\mathbf{T}^h = J(dA/dJ)\mathbf{I}$ in Equation (33) can then be written as: $\mathbf{T}^h = K(J - 1)\mathbf{I}$, where K is the bulk modulus. Choosing $\tilde{\alpha}_2 = 0$ (only a linear dependence of \mathbf{T}^d on $\tilde{\mathbf{B}}_e$) and identifying $2\tilde{\alpha}_1$ to the shear modulus G , the constitutive formulation (33) reduces to:

$$\mathbf{T} = K(J - 1)\mathbf{I} + G\tilde{\mathbf{B}}_e^d, \quad (34a)$$

$$\dot{\tilde{\mathbf{B}}} = (\mathbf{D}^d - \mathbf{D}_p) \cdot \tilde{\mathbf{B}}_e + \tilde{\mathbf{B}}_e \cdot (\mathbf{D}^d - \mathbf{D}_p), \quad (34b)$$

$$\dot{J} \mathbf{I} = J \text{tr}(\mathbf{D}) \mathbf{I}, \quad (34c)$$

$$\mathbf{D}_p = \frac{\mathbf{T}^d}{2\eta(\tau_{eq})}, \quad (34d)$$

$$\eta(\tau_{eq}) = A\tau_0 \frac{(\tau_{eq}/\tau_0)}{\sinh(\tau_{eq}/\tau_0)}. \quad (34e)$$

Although derived in a different way, this model is similar to Leonov models as discussed by Rubin (1994) and Baaijens (1991).

3. Experimental

All experiments were performed on test samples produced from extruded sheets of Makrolon (bisphenol A polycarbonate) on a Frank 81565 tensile tester. Tensile tests were performed according to ASTM-D638. The planar extension experiments were performed as described by Whitney and Andrews (1967), using a sample length-to-width ratio of two, rather than one. Shear experiments were performed according to ASTM-D4255-83. All experiments were performed on separate samples of identical thermal history, their age exceeding by far the longest times in the experiments, to minimize the effect of physical aging.

4. Results

Some features of the “compressible Leonov model”, which was derived in the previous section, are demonstrated in this section, using polycarbonate as a model polymer.

4.1. MATERIAL PARAMETERS

The material parameters required by the compressible Leonov model are the linear elastic constants K and G in Hooke's law and two non-linearity parameters in the Eyring viscosity function: A and τ_0 . The elastic constants were obtained by measuring the Young's (glassy) modulus E and the Poisson constant ν in a tensile test, at low stresses and strains, which resulted in $E = 2350$ [MPa] and $\nu = 0.41$ [–]. The shear modulus is related to E and ν by: $G = E/2(1 + \nu) = 830$ [MPa], and the bulk modulus by: $K = E/3(1 - 2\nu) = 4600$ [MPa].

At the yield point, the plastic rate-of-strain is approximately equal to the total rate-of-strain. Therefore, according to the Leonov model, at the yield point, a material behaves as a generalized Newtonian fluid:

$$\mathbf{T} = -p\mathbf{I} + 2\eta\mathbf{D}_p = -p\mathbf{I} + 2\eta\mathbf{D}. \quad (35)$$

Because of the incompressibility constraint, the hydrostatic stress p depends only on the boundary conditions. The yield point is defined by the moment the stress remains constant at a constant applied rate-of-strain and is, therefore, completely determined by the viscosity function (Equation (30)):

$$\eta = \frac{\tau_0}{\dot{\gamma}_{\text{eq}}} \operatorname{arcsinh}(A\dot{\gamma}_{\text{eq}}), \quad \dot{\gamma}_{\text{eq}} = \sqrt{2(\mathbf{D}_p \cdot \mathbf{D}_p)}. \quad (36)$$

If the yield point σ_y is measured in a tensile experiment at a (Hencky) rate-of-strain $\dot{\epsilon}$ in the axial direction, Equation (35) leads to:

$$\begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & \sigma_y \end{bmatrix} = \begin{bmatrix} -p & 0 & 0 \\ 0 & -p & 0 \\ 0 & 0 & -p \end{bmatrix} + 2\eta(\dot{\gamma}_{\text{eq}}) \begin{bmatrix} -\frac{1}{2}\dot{\epsilon} & 0 & 0 \\ 0 & -\frac{1}{2}\dot{\epsilon} & 0 \\ 0 & 0 & \dot{\epsilon} \end{bmatrix}. \quad (37)$$

From this equation it can be seen that the equivalent plastic rate-of-strain becomes $\dot{\gamma}_{\text{eq}} = \dot{\epsilon}\sqrt{3}$. The yield stress as a function of rate-of-strain, therefore, equals:

$$\sigma_y = \tau_0\sqrt{3} \operatorname{arcsinh}(A\dot{\epsilon}\sqrt{3}). \quad (38)$$

If the argument of the hyperbolic sine function is large, it can be approximated by an exponential function and relation (38) may be transformed to:

$$\sigma_y = \tau_0\sqrt{3} \ln(2A\sqrt{3}) + \tau_0\sqrt{3} \ln \dot{\epsilon}. \quad (39)$$

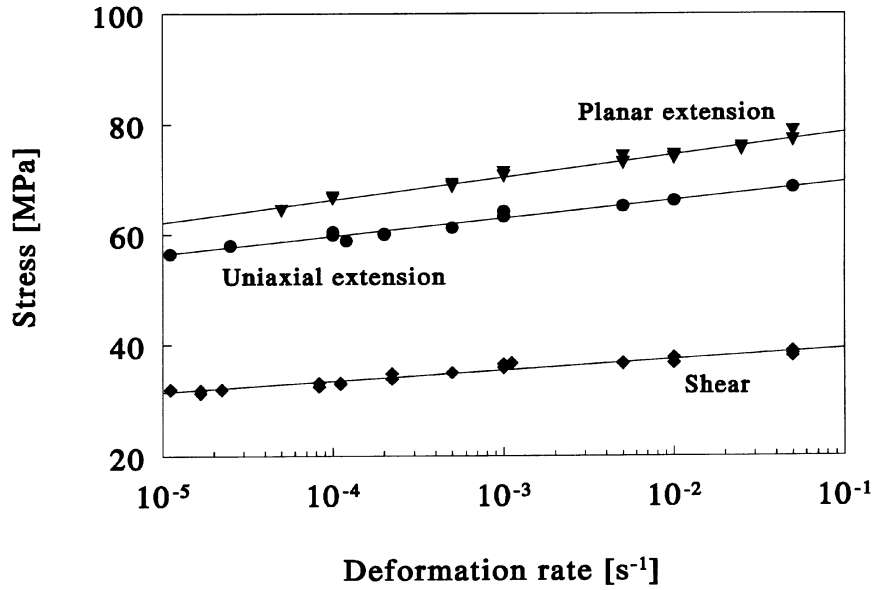


Figure 4. Eyring plot for polycarbonate constructed from yield points in various deformation modes. The solid lines are a best fit using a single set of Eyring parameters.

From the last equation it follows that the Eyring parameters from the Leonov model can be determined by linear regression, plotting the yield stress *versus* the logarithmic of the rate-of-strain. This is called an Eyring plot. Note that Equation (39) depends on the mode-of-deformation, for example, in shear, the Newtonian flow Equation (35) relates the shear-yield stress τ_y to the applied rate-of-shear $\dot{\gamma}$ by:

$$\tau_y = \tau_0 \ln(2A) + \tau_0 \ln \dot{\gamma}. \quad (40)$$

In a planar extension test, the Newtonian flow rule reduces to:

$$\sigma_y^{\text{pl}} = 2\tau_0 \ln(4A) + 2\tau_0 \ln \dot{\epsilon}^{\text{pl}}, \quad (41)$$

where σ_y^{pl} is the yield stress in planar extension at a rate-of-planar extension $\dot{\epsilon}^{\text{pl}}$.

Eyring plots for polycarbonate in various deformation modes are depicted in Figure 4. The solid lines in this figure are the best fit of a single set of Eyring parameters: $\tau_0 = 0.9$ [MPa] and $A = 1.75 \cdot 10^{20}$ [s]. From this figure it is clear that at the yield point polycarbonate behaves like a generalized Newtonian fluid.

Having determined all the material constants, it is now possible to calculate any response from the compressible Leonov model. First, a standard uniaxial tensile test will be considered, in which a tensile bar is elongated in the axial direction at two different rates of deformation. The tensile bar is stress free in the radial and tangential direction (see Figure 5a). As a second deformation mode, a plane-stress shear test, also called “laboratory shear”, is chosen. The configuration of a plane-stress shear test is shown in Figure 5b, the shear strain $\gamma_{xy} = \tan(\phi)$.

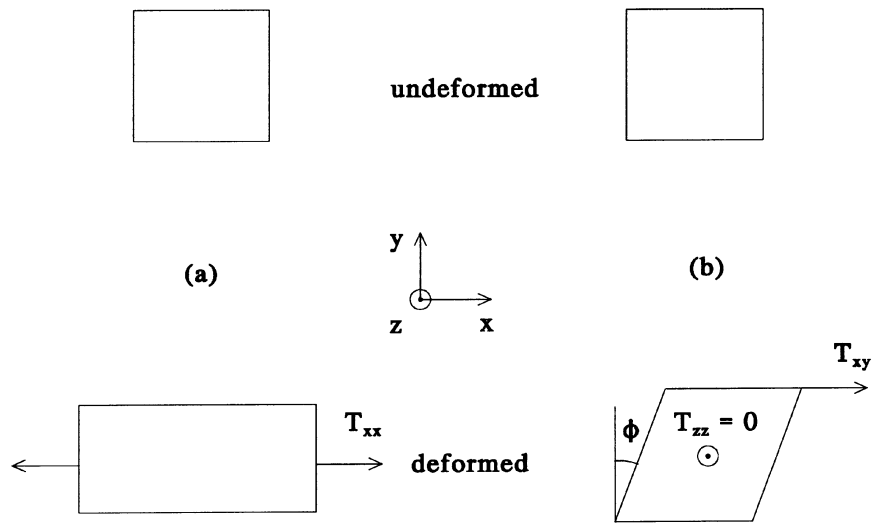


Figure 5. Schematic drawing of (a) the uniaxial tensile test and (b) the plane-stress shear test, the shear strain $\gamma = \tan(\phi)$.

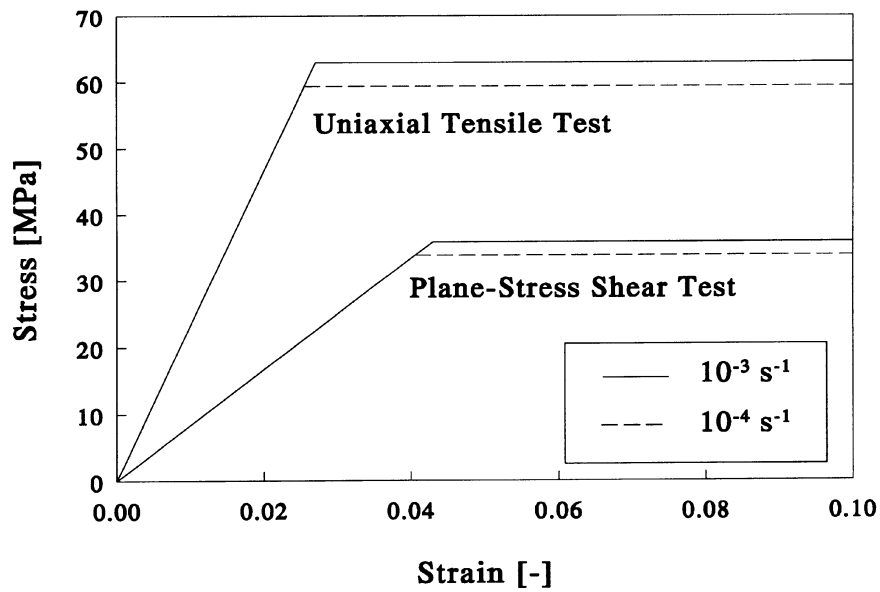


Figure 6. Calculated response from the Leonov model for polycarbonate in uniaxial-tensile and plane-stress shear deformation, at two rates-of-strain.

The response of the Leonov model (34) for these deformation modes, a uniaxial tensile and a plane-stress shear test, is given in Figure 6. In this figure it can be observed that the Leonov model predicts a sharp instead of a gradual transition from elastic to plastic behaviour, which is very similar to that of an elastic-perfectly plastic material with a rate-dependent von Mises yield criterion. This similarity originates from the proportionality of the equivalent stress τ_{eq} with the von Mises equivalent stress τ_{VM} ($\tau_{eq} = \tau_{VM}/3\sqrt{3}$).

4.2. COMPARISON WITH OTHER MODELS

A common way to describe viscoelastic behaviour is the so-called *generalized Maxwell model*, often depicted as a number of springs and dashpots in series. In a Maxwell model it is assumed that the velocity gradient is decomposed in an elastic and a plastic part:

$$\mathbf{L} = \mathbf{L}_e + \mathbf{L}_p = (\mathbf{D}_e + \mathbf{W}_e) + (\mathbf{D}_p + \mathbf{W}_p). \quad (42)$$

For the kinematic interpretation of \mathbf{L}_e and \mathbf{L}_p usually a so-called unloaded state or “natural reference state” is introduced (Besseling and van der Giessen, 1994).

In case of isotropic materials, the orientation of the unloaded state is irrelevant and the plastic spin \mathbf{W}_p is set equal to the null tensor. Furthermore, it is an experimental fact that to a good approximation, polymers, like most other materials, show negligible volume deformation during plastic flow, i.e. $\text{tr} \mathbf{D}_p = 0$. Therefore, the (deviatoric) plastic rate-of-strain tensor \mathbf{D}_p is assumed to be codirectional to the deviatoric Cauchy-stress tensor:

$$\mathbf{T}^d = 2\eta(p, \tau_{eq})\mathbf{D}_p \quad (43)$$

with p the pressure ($p = 1/3 \text{tr}(\mathbf{T})$). This equation reflects that the viscosity may be pressure dependent although the volume response is purely elastic.

The elastic part of the deformation is usually modelled by a rate formulation of Hooke's law for isotropic materials. This results in an isotropic relationship between an objective time derivative of the Cauchy-stress tensor and the elastic rate-of-strain tensor:

$$\overset{\diamond}{\mathbf{T}} = \lambda \text{tr}(\mathbf{D}_e)\mathbf{I} + 2\mu\mathbf{D}_e = \underline{\mathcal{L}}^e : \mathbf{D}_e. \quad (44)$$

Here, \diamond denotes an objective rate, λ and μ are the Lamé constants and $\underline{\mathcal{L}}^e$ is a tensor of rank four.

Combining Equations (42), (43) and (44), leads to a standard viscoelastic rate equation:

$$\begin{cases} \overset{\diamond}{\mathbf{T}} = \underline{\mathcal{L}}^e : (\mathbf{D} - \mathbf{D}_p), \\ \mathbf{D}_p = \frac{\mathbf{T}^d}{2\eta(I_T, \tau_{eq})}. \end{cases} \quad (45)$$

The subject of objective rates is a controversial one in continuum mechanics. By far the most common choice in plasticity theory is the Jaumann rate or corotational derivative, which is the time derivative with respect to a corotating reference frame (Neale, 1981). Applying the Jaumann derivative in Equation (45) results in the so-called *corotational Maxwell model*:

$$\frac{\eta(I_T, \tau_{eq})}{G} \overset{\circ}{\mathbf{T}} + \mathbf{T}^d = 2\eta(I_T, \tau_{eq})\mathbf{D} + \lambda \left(\frac{\eta(I_T, \tau_{eq})}{G} \right) \text{tr}(\mathbf{D}). \quad (46)$$

Another well-known rate is the Truesdell or upper-convected time derivative. As already mentioned above, this is the time derivative with respect to a codeforming reference frame (Bird et al., 1987, chapter 9). Using the Truesdell derivative in Equation (45) results in what will be denoted as the “Truesdell-rate model”:

$$\frac{\eta(I_T, \tau_{eq})}{G} \overset{\nabla}{\mathbf{T}} + \mathbf{T}^d = 2\eta(I_T, \tau_{eq})\mathbf{D} + \lambda \left(\frac{\eta(I_T, \tau_{eq})}{G} \right) \text{tr}(\mathbf{D}). \quad (47)$$

It can be shown that integration of the Truesdell-rate formulation of Hooke’s law results in hyperelastic behaviour, whereas integration of the Jaumann rate results in a hypoelastic law (van Wijngaarden, 1988; Sansour and Bednarczyk, 1993) (in contrast to a hypoelastic relation, a hyperelastic law is a constitutive equation for elastic behaviour, which can be derived from a strain-energy potential). Therefore, if large elastic deformations occur like in polymer flow, the Truesdell-rate is more attractive from a physics point of view. This was, for instance, shown by Beris and Edwards (1990), who found that their Poisson-bracket formulation of continuum mechanics could only accommodate the upper-convected time derivative (and its counterpart, the lower-convected derivative).

From the Truesdell-rate model (47) and the corotational Maxwell model (46), only the latter is approximately equal to the compressible Leonov model (34) in the limit of small elastic strains. This can be shown by taking the Jaumann derivative of the expression for the stress tensor in the Leonov formulation, Equation (34a):

$$\overset{\circ}{\mathbf{T}} = K J \dot{\mathbf{I}} + G \overset{\circ}{\tilde{\mathbf{T}}}_e - \frac{G}{3} \text{tr}(\dot{\tilde{\mathbf{B}}}_e) \mathbf{I}. \quad (48)$$

Substitution of the evolution equations for $\tilde{\mathbf{B}}_e$ and J , Equations (34b) and (34d) at small isochoric-elastic and volume strains ($\tilde{\mathbf{B}}_e \approx \mathbf{I}$ and $J \approx 1$), then results in the corotational Maxwell model:

$$\overset{\circ}{\mathbf{T}} = K \text{tr}(\mathbf{D}) \mathbf{I} + 2G(\mathbf{D}^d - \mathbf{D}_p) = \underline{\mathcal{L}}^e : (\mathbf{D} - \mathbf{D}_p). \quad (49)$$

However, taking the Truesdell derivative of Equation (34a), results in:

$$\overset{\nabla}{\mathbf{T}} = K J \dot{\mathbf{I}} - 2K(J - 1)\mathbf{D} + G \overset{\nabla}{\tilde{\mathbf{T}}}_e - \frac{G}{3} \text{tr}(\dot{\tilde{\mathbf{B}}}_e) \mathbf{I}. \quad (50)$$

Again substituting the evolution equations for $\tilde{\mathbf{B}}_e$ and J at small elastic strains, now results in:

$$\begin{aligned}\overset{\nabla}{\mathbf{T}} &= 2G(\mathbf{D}^d - \mathbf{D}_p) + K \operatorname{tr}(\mathbf{D})\mathbf{I} - 2K(J - 1)\mathbf{D} \\ &= \underline{\mathcal{L}}^e : (\mathbf{D} - \mathbf{D}_p) - 2K(J - 1)\mathbf{D}.\end{aligned}\quad (51)$$

In this expression an extra term appears, compared to the Truesdell-rate model (47), which cannot be neglected when the elastic rate-of-strain tensor \mathbf{D}_e is small ($\mathbf{D} \approx \mathbf{D}_p$). In contrast to the Jaumann derivative, the Truesdell derivative of a deviatoric tensor, in general, is not deviatoric. Therefore, the Truesdell derivative fails to preserve the (physically meaningful) distinction between the hydrostatic part and the deviatoric part of the Cauchy-stress tensor (Sansour and Bednarczyk, 1993).

It is possible, however, to reduce the compressible Leonov model (34), at small elastic strains, to a slightly modified Truesdell-rate model. For this purpose, an extra-stress tensor \mathbf{T}_E is defined, of which the deviatoric part is equal to the deviatoric part of the Cauchy-stress tensor:

$$\mathbf{T}_E = G(\tilde{\mathbf{B}}_e - \mathbf{I}); \quad \mathbf{T}_E^d = \mathbf{T}^d. \quad (52)$$

Taking the Truesdell derivative of this expression, followed by substitution of the flow rule for \mathbf{D}_p , Equation (43), and the evolution laws for $\tilde{\mathbf{B}}_e$ and J , Equations (34b) and (34d), at small elastic strains, results in:

$$\left[\begin{array}{l} \mathbf{T} = K(J - 1)\mathbf{I} + \mathbf{T}_E^d, \\ \frac{\eta(I_T, \tau_{eq})}{G} \overset{\nabla}{\mathbf{T}}_E + \mathbf{T}_E^d = 2\eta(I_T, \tau_{eq})\mathbf{D} \\ \dot{J} = \operatorname{tr}(\mathbf{D}). \end{array} \right. \quad (53)$$

Apart from the stress dependence of the viscosity, the Truesdell-rate equation for the extra-stress tensor \mathbf{T}_E , Equation (53), corresponds to the upper-convected Maxwell model, well known from polymer rheology (Larson, 1988, chapter 1). In the next section, this model, to be denoted as the UCM model, will be evaluated as well. Note that the corotational Maxwell model, Equation (46), can be written in a similar form as Equation (53), using only the Cauchy-stress tensor, due to the fortunate fact that the Jaumann derivative of a deviatoric tensor is always deviatoric:

$$\left[\begin{array}{l} \mathbf{T} = \mathbf{T}^d + K(J - 1)\mathbf{I}, \\ \frac{\eta(I_T, \tau_{eq})}{G} \overset{\circ}{\mathbf{T}} + \mathbf{T}^d = 2\eta(I_T, \tau_{eq})\mathbf{D}, \\ \dot{J} = \operatorname{tr}(\mathbf{D}). \end{array} \right. \quad (54)$$

The performance of the compressible Leonov model and the “standard” rate equations involving the Truesdell and the Jaumann derivative are mutually compared and evaluated by means of two simple homogeneous deformation tests, using

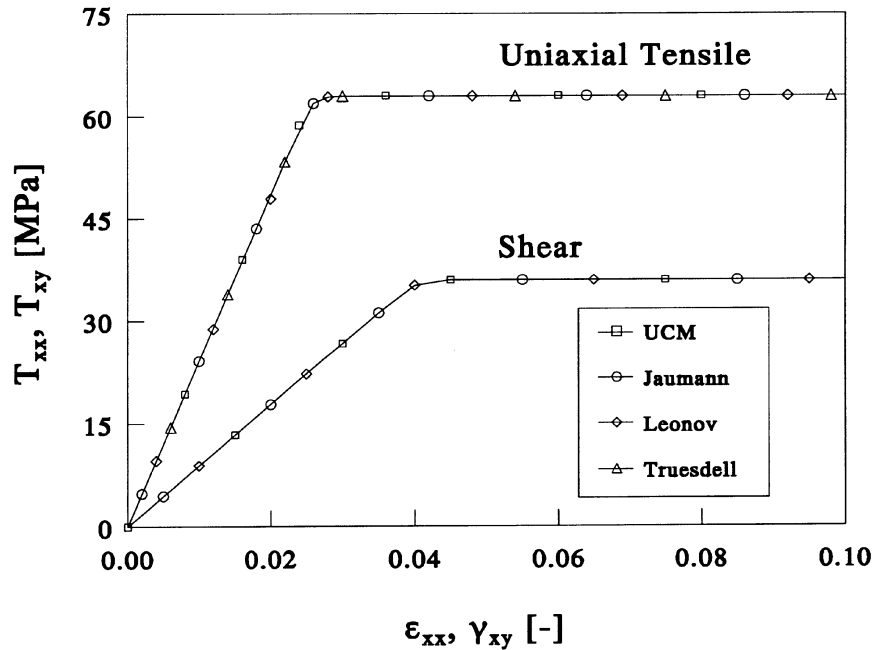


Figure 7. Stress-strain curves for a uniaxial tensile test (T_{xx} versus ϵ_{xx}) and a plane-stress shear test (T_{xy} versus γ_{xy}), both at a rate-of-deformation of $10^{-3} \text{ [s}^{-1}\text{]}$.

polycarbonate as a model polymer. The material parameters are $G = 830 \text{ [MPa]}$, $K = 4600 \text{ [MPa]}$ (which is equivalent to $E = 2350 \text{ [MPa]}$ and $\nu = 0.41 \text{ [-]}$), $A = 1.75 \cdot 10^{21} \text{ [s}^{-1}\text{]}$ and $\tau_0 = 0.89 \text{ [MPa]}$. First, a standard uniaxial tensile test will be considered, in which a tensile bar, stress-free in the radial and the tangential direction, is elongated in the x -direction at a rate-of-deformation of 10^{-3} (see Figure 7). As might be expected from these single mode models, they all show a sharp instead of a gradual transition from elastic to plastic behaviour.

The calculated volume response as a function of logarithmic strain, is depicted in Figure 8. All four models show a “correct” volume response in the elastic region, according to Hooke’s law. However, the Truesdell-rate model displays a volume decrease during plastic flow, which is not in accordance with the assumption of incompressible flow during plastic deformation.

Second, a plane-stress shear test will be calculated. The Truesdell-rate model is not considered anymore because of its anomalous volume decrease in a tensile test. Virtually the same behaviour is obtained for all three models, Figure 7. However, the calculated normal stress in the y -direction, T_{yy} , differs markedly for the three models considered, as is depicted in Figure 9. In contrast to the corotational Maxwell model, both the compressible Leonov model and the UCM model display “correct” neo-Hookean behaviour in the elastic region, where the normal stress in the y -direction is a quadratic function of the shear strain. This is to be expected,

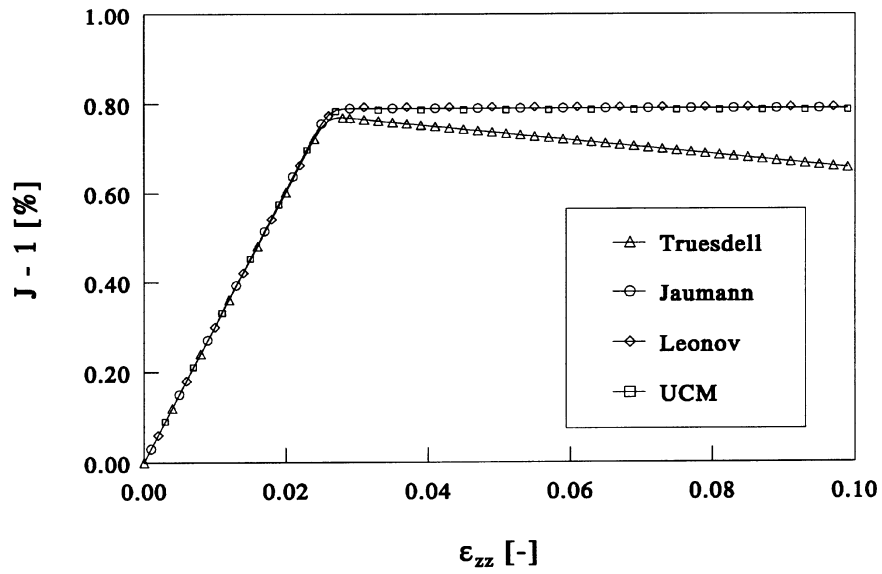


Figure 8. Relative volume deformation as a function of logarithmic strain for a uniaxial tensile test at a rate-of-deformation of $10^{-3} \text{ [s}^{-1}\text{]}$.

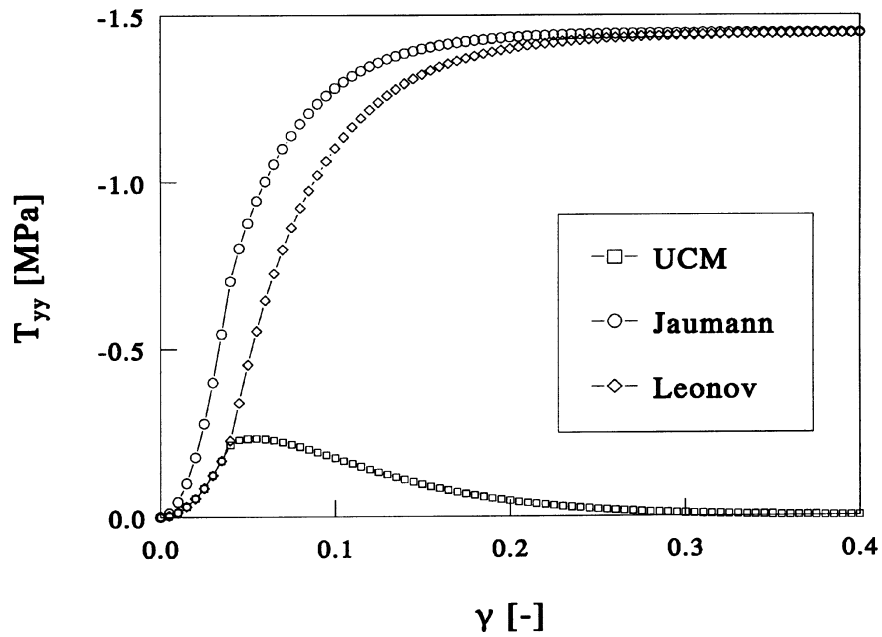


Figure 9. Normal stress in the y-direction as a function of shear strain at a rate-of-deformation of $10^{-3} \text{ [s}^{-1}\text{]}$.

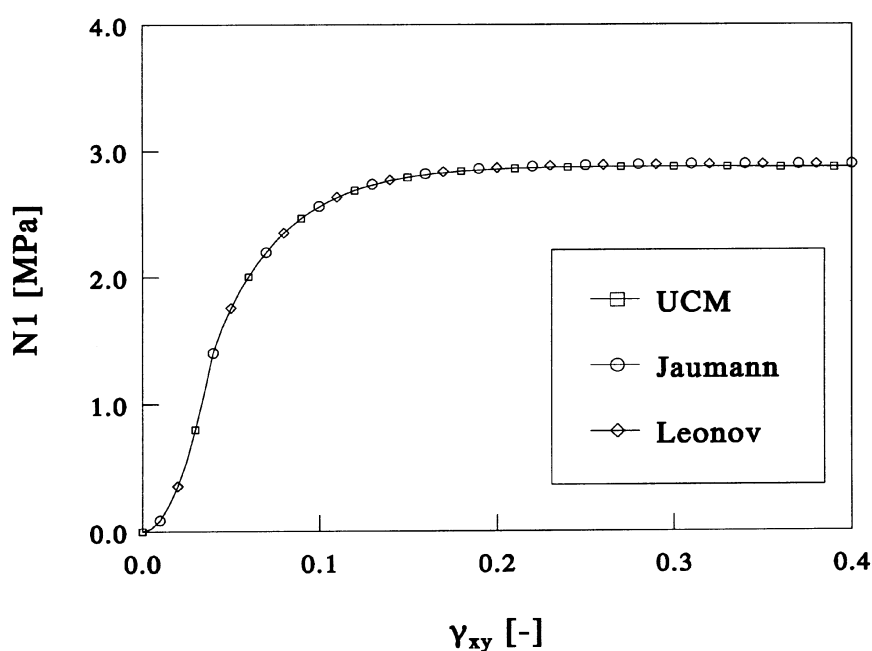


Figure 10. First normal stress difference $N1$ ($N1 = \mathbf{T}_{xx} - \mathbf{T}_{yy}$) as a function of shear strain at a deformation rate of $10^{-3} \text{ [s}^{-1}\text{]}$.

since integration of the Jaumann-rate version of Hooke's law does not result in hyperelastic behaviour. In contrast, at higher strains, the UCM model predicts zero normal stress in the y -direction, whereas shear flow of a polymeric substance normally results in negative normal stresses (Bird et al., 1987, chapter 3), as it is displayed by the corotational Maxwell model and the compressible Leonov model. The Leonov model provides a smooth transition from neo-Hookean behaviour in the elastic region, to the more realistic response of the corotational Maxwell element during yielding.

It is interesting to note that the first normal stress difference, $N1$ ($N1 = \mathbf{T}_{xx} - \mathbf{T}_{yy}$), is virtually equal for all three models considered, as can be concluded from Figure 10.

Apparently, at small elastic strains, all three models differ mainly in the hydrostatic-stress contribution, resulting in different absolute values of the normal stress themselves. This can also be derived from the calculated volume response, see Figure 11, recalling that in these models, the relative volume change is directly related to the hydrostatic stress.

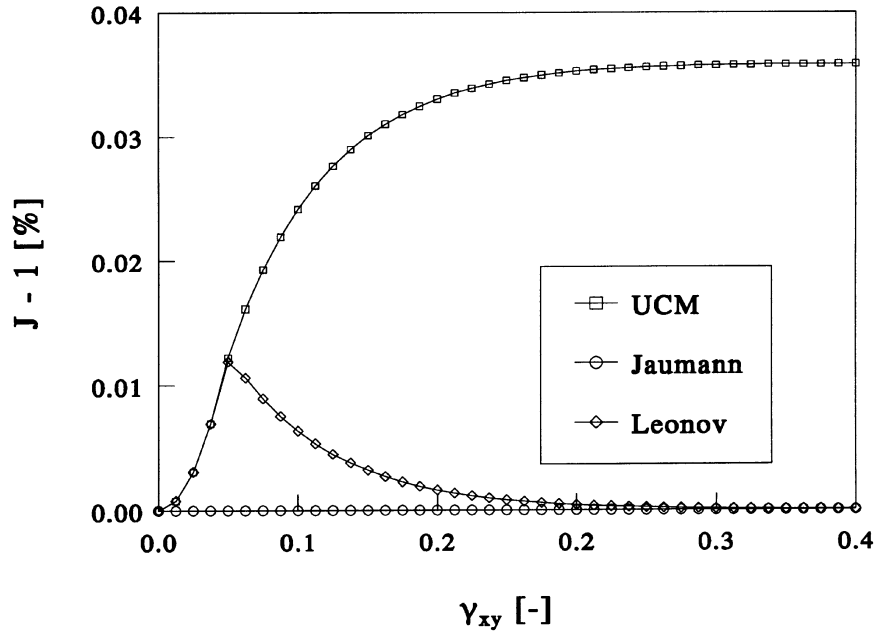


Figure 11. Relative volume deformation as a function of shear strain for a plane-stress shear test at a rate-of-deformation of $10^{-3} \text{ [s}^{-1}\text{]}$.

5. Discussion and Conclusions

In this study a so-called “compressible Leonov model” has been introduced which can be depicted as a single Maxwell model employing a relaxation time dependent on an equivalent stress proportional to the von Mises stress. The model has been derived using a generic formalism for the development of thermodynamically consistent constitutive equations. It was assumed that the free energy of the system at constant temperature, which is a measure for the amount of stored energy, is determined by two state variables, the isochoric elastic strain and the volume strain. The plastic rate-of-strain was constitutively described by stress-activated Eyring flow.

A comparison has been made between the Leonov model and two standard constitutive equations for the description of relaxation behaviour, the Truesdell-rate and the corotational Maxwell model. It was concluded that neither of these two standard models is able to describe plastic deformation accompanied by large elastic deformations, as it can occur during strain hardening of glassy polymers. Integration of the corotational Maxwell model is known the result in hypoe-lastic elastic behaviour, whereas integration of the Truesdell model results in a volume decrease during plastic flow in a tensile test. Based upon the Leonov model, a slightly modified Truesdell-rate model was proposed, the so-called upper-

convected Maxwell model (UCM model), for which the volume remains constant during plastic flow in a tensile experiment.

In a plane-stress shear test, the UCM model, the corotational Maxwell model and the Leonov model only seem to differ in their volume response. The corotational Maxwell model shows no volume response at all, which is somewhat unrealistic for a plane-stress configuration. Contrary, the compressible Leonov model and the UCM model display a volume increase in the elastic region, but the volume does not remain constant after yielding as in the tensile test. It is doubtful whether experimental data can shed any light on these results. In principle, the normal stress in the y -direction can be measured experimentally up to the yield point. After the yield point however, shearbands will develop, prohibiting a straightforward interpretation of the data. Furthermore, even if it would be possible to extract useful data after the yield point, the effects mentioned would probably be overwhelmed by the strain-hardening response. Since the models considered here are all "single mode" models, even the response in the linear viscoelastic region will not be predicted realistically. Also, the strain-hardening response is not captured by the models discussed in this paper. Furthermore, in all the single mode models discussed in this paper, the plastic deformation is irreversible. This is realistic for metals, but does not necessarily apply to polymers, which can return to their undeformed shape upon heating the sample. It must be emphasized, however, that the compressible Leonov model can easily be extended to include multiple relaxation times, in which case a realistic non-linear viscoelastic description of the deformation behavior (including strain hardening) of polymers can be obtained. A theoretical and experimental study of the full non-linear viscoelastic response up to the yield point of polycarbonate, is discussed by Tervoort et al. (1996).

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