On the dynamic behaviour of polymers under finite strains: constitutive modelling and identification of parameters

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Abstract

In this paper we apply a model of finite viscoelasticity and propose an identification technique to represent the dynamic properties of polymers. The model is based on a multiplicative split of the deformation gradient into a thermal and a mechanical part, the latter being decomposed further into elastic and viscous parts. In order to formulate the constitutive equations we transfer the concept of discrete relaxation spectra to finite strains, specify the free energy as a function of elastic strain tensors and evaluate the dissipation principle of thermodynamics in the form of the Clausius–Duhem inequality. Then we investigate the dynamic moduli of a polyethylene melt under harmonic shear deformations and determine the material parameters. To this end we linearise the constitutive model and calculate the analytical solution of the evolution equations. In addition we formulate a second model which represents the experimental data on the basis of a fairly small number of fitting parameters. This so-called substitute model is based on the fractional calculus and corresponds to a continuous relaxation spectrum. In order to identify the material constants of the finite strain model we are looking for, we proceed as follows. We determine the parameters of the substitute model, calculate the so-called cumulative relaxation spectrum and approximate it by means of a series of step functions: the height of the steps corresponds to the stiffness parameters of the finite strain model and their locations to the inverse relaxation times. © 2000 Elsevier Science Ltd. All rights reserved.

1. Introduction

For the purpose of modelling static and dynamic mechanical properties of polymers when subjected to small strains, the phenomenological theory of linear viscoelasticity is a very powerful and familiar tool (cf Tobolsky, 1967; Gross, 1968; Findley et al., 1976; Ferry, 1980; Tschoegl, 1989 among others). If the corresponding relaxation function $G(t)$ is completely monotonic, i.e. the condition $(-1)^n \, \mathrm{d}^n G/\mathrm{d}t^n \geq 0$

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is satisfied for any natural number n or, equivalently, the relaxation spectrum is non-negative, the compatibility with the second law of thermodynamics is ensured (see, for example, Beris and Edwards, 1993 and literature citations therein). This is the case, for example, if the mathematical form of the constitutive model is based on discretely or continuously distributed rheological elements, i.e. on linear springs and dampers with positive stiffness parameters and viscosities. If, for comparison, the model is formulated purely mathematically on the basis of linear differential operators, i.e. $a_0\sigma + a_1 \, \mathrm{d}\sigma/\mathrm{d}t + a_2 \, \mathrm{d}^2\sigma/\mathrm{d}t^2 + \cdots = \epsilon + b_1 \, \mathrm{d}\epsilon/\mathrm{d}t + b_2 \, \mathrm{d}^2\epsilon/\mathrm{d}t^2 + \cdots$, it can happen that the thermodynamical compatibility is violated under certain circumstances. Akyildiz et al. (1990) analysed such an example.

In addition to the classical rheological model approach, the fractional calculus, which was transferred to linear viscoelasticity by Caputo and Mainardi (1971), can also be successfully applied to describe the relaxation, creep or dynamic properties of polymeric materials over fairly large ranges in the time or the frequency domain (see, for example, Koeller, 1984; Bagley and Torvik, 1986). If these models are formulated on the basis of so-called fractional rheological elements (see Schiessel et al., 1995) they are compatible with the second law of thermodynamics as well (see Lion, 1997a,b).

If the deformations are larger, for example, in the case of extrusion or injection moulding, linear theories are no longer applicable to simulate the material properties in thermomechanical boundary value problems. Many polymers have a vanishing equilibrium stress; they show pronounced relaxation and creep effects and have an off-zero storage modulus. Therefore, the concepts of linear or non-linear viscous fluids are also invalid. We therefore intend to propose a thermodynamically consistent approach capable of describing complicate viscoelastic behaviour. The deformations can be finite and both the equilibrium stress and the low-frequency limit of the storage modulus can either be different from zero or not. In order to determine the material constants, we propose a method which is based on dynamic shear tests under small strains.

2. Constitutive approach

The details of our constitutive approach are described in earlier papers (cf Lion, 1997a, 1998). In order to separate physical phenomena of a different nature we introduced multiple intermediate configurations. The push-forward and pull-back transformations of the associated stress and strain variables between the different sets of configurations are carried out using the concept of dual variables developed by Haupt and Tsakmakis (1989).

We begin with the multiplicative decomposition of the deformation gradient $\mathbf{F}$ into a stress-producing mechanical part $\mathbf{F}_M$ and a thermal part $\mathbf{F}_\theta$ as originally proposed by Lu and Pister (1975):

$$\mathbf{F} = \mathbf{F}_M \mathbf{F}_\theta. \tag{1}$$

Isotropic thermal expansion leads to $\mathbf{F}_\theta = \varphi(\theta)\mathbf{1}$, where φ describes the temperature dependence of the mass density. In addition we define the following set of mechanical stress and strain measures

$$\mathbf{E}_M = \tfrac{1}{2}[\mathbf{C}_M - \mathbf{1}], \quad \mathbf{C}_M = \mathbf{F}_M^{\mathrm{T}}\mathbf{F}_M, \quad \tilde{\mathbf{T}}_M = (\det \mathbf{F}_M)\mathbf{F}_M^{-1}\mathbf{T}\mathbf{F}_M^{\mathrm{T}-1}, \tag{2}$$

where $\mathbf{E}_M$ is the mechanical Green strain tensor, $\mathbf{C}_M$ the Cauchy–Green tensor, $\mathbf{T}$ the Cauchy stress and $\tilde{\mathbf{T}}_M$ the mechanical second Piola–Kirchhoff stress tensor. If we express the dissipation in the form of the Clausius–Duhem inequality (see, for example, Haupt, 1992) in terms of these variables we obtain the relation

$$\rho_{R\theta}\theta\Gamma = -\rho_{R\theta}\dot{\psi} + \tilde{\mathbf{T}}_M \cdot \dot{\mathbf{E}}_M + \mathbf{C}_M\tilde{\mathbf{T}}_M \cdot \mathbf{L}_\theta - \rho_{R\theta}s\dot{\theta} - \frac{\mathbf{q}_R \cdot \mathrm{Grad}\,\theta}{\theta \ \det(\mathbf{F}_\theta)} \geq 0, \tag{3}$$

$$\mathbf{L}_\theta = \dot{\mathbf{F}}_\theta \mathbf{F}_\theta^{-1}, \quad \rho_{R\theta} = \frac{\rho_R}{\det(\mathbf{F}_\theta)}, \tag{4}$$

which has to be satisfied for arbitrary thermomechanical processes. In the above relations ψ is the free energy per unit mass, s the specific entropy, θ the thermodynamic temperature, $\mathbf{q}_R$ the vector of heat flux, and Γ the rate of entropy production. The quantities $\rho_{R\theta}$ and ρ_R are the mass densities of the unloaded configuration at the temperatures θ and θ_0. The vector $\mathrm{Grad}\theta$ is the material temperature gradient and a superscript dot denotes the material time derivative.

Formulating the constitutive model we assume that all dependent variables ψ, $\tilde{\mathbf{T}}_M$ and s are functionals of the history of the mechanical Green strain tensor $\mathbf{E}_M$ and the thermodynamic temperature θ:

$$\psi(t) = \underset{s\geq 0}{h}(\mathbf{E}_M(t-s), \theta(t-s)), \quad \tilde{\mathbf{T}}_M(t) = \underset{s\geq 0}{\mathbf{H}}(\mathbf{E}_M(t-s), \theta(t-s)),$$

$$s(t) = \underset{s\geq 0}{k}(\mathbf{E}_M(t-s), \theta(t-s)). \tag{5}$$

Motivated by the structure of rheological models with discrete relaxation spectra and further physical arguments (see, for example, Lubliner, 1985; Haupt, 1993; Lion, 1997a, 1998) we decompose the free energy ψ and the stress $\tilde{\mathbf{T}}_M$ as follows:

$$\psi = \psi_{\mathrm{eq}}(\mathbf{E}_M, \theta) + \sum_{k=1}^{N}\psi_{ovk}(\boldsymbol{\epsilon}_{evk}, \theta) + \zeta(\theta), \quad \tilde{\mathbf{T}}_M = \tilde{\mathbf{T}}_{\mathrm{eq}} + \sum_{k=1}^{N}\tilde{\mathbf{T}}_{ovk}. \tag{6}$$

The equilibrium parts ψ_{eq} and $\tilde{\mathbf{T}}_{\mathrm{eq}}$ describe the equilibrium properties of the material and depend on the total mechanical deformation $\mathbf{E}_M$ and the temperature, whereas $\zeta(\theta)$ is related to the temperature dependence of the specific heat capacity. The non-equilibrium part ψ_{ov} is the sum of energy functions of the elastic strain tensors $\boldsymbol{\epsilon}_{evk}$ defined by the following set of multiplicative decompositions:

$$\mathbf{F}_M = \mathbf{F}_{evk}\mathbf{F}_{vk}, \quad \boldsymbol{\epsilon}_{evk} = \tfrac{1}{2}(\mathbf{C}_{evk} - 1), \quad \mathbf{C}_{evk} = \mathbf{F}_{evk}^{\mathrm{T}}\mathbf{F}_{evk}, \quad \mathbf{C}_{vk} = \mathbf{F}_{vk}^{\mathrm{T}}\mathbf{F}_{vk}. \tag{7}$$

As a consequence of the dissipation inequality (3) and the concept of dual variables proposed by Haupt and Tsakmakis (1989), the potential relations for the stresses and the evolution laws for the inelastic deformations, acting on the thermomechanical intermediate configuration introduced by (1), can be written as

$$\tilde{\mathbf{T}}_{\mathrm{eq}} = \rho_{R\theta}\frac{\partial\psi_{\mathrm{eq}}}{\partial\mathbf{E}_M}, \quad \tilde{\mathbf{T}}_{ovk} = \rho_{R\theta}\mathbf{F}_{vk}^{-1}\frac{\partial\psi_{ovk}}{\partial\boldsymbol{\epsilon}_{evk}}\mathbf{F}_{vk}^{\mathrm{T}-1} \quad \text{and} \quad \dot{\mathbf{C}}_{vk} = \frac{4\rho_{R\theta}}{\eta_k(\dots)}\mathbf{F}_{vk}^{\mathrm{T}}\left(\mathbf{C}_{evk}\frac{\partial\psi_{ovk}}{\mathbf{C}_{evk}}\right)\mathbf{F}_{vk}. \tag{8}$$

The potential relation for the specific entropy s has been omitted here. It is specified in an earlier work (cf Lion, 1998). The quantities $\eta_k > 0$ are viscosity functions which may depend on the temperature, the stress or other internal variables. These can be introduced, for example, to describe thixotropic effects depending on the deformation process (cf Lion, 1998). If the material is incompressible with respect to mechanical loads we have $\det(\mathbf{F}_M) = 1$ so that the Cauchy stress tensor $\mathbf{T}$ reads

$$\mathbf{T} = -p\mathbf{1} + \mathbf{T}_{\mathrm{eq}} + \sum_{k=1}^{N}\mathbf{T}_{ovk}, \tag{9}$$

$$\mathbf{T}_{\mathrm{eq}} = \mathbf{F}_M\tilde{\mathbf{T}}_{\mathrm{eq}}\mathbf{F}_M^{\mathrm{T}} \quad \text{and} \quad \mathbf{T}_{ovk} = \mathbf{F}_M\tilde{\mathbf{T}}_{ovk}\mathbf{F}_M^{\mathrm{T}}. \tag{10}$$

The pressure p is not determine constitutively but by the balance of momentum. Well-tested strain energy functions for viscoelastic polymers and elastomers are given by modified Mooney–Rivlin and Neo–Hooke models

$$\psi_{\text{eq}} = \frac{\theta}{\theta_0}(c_1(I_M - 3) + c_2(II_M - 3)), \quad \psi_{ovk} = \frac{\theta}{\theta_0}\mu_k(\hat{\mathbf{C}}_{evk} \cdot \mathbf{1} - 3), \quad \hat{\mathbf{C}}_{evk} = \frac{\mathbf{C}_{evk}}{\det(\mathbf{C}_{evk})^{1/3}}. \tag{11}$$

The variables $I_M = \text{tr}(\mathbf{C}_M)$ and $II_M = 1/2(\text{tr}(\mathbf{C}_M)^2 - \mathbf{C}_M \times \mathbf{C}_M)$ are the invariants of the mechanical Cauchy–Green tensor $\mathbf{C}_M$ and the parameters c_k and μ_k are material constants.

3. Linearised model

In order to determine the material constants of the constitutive model it is expedient to carry out dynamic tests in uniaxial tension, shear or compression. To this end it is common practice to apply a time-independent pre-deformation γ_0 which is superimposed by small sinusoidal oscillations with an angular frequency ω and an amplitude $\Delta\gamma$:

$$\gamma(t) = \gamma_0 + \Delta\gamma \, \sin(\omega t). \tag{12}$$

In this case the mechanical deformation gradient can be written as $\mathbf{F}_M = \mathbf{F}_0(\mathbf{1} + \mathbf{h}(t))$ with $\mathbf{F}_0 = \text{const}$ and $\|\mathbf{h}(t)\| \ll 1$.[1] As a consequence of this assumption the model can be linearised with respect to the incremental displacement gradient $\mathbf{h}$. If we introduce the definition $\mathbf{B}_0 = \mathbf{F}_0\mathbf{F}_0^{\text{T}}$ and the incremental strain tensor $\mathbf{e} = 1/2(\mathbf{h} + \mathbf{h}^{\text{T}})$ we obtain for the Cauchy stress tensor $\mathbf{T}$ the following set of linearised equations (for more details, see Lion, 1998; Horz, 1994):

$$\mathbf{T}_{\text{eq}} = 2\rho_{R\theta}\frac{\theta}{\theta_0}[c_1\mathbf{B}_0 - c_2\mathbf{B}_0^{-1} + c_1[\mathbf{h}\mathbf{B}_0 + \mathbf{B}_0\mathbf{h}^{\text{T}}] + c_2[\mathbf{B}_0^{-1}\mathbf{h} + \mathbf{h}^{\text{T}}\mathbf{B}_0^{-1}]] \tag{13}$$

$$\mathbf{T}_{ovk} = 4\mu_k\rho_{R\theta}(\mathbf{e} - \mathbf{e}_{vk})^{\text{D}}, \quad \dot{\mathbf{e}}_{vk} = \nu_k(\mathbf{e} - \mathbf{e}_{vk})^{\text{D}}, \quad \nu_k = \frac{4\mu_k\rho_{R\theta}}{\eta_k(\ldots)} \tag{14}$$

$$\mathbf{T} = -p\mathbf{1} + \mathbf{T}_{\text{eq}} + \sum_{k=1}^{N}\mathbf{T}_{ovk}, \quad \mathbf{T}_{RM} = \mathbf{T}(\mathbf{1} + \mathbf{h})^{-1} \approx \mathbf{T}(\mathbf{1} - \mathbf{h}). \tag{15}$$

The superscript 'D' denotes the deviatoric part of a tensor, the quantities $\mathbf{e}_{vk}$ are internal variables of strain type, $\mathbf{T}_{RM}$ is a linearised version of the first Piola–Kirchhoff stress tensor, related to the statically pre-deformed configuration. The parameters ν_k are inverse relaxation times or relaxation frequencies. Obviously, this interpretation is only valid in the linearised model.

For the sake of simplicity, we omit the static pre-deformation $\mathbf{F}_0$ in the following considerations, assume that all viscosities η_k are constant, and we apply a harmonic shear deformation $\gamma(t)$. Thus, we have $\gamma(t) = \Delta\gamma \, \sin(\omega t)$, $\mathbf{h}(t) = \gamma(t)\mathbf{e}_x \otimes \mathbf{e}_y$, $\theta = \theta_0$ and $\mathbf{F}_0 = \mathbf{1}$. Since the amplitude $\Delta\gamma$ is small, normal stress effects can be disregarded and the stationary stress response can be written as

$$\mathbf{T}(t) = \tau(t)(\mathbf{e}_x \otimes \mathbf{e}_y + \mathbf{e}_y \otimes \mathbf{e}_x), \tag{16}$$

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[1] $\|\mathbf{h}\| = \sqrt{\mathbf{h} \cdot \mathbf{h}}$.

$$\tau(t) = \Delta\gamma(G'(\omega)\sin(\omega t) + G''(\omega)\cos(\omega t)) \tag{17}$$

and

$$G'(\omega) = 2\rho_{R\theta}(c_1 + c_2) + 2\rho_{R\theta}\sum_{k=1}^{N}\frac{\mu_k\omega^2}{\nu_k^2 + \omega^2}, \quad G''(\omega) = 2\rho_{R\theta}\sum_{k=1}^{N}\frac{\mu_k\omega\nu_k}{\nu_k^2 + \omega^2}. \tag{18}$$

The two frequency-dependent functions G' and G'' are the dynamic shear moduli of the linearised finite strain model. They are similar to the corresponding expressions of linear viscoelastic models with discrete relaxation spectra (see, for example, Tobolsky, 1967). In the following we employ these expressions to determine the material parameters c_1, c_2, μ_k, η_k occurring in the constitutive model and the number N of Maxwell elements. For incremental deformations of filled elastomers, loaded with finite pre-deformations, i.e. $\mathbf{F}_0 \neq \mathbf{1}$, we recommend the interested reader to consult the work of Lion (1998).

In order to illustrate the physical meaning of the constitutive theory we investigate the mechanical behaviour of a polyethylene melt at a temperature level of 473 K and determine the material constants. To this end the dynamic moduli of shear have to be measured. Fig. 1 illustrates given experimental data in a double logarithmic diagram. As we see, the data points of the storage and dissipation moduli can be rather well approximated by straight lines. This behaviour corresponds to a power law. As a consequence the fractional calculus can be successfully applied to describe the data by means of a fairly simple functional relation.

4. Identification of material parameters

The linearised constitutive equations (17) and (18) are analogous to those of linear viscoelasticity with a discrete relaxation spectrum. In view of the experimental data points depicted in Fig. 1, the number N of material parameters μ_k and η_k required to represent them is presumably quite large. Moreover, due to the mathematical structure of the expressions (18) for the dynamic moduli, the problem of the parameter identification is strongly non-linear. However, we can avoid this dilemma: instead of determining the parameters μ_k, η_k by means of a non-linear optimisation algorithm, a simpler procedure is possible. In fact Fig. 1 suggests that only a few parameters (at the most four) is required to fit the experimental data into a good approximation. Therefore, we formulate an additional uniaxial model of linear viscoelasticity, which corresponds to a power law and serves as a substitute model. If we calculate
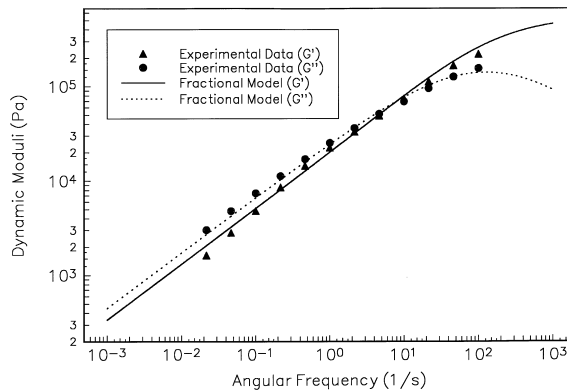

Fig. 1. Dynamic moduli of polyethylene at $\theta = 473$ K.

the dynamic moduli of the substitute model analytically, we are able to compute a continuous relaxation spectrum on the basis of a Stieltjes transformation. In the final step we approximate this continuous spectrum by the discrete spectrum of the linearised finite strain model.

4.1. Substitute model

Appropriate models to describe the power law-type frequency-dependence of the dynamic moduli of polymeric media can be formulated on the basis of the fractional calculus (see, for example, Caputo and Mainardi, 1971; Koeller, 1984; Bagley and Torvik, 1986). As usual, we define the fractional derivative $\mathrm{d}^\alpha f/\mathrm{d}t^\alpha$ of order $0 < \alpha < 1$ by the linear integral operator

$$\frac{\mathrm{d}^\alpha f}{\mathrm{d}t^\alpha} = \frac{1}{\Gamma(1-\alpha)}\int_0^t \frac{f'(s)}{(t-s)^\alpha}\mathrm{d}s, \quad f(0) = 0, \tag{19}$$

where the kernel function is a weakly singular power law and $\Gamma(x)$ the Eulerian Gamma function. A simple way to formulate thermodynamically consistent constitutive laws based on (19) is to define a so-called fractional damping element (see Lion, 1997b). It can be used as an additional rheological element to create more complex models. It assumes proportionality between the fractional derivative $\mathrm{d}^\alpha \epsilon/\mathrm{d}t^\alpha$ of the strain ϵ which acts on it and the corresponding stress σ, i.e. $\mathrm{d}^\alpha \epsilon/\mathrm{d}t^\alpha = \sigma/(E\zeta^\alpha)$. The constants E, ζ and α are non-negative material parameters. In the limit case of $\alpha = 1$ the fractional element corresponds to the linear Newtonian damper and for $\alpha = 0$ to Hookean elasticity.

In particular, the fractional generalisation of the standard linear solid can be obtained by replacing the Newtonian damper by a fractional damping element as sketched in Fig. 2 (cf Schiessel et al., 1995):

$$\tau = \tau_{eq} + \tau_{ov}, \quad \tau_{eq} = C\gamma, \quad \tau_{ov} = E(\gamma - \gamma_{in}), \quad \frac{\mathrm{d}^\alpha \gamma_{in}}{\mathrm{d}t^\alpha} = \frac{1}{E\zeta^\alpha}\tau_{ov} \tag{20}$$

$$\frac{\mathrm{d}^\alpha \tau}{\mathrm{d}t^\alpha} + \frac{1}{\zeta^\alpha}\tau = (E+C)\frac{\mathrm{d}^\alpha \gamma}{\mathrm{d}t^\alpha} + \frac{1}{\zeta^\alpha}C\gamma. \tag{21}$$

In the above equations τ_{eq} is the equilibrium stress, C the corresponding stiffness constant and τ_{ov} the rate-dependent overstress. Computing the fractional derivative of $(20)_3$ and eliminating the variable γ_{in} we obtain the representation in the form of (21).

The storage and dissipation moduli G' and G' belonging to this model are quite easy to work out. For this purpose we apply the integral operator (19) and calculate the fractional derivative of the complex harmonic function $f(t) = \Delta f\, e^{i\omega t}\Theta(t)$

$$\frac{\mathrm{d}^\alpha f}{\mathrm{d}t^\alpha} = \frac{\Delta f}{\Gamma(1-\alpha)t^\alpha} + \frac{i\omega}{\Gamma(1-\alpha)}\int_0^t \frac{e^{-i\omega s}}{s^\alpha}\mathrm{d}s\Delta f\, e^{i\omega t}, \tag{22}$$
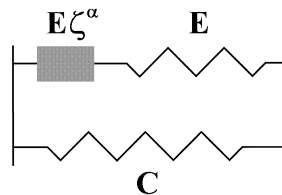
Fig. 2. Model of fractional viscoelasticity.

where $i = \sqrt{-1}$ is the imaginary unit, $\Theta(t) = 0$ if $t \leq 0$ and $\Theta(t) = 1$ if $t > 0$. In the stationary case, i.e. for large values of t, the upper limit of integration in (22) can be replaced by $+\infty$ and the first term vanishes, so that the right-hand-side becomes periodic with respect to time t:

$$\frac{d^\alpha}{dt^\alpha}(\Delta f\, e^{i\omega t}\Theta(t)) = \frac{i\omega}{\Gamma(1-\alpha)}\int_0^\infty \frac{e^{-i\omega s}}{s^\alpha}ds\Delta f\, e^{i\omega t} \implies \frac{d^\alpha}{dt^\alpha}(\Delta f\, e^{i\omega t}\Theta(t)) = (i\omega)^\alpha \Delta f\, e^{i\omega t}. \tag{23}$$

As we see, the fractional derivative of the function $f(t) = \Delta f\, e^{i\omega t}\Theta(t)$ is proportional to $f(t)$ itself in the stationary case. A relation similar to $(23)_2$ holds for the Fourier transformation of the fractional derivative (see Schiessel et al., 1995).

In the following consideration we assume $t > 0$ and stationary conditions, i.e. $\Theta(t) = 1$, $\gamma(t) = \Delta\gamma\, e^{i\omega t}$ and $\tau(t) = \Delta\tau\, e^{i\omega t}$, where $\Delta\tau$ is the complex stress amplitude. Inserting the harmonic deformation $\gamma(t)$ in combination with the stress $\tau(t)$ into (21), while bearing $(23)_2$ in mind and rearranging the terms we obtain the expression

$$\left((i\omega)^\alpha + \frac{1}{\zeta^\alpha}\right)\Delta\tau\, e^{i\omega t} = \left((E+C)(i\omega)^\alpha + \frac{1}{\zeta^\alpha}C\right)\Delta\gamma\, e^{i\omega t} \tag{24a}$$

and finally

$$\Delta\tau = G^*(i\omega)\Delta\gamma, \quad G^* = C + \frac{E(i\omega\zeta)^\alpha}{1 + (i\omega\zeta)^\alpha} \tag{24b}$$

for the stationary stress response. The quantity $G^*(i\omega)$ is the complex dynamic modulus whose real and imaginary parts $G' = \mathrm{Re}(G^*)$ and $G'' = \mathrm{Im}(G^*)$ read as follows:

$$G'(\omega) = C + \frac{E((\omega\zeta)^{2\alpha} + (\omega\zeta)^\alpha\,\cos(\alpha\pi/2))}{1 + (\omega\zeta)^{2\alpha} + 2(\omega\zeta)^\alpha\,\cos(\alpha\pi/2)}, \quad G''(\omega) = \frac{E(\omega\zeta)^\alpha\,\sin(\alpha\pi/2)}{1 + (\omega\zeta)^{2\alpha} + 2(\omega\zeta)^\alpha\,\cos(\alpha\pi/2)}. \tag{25}$$

The four parameters C, E, α and ζ of this model were determined using a Monte Carlo identification technique (Bronstein and Semendjajew, 1997, p. 720 ff.). In order to minimise the quadratic error norm between the test data of $\log(G')$ and $\log(G'')$ and the formulae (25), the parameters C, E, α and ζ were varied statistically in given limits. The final result of fitting the analytical expressions (25) to the experimental data of Fig. 1 is $C = 8$ Pa, $E = 32{,}424$ Pa, $\alpha = 0.586$ and $\zeta = 7.7 \times 10^{-3}$ s. Since the equilibrium modulus C of the fractional model is approximately zero we cannot go far wrong by equating C to zero and concluding $c_1 = c_2 = 0$ [see (18)].

In order to determine the parameters of the finite strain model we have to compute the relaxation spectrum of the fractional model (21). To this end we follow Gross (1968) or Tschoegl (1989) and apply the general relation between the complex modulus G^* of a linear viscoelastic system and its spectrum $h(v)$ as a function of the relaxation frequency $v > 0$. This spectrum is related to the relaxation function $G(t)$ via

$$G(t) = \int_0^\infty h(v)e^{-vt}\,dv. \tag{26}$$

Inserting the harmonic deformation process $\gamma(t) = \Delta\gamma\, e^{i\omega t}$ into the linear functional relation

$$\tau(t) = \int_{-\infty}^t G(t-s)\gamma'(s)ds, \tag{27}$$

between stress and strain, taking (26) into consideration and altering the sequence of integration, we

arrive at the formula we are looking for

$$\frac{G^*(i\omega)}{i\omega} = \int_0^\infty \frac{h(\nu)}{\nu + i\omega} d\nu. \tag{28}$$

As we see, the function $G^*(i\omega)/i\omega$ is the Stieltjes transformation of the relaxation spectrum $h(\nu)$. Following Gross (1968) or Tschoegl (1989) the inverse of the Stieltjes transformation of (28) can be worked out using quite a simple limit transition. It reads as

$$h(\nu) = \frac{1}{2\pi i} \lim_{\epsilon \to 0} \left(\frac{G^*(-\nu - i\epsilon)}{-\nu - i\epsilon} - \frac{G^*(-\nu + i\epsilon)}{-\nu + i\epsilon} \right), \tag{29}$$

where $\nu > 0$ and $\epsilon > 0$ is stipulated. In the context of our present task it is appropriate to express the complex arguments $-\nu \pm i\epsilon$ of (29) in the form of the complex exponential function

$$-\nu \pm i\epsilon = \sqrt{\epsilon^2 + \nu^2}\ e^{\pm i(\pi - \arctan(\epsilon/\nu))}, \tag{30}$$

and to carry out the limit transition $\epsilon \to 0$. As an intermediate result we obtain the general formula

$$h(\nu) = \frac{1}{2\pi i} \left(\frac{G^*(\nu\ e^{-i\pi})}{\nu\ e^{-i\pi}} - \frac{G^*(\nu\ e^{+i\pi})}{\nu\ e^{+i\pi}} \right), \tag{31}$$

which can be utilised to compute the relaxation spectrum if the dynamic modulus is known. Taking the modulus $(24b)_2$ into account and bearing $C = 0$ in mind, the relaxation spectrum of the fractional model (21) reads as

$$h(\nu) = \frac{E(\nu\zeta)^\alpha\ \sin(\alpha\pi)}{\pi\nu(1 + (\nu\zeta)^{2\alpha} + 2(\nu\zeta)^\alpha\ \cos(\alpha\pi))}. \tag{32}$$

Due to $h(\nu) > 0$ the fractional model is compatible with the second law of thermodynamics as well (see, for example, Beris and Edwards, 1993; Lion, 1997b).

In order to determine the material constants of the linearised finite strain model we are looking for, we apply an extremely effective method which was devised by Backhaus (1997). To this end we define the so-called cumulative relaxation spectrum

$$H(\nu) = \int_0^\nu h(z) dz, \tag{33}$$

which possesses the advantageous characteristic of being a monotonic function of its argument ν. Due to the simple mathematical form of (32) the integration can be carried out analytically:

$$H(\nu) = \frac{E}{\alpha\pi} \left(\arctan\left(\frac{(\nu\zeta)^\alpha + \cos(\alpha\pi)}{\sin(\alpha\pi)} \right) - \pi\left(\frac{1}{2} - \alpha \right) \right). \tag{34}$$

If the relaxation spectrum $h(\nu)$ has a more complex mathematical form, the integration can be carried out using a numerical method.

4.2. Approximation of the cumulative relaxation spectrum

The technique we use to determine the real material constants μ_k and ζ_k of the constitutive model (13)–(15) consists of approximating the cumulative spectrum $H(\nu)$ of the substitute model by the

cumulative spectrum $H_{\text{lin}}(v)$ of the uniaxial version (17) and (18) of the linearised model. In order to explain the general method we integrate (28) by parts and express the complex modulus $G^*(i\omega)$ as a linear functional of the cumulative spectrum H:

$$G^*(i\omega) = \int_0^\infty h(v) \frac{i\omega}{v + i\omega} \mathrm{d}v = \left(\frac{H(v)i\omega}{v + i\omega} \right)_0^\infty + \int_0^\infty H(v) \frac{i\omega}{(v + i\omega)^2} \mathrm{d}v = \int_0^\infty H(v) \frac{i\omega}{(v + i\omega)^2} \mathrm{d}v. \tag{35}$$

The relaxation spectrum, which can be attributed to the linearised finite strain model (17) and (18), is given by a series of Diracean Delta functions. Therefore, the corresponding cumulative spectrum $H_{\text{lin}}(v)$, calculated on the basis of (33) is given by a series of step functions:

$$H_{\text{lin}}(v) = 2\rho_{R\theta} \sum_{k=1}^{N} \mu_k \langle v - v_k \rangle \tag{36}$$

with

$$\langle x \rangle = 0 \quad \text{if } x < 0 \quad \text{and} \quad \langle x \rangle = 1 \quad \text{if } x \geq 0. \tag{37}$$

The problem now is to determine the constants μ_k and v_k as well as the number N of elements, so that the function $H(v)$ of the substitute model (34) is represented by $H_{\text{lin}}(v)$ in a given domain of relaxation frequencies $v_{\min} \leq v \leq v_{\max}$. In order to simplify the approximation procedure we prescribe the numerical values of constants v_k and take the following power law distribution:

$$v_k = v_{\min} \left(\frac{v_{\max}}{v_{\min}} \right)^{(k-1)/(N-1)}. \tag{38}$$

To specify the numerical values of $v_{\min}$, $v_{\max}$, N and the parameters μ_k we proceed as follows: due to (36) the function $H_{\text{lin}}(v)$ vanishes for $0 \leq v \leq v_{\min}$ and is constant for $v_{\max} \leq v$. In the intermediate regions we define the value of $H_{\text{lin}}(v)$ as the mean value $1/2(H(v_i) + H(v_{i+1}))$ with $v_i \leq v \leq v_{i+1}$:

$$0 \leq v < v_1: \quad H_{\text{lin}}(v) = 0 \tag{39a}$$

$$v_1 \leq v < v_2: \quad H_{\text{lin}}(v) = 2\rho_{R\theta}\mu_1 := \tfrac{1}{2}(H(v_1) + H(v_2)) \tag{39b}$$

$$v_i \leq v < v_{i+1}: \quad H_{\text{lin}}(v) = 2\rho_{R\theta} \sum_{k=1}^{i} \mu_k := \frac{1}{2}(H(v_i) + H(v_{i+1})) \tag{39c}$$

$$v_N \leq v: \quad H_{\text{lin}}(v) = 2\rho_{R\theta} \sum_{k=1}^{N} \mu_k := \frac{1}{2}(H(v_N) + H(v_{N+1})). \tag{39d}$$

As a consequence, it is easy to calculate the numerical values of the stiffness parameters μ_k and viscosities η_k:

$$\mu_1 = \frac{H(v_1) + H(v_2)}{4\rho_{R\theta}} \quad \text{if } k = 1 \quad \text{and} \quad \mu_k = \frac{H(v_{k+1}) - H(v_{k-1})}{4\rho_{R\theta}} \quad \text{if } k > 1, \quad \eta_k = \frac{4\mu_k\rho_{R\theta}}{v_k}. \tag{40}$$

In order to represent the dynamic behaviour of the material in the frequency domain $\omega_{\min} \leq \omega \leq \omega_{\max}$

we have to estimate the lower and upper limits $v_{\min}$ and $v_{\max}$ of relaxation frequencies as well as the number N of Maxwell elements.

To this end we estimate the error Φ between the complex moduli G^* and $G^*_{\lin}$ of the substitute model and the linearised finite strain model:

$$\Phi = \mid G^*(i\omega) - G^*_{\lin}(i\omega) \mid = \left| \int_0^\infty (H(v) - H_{\lin}(v))\frac{i\omega}{(v+i\omega)^2} dv \right|. \tag{41}$$

By splitting the integral domain into three parts and applying the triangle inequality we arrive at

$$\Phi \leq \left| \int_0^{v_{\min}} \frac{(H(v) - H_{\lin}(v))i\omega}{(v+i\omega)^2} dv \right| + \left| \int_{v_{\min}}^{v_{\max}} \frac{(H(v) - H_{\lin}(v))i\omega}{(v+i\omega)^2} dv \right| + \left| \int_{v_{\max}}^\infty \frac{(H(v) - H_{\lin}(v))i\omega}{(v+i\omega)^2} dv \right|$$
$$:= \Phi_1 + \Phi_2 + \Phi_3. \tag{42}$$

Since $|i\omega/(v+i\omega)^2| = \omega/(v^2+\omega^2)$ is valid and the cumulative spectrum $H_{\lin}(v)$ of the linearised finite strain model vanishes in the first domain, the term Φ_1 can be estimated:

$$\Phi_1 \leq \int_0^{v_{\min}} \frac{H(v)\omega}{v^2+\omega^2} dv \leq H(v_{\min})\arctan(v_{\min}/\omega_{\min}). \tag{43}$$

As we see, the contribution Φ_1 can be made arbitrarily small if the bottom limit $v_{\min}$ of the relaxation frequency domain is chosen so that the inequality $v_{\min} \ll \omega_{\min}$ is satisfied. In the third domain of integration we have $|H(v)-H_{\lin}(v)| \leq H(\infty)$ and obtain

$$\Phi_3 \leq \int_{v_{\max}}^\infty \frac{\mid H(v) - H_{\lin}(v) \mid \omega}{v^2+\omega^2} dv \leq H(\infty)(1 - \arctan(v_{\max}/\omega_{\max})), \tag{44}$$

which tends to zero in the case of $v_{\max} \gg \omega_{\max}$. In order to evaluate Φ_2 let us consider the estimation $\omega/(v^2+\omega^2) \leq 1/\omega$ and split the integral domain between the limits between $v_{\min}$ and $v_{\max}$ into $N-1$ parts. In addition, we take the estimation $|H(v)-H_{\lin}(v)| \leq H(v_{k+1})-H(v_k) \leq M(v_{k+1}-v_k)$ into account where M is the maximum of the derivative $H'(v)$ in the relaxation frequency domain $v_{\min} \leq v \leq v_{\max}$:

$$\Phi_2 \leq \frac{1}{\omega} \int_{v_{\min}}^{v_{\max}} \mid H(v) - H_{\lin}(v) \mid dv \leq \frac{1}{\omega} \sum_{k=1}^{N-1} \int_{v_k}^{v_{k+1}} \mid H(v) - H_{\lin}(v) \mid dv \leq \frac{M}{\omega} \sum_{k=1}^{N-1} (v_{k+1} - v_k)^2. \tag{45}$$

On the basis of the power law distribution (38) we can find out the differences between adjacent relaxation frequencies

$$v_{k+1} - v_k = v_{\min}(\eta - 1)\eta^{k-1} \quad \text{with } \eta = \left(\frac{v_{\max}}{v_{\min}}\right)^{1/(N-1)}, \tag{46}$$

insert them into (45), evaluate the geometric series, consider the estimation $(\eta+1) \geq 2$ and obtain

$$\frac{\omega}{Mv_{\min}^2}\Phi_2 \leq (\eta - 1)^2 \sum_{k=1}^{N-1} \eta^{2(k-1)} = (\eta - 1)^2 \frac{\eta^{2N}-1}{\eta^2-1} \leq \frac{\eta-1}{\eta+1}(\eta^{2N}-1) \leq \frac{1}{2}(\eta-1)(\eta^{2N}-1). \tag{47}$$

Since the term $\eta^{2N}-1$ has the top limit $(v_{\max}/v_{\min})^4$ we find the final result

$$\Phi_2 \leq \frac{M v_{\min}^2}{2\omega_{\min}} \left(\frac{v_{\max}}{v_{\min}}\right)^4 \left(\left(\frac{v_{\max}}{v_{\min}}\right)^{1/(N-1)} - 1\right) = O\left(\frac{1}{N}\right) \tag{48}$$

which tends asymptotically to zero as $O(1/N)$, i.e. $\Phi_2 \leq K/N$ for sufficiently large values of N. The most important outcome of this investigation are the following conditions for the bottom and top limits $v_{\min}$ and $v_{\max}$ of the relaxation frequency range and the number N of elements:

Smallest relaxation frequency: $v_{\min} \ll \omega_{\min}$ $\tag{49a}$

Largest relaxation frequency: $v_{\max} \gg \omega_{\max}$ $\tag{49b}$

Number of elements : $N \gg 1 + \dfrac{\log(v_{\max}) - \log(v_{\min})}{\log 2}.$ $\tag{49c}$

Fig. 3 illustrates the approximation of the cumulative spectrum $H(v)$ of the substitute model with the step function series $H_{\mathrm{lin}}(v)$ specified in (36) and $N = 10$ elements. The lower and upper limits are given by $v_{\min} = 10^{-3}$ s^{-1} and $v_{\max} = 10^3$ s^{-1} so that the conditions (49a,b) are practically satisfied. The numerical values of the stiffness parameters are calculated on the basis of (40). They correspond to the height of the steps at the locations of the relaxation frequencies v_k. The viscosities η_k can be calculated using (14) and (38).

In order to discuss the accuracy of the dynamic moduli represented let us look at Fig. 4 for comparison, where the test data as well as two different approximations with $N = 4$ and $N = 10$ elements are shown. If the number of elements is to small, we observe pronounced oscillations in the dissipation modulus G'', a stepped shape of the storage modulus G', and the quality of data approximation is quite poor. If the number of elements is sufficiently large, the data approximation is fairly accurate and the oscillations vanish.

In addition to this, we ought to analyse the quality of approximation of the fractional substitute model using the linearised finite strain model. The dynamic moduli of the substitute model are shown in Fig. 1 as continuous and dotted curves and the moduli belonging to $N = 10$ elements of the finite strain model as continuous lines in Fig. 4. If we compare the plots, we see that the discrete approximation is only satisfactory if the condition $v_{\min} < \omega < v_{\max}$ is satisfied. It definitely deteriorates outside the specified frequency range.
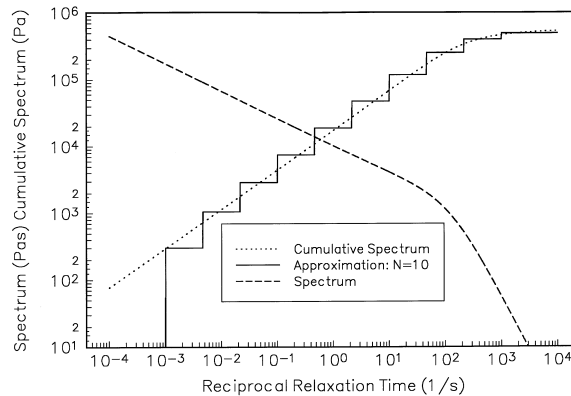

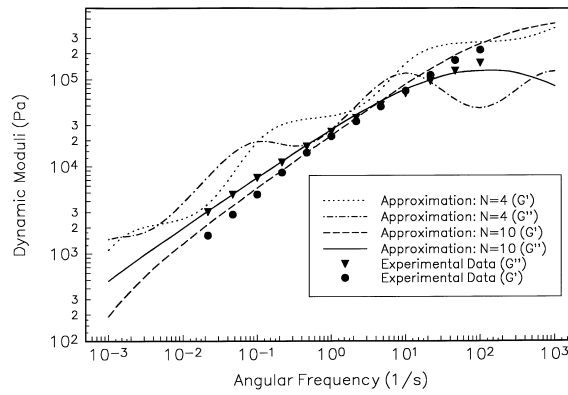Fig. 3. Spectrum and cumulative spectrum.

Fig. 4. Approximations with $N = 10$ and $N = 4$.

On the basis of the identified parameters μ_k and η_k for $N = 4$ and $N = 10$ elements, we may calculate the stress response in tension of the finite deformation model belonging to monotonic strain controlled processes.

The rate $\dot{\epsilon} = \dot{l}/l_0$ of the engineering strain is constant and varies in five steps between 10^{-2} s^{-1} and 10^2 s^{-1}. The curves of the engineering stress are plotted in Figs. 5 and 6. Due to the constant rate of the engineering strain we observe a non-monotonic behaviour, i.e. a decrease in the engineering stress for large deformations. It can be shown, however, that this is not the case if the logarithmic strain rate $\dot{l}/l(t)$ is held constant and the model response of the Cauchy stress is calculated. If we compare the numerical simulations with $N = 4$ and $N = 10$ elements we see that the curvature of the stress response depends significantly on the number of non-linear Maxwell elements introduced to approximate the continuous relaxation spectrum. An explanation for the behaviour illustrated here is to be found in the widely spaced-out relaxation frequencies, i.e. the ratio between them and the duration of the loading process.

The comparison between these predictions and experimental data under large deformations is not provided in this work because no test data is available. In addition the validation of the finite strain model under two- and three-dimensional states of stress and strain is an interesting research project which should be investigated in the future.
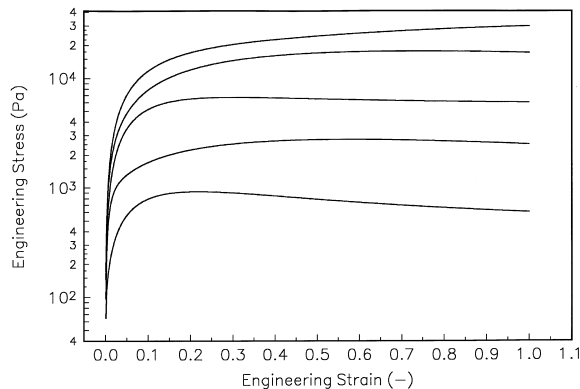

Fig. 5. Simulation of tension tests, $N = 4$.

5. Closure

In this paper we applied a physically based constitutive theory of finite viscoelasticity to describe the dynamic behaviour of polymers in combination with a fairly simple identification technique. It is a well-known fact that the long-term and short-term properties of polymers under small strains can be adequately described by the models of linear viscoelasticity with continuous relaxation spectra. The reason for this is that the characteristic time constants of the relaxation mechanisms of many polymers are very close together. In these cases there is no risk involved in replacing the discrete relaxation time distribution by a continuous one.

When representing the material properties by means of a discrete spectrum we have to incorporate a very large number of material parameters, and the identification process becomes quite complicated. The above investigation suggests that the number of parameters can be considerably reduced, if a substitute model of the fractional type is applied. In our opinion other models of linear viscoelasticity can also be utilised as substitute models. The only requirement is the analytical calculability of the inverse Stieltjes transformation.

From the point of view of continuum thermomechanics it is easy to extend the concept of discrete spectra to include the case of finite thermomechanical deformations. As we know, each discrete Maxwell element corresponds, in the case of small deformations, to an additive decomposition of the strain into an elastic and viscous part. Thus, we have to introduce a set of N multiplicative decompositions of the deformation gradient, likewise split into elastic and viscous parts, and obtain a set of N intermediate configurations in parallel. Since the constitutive laws of the non-linear Maxwell elements are formulated taking thermodynamical aspects into consideration and applying the concept of dual variables, the compatibility with the second law of thermodynamics is satisfied.

Due to the discrete structure of the finite strain theory and the impossibility of expressing the current values of the internal variables as linear functionals of the deformation history, it would seem to be impracticable to extend the concept of continuous spectra to finite strains without loosing the thermodynamical consistency. For this reason we have chosen a well-established mathematical method and an identification technique to approximate a given continuous spectrum by the discrete spectrum of the finite strain model. The idea of this technique is taken from the theory of linear viscoelasticity and is based on the relation between the relaxation spectrum and the complex modulus, i.e. on the inverse Stieltjes transformation.
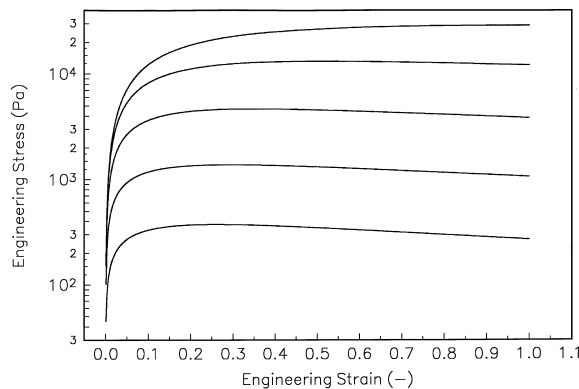

Fig. 6. Simulation of tension tests, $N = 10$.

Acknowledgements

References

Akyildiz, F., Jones, R.S., Walters, K., 1990. On the spring-dashpot representation of linear viscoelastic behaviour. Rheol. Acta 29, 482–484.

Backhaus, E., 1997. Progress report on the project DFG-Ha 2075/1. University of Dresden, Institute of Solid Mechanics.

Bagley, R.L., Torvik, P.J., 1986. On the fractional calculus model of viscoelastic behaviour. J. Rheol. 30, 133–155.

Beris, A.N., Edwards, B.J., 1993. On the admissibility criteria for linear viscoelasticity kernels. Rheol. Acta 32, 505–510.

Bronstein, I.N., Semendjajew, K.A., 1997. Taschenbuch der Mathematik. Verlag Harri Duetsch.

Caputo, M., Mainardi, F., 1971. Linear Models of Dissipation in Anelastic Solids. Rivista del Nuovo Cimento, pp. 1,161–1,198.

Ferry, J.D., 1980. Viscoelastic Properties of Polymers. John Wiley and Sons.

Findley, W.N., Lai, J.S., Onaran, K., 1976. Creep and Relaxation of Nonlinear Viscoelastic Materials with an Introduction to Linear Viscoelasticity. North Holland, Amsterdam, New York, Oxford.

Gross, B., 1968. Mathematical Structure of the Theories of Linear Viscoelasticity. Hermann, Paris.

Haupt, P., Tsakmakis, C., 1989. On the application of dual variable in continuum mechanics. Continuum Mech. Thermodyn. 1, 165–196.

Haupt, P., 1992. Thermodynamics of Solids. Non-Equilibrium Thermodynamics with Application to Solids. Springer CISM-Kurs in Udine (Italy).

Haupt, P., 1993. On the mathematical modelling of material behaviour in continuum mechanics. Acta Mechanica 100, 129–154.

Horz, M., 1994. Linear-elastische Wellen in vordeformierten Medien. Dr.-Ing. thesis, University of Kassel, Germany, Report No. 2/1994.

Koeller, R.C., 1984. Applications of fractional calculus to the theory of viscoelasticity. J. Appl. Mech. 51, 299–307.

Lion, A., 1997a. On the large deformation behaviour of reinforced rubber at different temperatures. J. Mech. Phys. Solids 45, 1805–1834.

Lion, A., 1997b. On the thermodynamics of fractional damping elements. Continuum Mech. Thermodyn. 9, 83–96.

Lion, A., 1998. Thixotropic behaviour of rubber under dynamic loading histories: experiments and theory. J. Mech. Phys. Solids 46, 895–930.

Lu, S.C.H., Pister, K.D., 1975. Decomposition of deformation and representation of the free energy function for isotropic thermoelastic solids. Int. J. Solids Struct. 11, 927–934.

Lubliner, J., 1985. A model for rubber viscoelasticity. Mech. Res. Com. 12, 93–99.

Schiessel, H., Metzler, R., Blumen, A., Nonnenmacher, T.F., 1995. Generalised viscoelastic models: their fractional equations with solutions. J. Phys. A: Math. Gen. 28, 6567–6584.

Tobolsky, A., 1967. Mechanische Eigenschaften von Polymeren. Berliner Union.

Tschoegl, N.W., 1989. The Phenomenological Theory of Linear Viscoelastic Material Behaviour. Springer Verlag.