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Fractional Calculus Description of Non-Linear Viscoelastic Behaviour of Polymers

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Abstract. In recent decades, constitutive equations for polymers involving fractional calculus have been the object of ever increasing interest, due to their special suitability for describing self-similarity and memory effects, which are typical of viscoelastic behaviour in polymers. Thermodynamic validity of these equations can be ensured by obtaining them from analog models containing spring-pots with positive front factors. Failure of self-similarity in real polymers at short (local) and long (whole chain) scales has been addressed previously. In the past, interest in fractional differential descriptions of polymer viscoelasticity has been mainly concerned with linear viscoelasticity, despite the fact that in processing and end use conditions are largely in the non-linear range. In this paper, extension of fractional calculus models to the non-linear range of viscoelasticity is attempted, by accounting for stress activation of deformation and strain acceleration of annealing. Calculated stress-strain curves are compared with experimental results on an amorphous polymer (polycarbonate). The model adequately describes the general trends of yield and post-yield behaviour, but does not properly describe the gentle approach to yield observed experimentally.

Key words: analog model, fractional calculus, non-linear viscoelasticity, plasticity, spring-pot

1. Introduction

Descriptions of polymer viscoelasticity involving fractional differential formulations have been developed for at least the past half century [1–5] (see the historical survey of Oldham and Spanier [1] for early work, and Friedrich et al. [2] for more recent developments [2]). Interest in such formulations, and also concern over their soundness and applicability, has been steadily increasing in recent years. The simplest fractional differential equation linking stress and strain is:

$$\sigma = K\frac{d^{\beta}}{dt^{\beta}}\varepsilon \quad \text{or} \quad \varepsilon = \frac{1}{K}\frac{d^{-\beta}}{dt^{-\beta}}\sigma \tag{1}$$

This equation describes linear elastic behaviour (Hookean spring) for $\beta = 0$ and Newtonian viscosity (dashpot) for $\beta = 1$. For intermediate values of the exponent, it describes viscoelastic behaviour. The corresponding analog element was called a “spring-pot” by Koeller [6]. K can also be expressed in the form $E\tau^{\beta}$, where E is an elastic modulus and τ is a characteristic time. This form is useful when spring-pots are associated with elastic elements.

The spring-pot is particularly well suited to a description of polymer viscoelasticity, as can be understood by examination of Grünwald’s definition of a fractional derivative of order β applied to the interval [0,*t*] [1, p. 48]:

$$\frac{d^{\beta}f}{dt^{\beta}} = \lim_{N\to\infty}\left\{\frac{(t/N)^{-\beta}}{\Gamma(-\beta)}\sum_{j=0}^{N-1}\frac{\Gamma(j-\beta)}{\Gamma(j+1)}f(t-jt/N)\right\} \tag{2}$$

This expression illustrates several features of fractional derivatives. First, to obtain the present value of the derivative, the entire history of the function f is required, indicating that fractional derivatives are particularly well adapted to description of materials with memory. (This is true also of integrals of real order; integer order derivatives, which are local, are the exception rather than the rule.) Second, the factor $\Gamma(j-\beta)/\Gamma(j+1)$ decreases with increasing j like $j^{-(1+\beta)}$ indicating fading memory if $\beta > -1$. Third, a spring-pot displays non-exponential relaxation and creep; the solutions to Equation (1) for constant strain ε_0 or constant stress σ_0 are

$$\sigma = \frac{K\varepsilon_0}{\Gamma(2-\beta)}t^{-\beta} \quad \text{and} \quad \varepsilon = \frac{\sigma_0}{K\Gamma(2+\beta)}t^{\beta} \tag{3}$$

This illustrates that a spring-pot can describe non-exponential relaxation without the need for a distribution of relaxation times and with a very low number of parameters. Clearly, a spring-pot on its own displays some rather unphysical behaviour. In particular, it is non-standard, has an infinite instantaneous modulus, and has a constant phase lag $\beta\pi/2$ independent of frequency. (The latter can be observed from the complex modulus of the spring-pot, which is $K(i\omega)^\beta = K\omega^\beta(\cos(\beta\pi/2) + i\sin(\beta\pi/2))$). To describe real viscoelastic behaviour, a spring-pot must be associated with at least one elastic element, in other words a fractional derivative term must be associated with at least one elastic term. In common practice, this is carried out by starting from a phenomenologically acceptable description, and replacing the ordinary derivatives by fractional derivatives. For example, generalization of the single mode Maxwell model,

$$\sigma + \tau\frac{d\sigma}{dt} = \tau E\frac{d\varepsilon}{dt} \tag{4}$$

leads to

$$\sigma + \tau^\alpha\frac{d^\alpha\sigma}{(dt)^\alpha} = E\tau^\beta\frac{d^\beta\varepsilon}{(dt)^\beta} \tag{5}$$

and generalization of the standard solid model (SMM) or Zener model which can be written

$$\sigma + \tau_\mathrm{E}\frac{d\sigma}{dt} = E\left(\varepsilon + \tau_\mathrm{D}\frac{d\varepsilon}{dt}\right) \tag{6}$$

leads to

$$\sigma + \tau_\mathrm{E}^\alpha\frac{d^\alpha\sigma}{(dt)^\alpha} = E\left(\varepsilon + {\tau_\mathrm{D}}^\beta\frac{d^\beta\varepsilon}{(dt)^\beta}\right) \tag{7}$$

where α and β are frequently assumed to be different [7–10]. Generalization is sometimes carried out using a fractional integral formulation [11] under the claim that this avoids problems with divergent initial conditions. It should be pointed out that once the fractional behaviour is incorporated into a standard model, divergence at short times or high frequencies is eliminated.

There has been some concern and also some confusion in recent years over thermodynamic validity of constitutive equations based on fractional derivatives, and also over stability of such formulations. Friedrich [7] noted that Equation (5) is thermodynamically valid for $\beta \geq \alpha$, and Glöckle and Nonnenmacher [11] noted that the fractional SMM, Equation (7) is thermodynamically valid only for $\alpha = \beta$, and that when $\beta > \alpha$ the thermodynamic condition $E'' > 0$ is respected only below some limiting frequency. The fractional SMM equation was obtained mathematically by Enelund and Lesieutre [12], obtaining $\alpha = \beta$. The same result was obtained by Heymans [13] and by Haupt et al. [14], by replacing the dashpot by a spring-pot in the classical Zener model. Rossikhin and Shitikova [15] modelled damped vibrations using a fractional Maxwell model rather than a fractional SMM, in order to be able to introduce two independent exponents while complying with the requirements of thermodynamic compatibility.

However, the question of admissible combinations of terms with different exponents remained open until proof was given by Beris and Edwards [16] that thermodynamically admissible constitutive equations are completely equivalent to analog models with all positive coefficients. This means that a fractional differential or integral constitutive equation is not thermodynamically valid unless it describes some combination of springs, dashpots and spring-pots. It was pointed out by Heymans [13] that the fractional Maxwell model with $\alpha < \beta$ describes the series association of two spring-pots and is therefore non-standard, and that the generalization of the SMM including two spring-pots with different exponents β_1 and β_2 leads to a constitutive equation containing fractional derivatives not of two but of three orders β_1, β_2 and $\beta_1 - \beta_2$, and therefore Equation (7) containing two different exponents cannot describe thermodynamically valid behaviour.

The question of stability of constitutive equations containing fractional derivatives was raised by Palade et al. [17], who showed that relaxation of an initial perturbation cannot be expressed in terms of a combination of exponential relaxations, questioning the usefulness of fractional calculus constitutive equations. However, this arises because of the self-similarity underlying fractional derivative descriptions, which breaks down on the scale of whole polymer chains. An appropriate treatment of this breakdown and the corresponding transition to pure flow has been given recently by Heymans [18].

All work recalled above applies to linear viscoelasticity, in the sense that all coefficients in the constitutive equations are independent of frequency, stress or strain. Few examples exist in the literature incorporating both fractional calculus and non-linearity [19, 20]. In the present work, existing models are generalized to account explicitly for effects such as strain softening, stress activation and stress-accelerated ageing.

2. Model

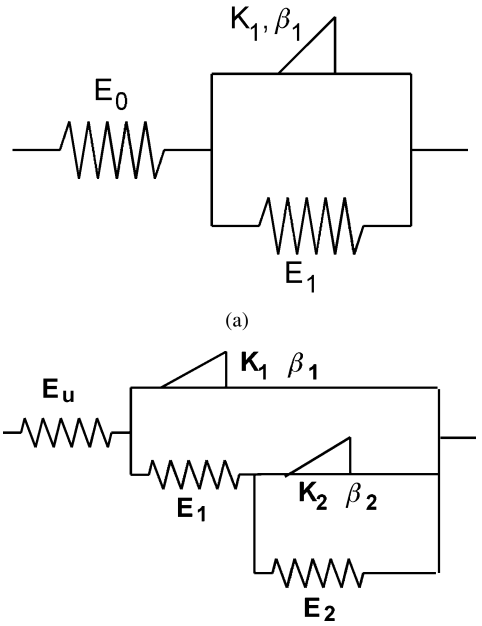
2.1. THE SPRING-POT AND MODELS FOR LINEAR VISCOELASTICITY

The fundamental building block that is used in this work is the spring-pot, whose complex modulus is

$$E^* = K(\mathrm{i}\omega)^\beta \tag{8}$$

with a corresponding constitutive equation given either by the fractional derivative or fractional integral form of Equation (1). Strictly speaking, these two forms are not mathematically equivalent for general initial conditions; however we shall assume here that all calculations are initiated from a state of rest in which case the fractional derivative and integral forms are equivalent [1]. Although spring-pots have been obtained from hierarchical arrangements of springs and dashpots, either exactly [21] or as a long time or low frequency approximation [22, 23], they will be treated here as viscoelastic elements in their own right. (Note that the tree model proposed by Heymans and Bauwens [21] is misrepresented in [5]).

To describe a viscoelastic transition such as the glass transition, a finite elastic modulus is required, both above and below the transition. The simplest model capable of describing this behaviour is the



(a)

(b)

Figure 1. (a) Modified Zener model including spring-pot. (b) Hierarchical nested model describing two viscoelastic transitions.

Zener model, or SSM, Figure 1a, in which the viscous element is replaced by a spring-pot [13]. Schiessel et al. have investigated the Zener model in which all three elements are replaced by spring-pots [24]. The advantage of this model is that it allows representation of the slight frequency (or time or temperature) dependence of the glassy and rubbery modulus. The drawback is that the model is no longer standard. In fact, close examination of experimental data will usually show that frequency dependence of the glassy storage modulus is an indicator of the proximity of a secondary transition. Multiple viscoelastic transitions have previously been modelled satisfactorily by introducing an extra spring and spring-pot for each transition, in a nested arrangement shown on Figure 1b, which ensures hierarchy [13, 18]. Such models lend themselves particularly well to analysis of dynamic (DMTA) measurements, and it is well known that in simple cases such as constant stress (creep) or constant strain (stress relaxation) the time-domain response can be obtained analytically in terms of a function of the Mittag–Leffler or Fox function family [2, 7, 11, 25]. However, for more general loading programs or in the presence of non-linear viscoelasticity, a numerical solution is required.

2.2. SOURCES AND TREATMENT OF NON-LINEARITY

Several sources of non-linear viscoelastic behaviour can arise. In previous work, stress activation of the deformation process has been taken into account to explain stress relaxation after strain reversal at high strains [20]. The effect of ageing, both prior to testing and also strain-accelerated ageing during creep, has been taken into account by allowing for a time-dependent characteristic time [19]. Other effects which are liable to cause deviations from linear behaviour include strain softening, annealing and non-linear rubbery elasticity. To treat stress activation, strain softening and annealing, it is appropriate to express the front factor K of the fractional element in the form $E\tau^{\beta}$, where E is the modulus of one or a combination of springs in the model. In this work based on the Zener model of Figure 1a, E is taken equal to the instantaneous modulus E_0.

2.2.1. *Strain Softening*

Strain softening, which has also been called "rejuvenation", can be expressed via a strain dependent characteristic time. However, because it has been shown previously that effects of strain softening and annealing on yield behaviour of polymers can both be expressed by means of the concept of structural temperature, the same will be carried out here. The structural temperature is a useful concept when describing properties of non-equilibrium materials such as organic or inorganic glasses, and is defined as the temperature at which the free energy or free volume of the actual material would be equivalent to that of a material at equilibrium. Thus, immediately after cooling a sample from above the glass transition range to a temperature far below it, the structural temperature is equal to the glass transition temperature T_g because the free energy and specific volume are equivalent to those of the equilibrium material at T_g. Annealing slightly below T_g produces enthalpy relaxation and volume contraction, resulting in a decrease in θ. The zero stress characteristic time is hence expressed as

$$\tau_\theta = \tau_0 \exp(-k_\theta(\theta - \theta_0)) \tag{9}$$

where τ_0 is the characteristic time at the reference structural temperature θ_0. No particular significance is given to the linear form of the argument of the exponential in Equation (10). It simply expresses that in a sufficiently limited range any expression may be linearized.

An increase in structural temperature can be produced by anelastic or plastic deformation. This effect is assumed to be instantaneous, and is also assumed as a first approximation to be proportional to the anelastic component of strain. This contribution to the increment in structural temperature can be expressed as:

$$d_\varepsilon \theta = k_\varepsilon d\varepsilon_r \tag{10}$$

where ε_r is the retarded deformation, i.e. the anelastic or plastic component and k_ε is a constant. (In common practice, anelastic deformation is defined as deformation, which can recover after unloading, on a time scale comparable to the time under load whereas plastic deformation cannot. Although there is some debate as to whether a single deformation process or two distinct processes are involved, in this work no difference is made between the two.) The structural temperature is also explicitly time-dependent: it relaxes towards the test temperature T, at a rate which depends both on the test temperature and the state of the sample, i.e. on the structural temperature θ itself. This is expressed here through a first-order annealing equation:

$$d_{\mathrm{a}}\theta = (T - \theta)\frac{dt}{\tau_\theta} \tag{11}$$

where subscript a stands for 'annealing'. This form of annealing equation has been used successfully to describe both isothermal annealing and change of structural temperature during a temperature sweep. In this paper, it is assumed that the temperature of the test piece remains constant at room temperature (23 °C).

The two contributions to the change in structural temperature are assumed to be independent, thus the increment during a time step is $d\theta = d_{\mathrm{a}}\theta + d_\varepsilon\theta$.

2.2.2. *Stress Activation*

Stress activation can be accounted for by introducing a stress-dependent characteristic time for the deformation process, e.g. using an Eyring-type equation which can be expressed as:

$$\tau = \tau_\theta \frac{\sigma/\sigma_0}{\sinh(\sigma/\sigma_0)} \tag{12}$$

where σ_0 is a stress sensitivity parameter depending on activation volume and test temperature, and τ_θ is the zero stress characteristic time, which may depend on the structural temperature θ. Use of a different time constant for deformation than for the change in structural temperature reflects the fact that deformation is regarded as a stress-activated flow process whereas enthalpy and volume relaxation are not stress-activated.

2.2.3. *Non-Linear Elasticity*

A final source of non-linearity which is likely to appear at high draw ratios is non-linear elasticity. As discussion here will be restricted to uniaxial extension, the appropriate form of the inverse Langevin expression for the entropic retractive stress is

$$\sigma = \frac{E_1\,\lambda_{\mathrm{M}}}{9}\left\{\mathcal{L}^{-1}\left(\frac{\lambda}{\lambda_{\mathrm{M}}}\right) - \frac{1}{\lambda^{3/2}}\mathcal{L}^{-1}\left(\frac{1}{\lambda_{\mathrm{M}}\lambda^{1/2}}\right)\right\} \tag{13}$$

where E_1 is the low-strain modulus, λ is the draw ratio of the "spring" (i.e. L/L_0, where L is current length and L_0 is initial length), $\mathcal{L}^{-1}$ is the inverse Langevin function and λ_M is the maximum allowable network draw ratio.

2.2.4. *Incorporation of Non-Linearities*

Except for this last source of non-linearity, all other effects lead to a dependence of the characteristic time of the process on stress state and history. How should this be properly accounted for when solving the constitutive equation? Because complete equivalence has been established between valid constitutive equations and analog models, it will not be attempted here to solve the complete constitutive equation. Instead, Equation (1) either in the integral or differential form is integrated numerically at each time step, giving either the current stress from the strain history, or the current strain from the stress history. However, it is not immediately clear how these equations should be formulated when K is not constant. The situation is analogous to that of a non-Newtonian dashpot, where viscosity may depend on stress or strain-rate. In this case the appropriate expression is

$$\sigma = \eta(t,\sigma)\frac{d\varepsilon}{dt} \quad \text{or} \quad \varepsilon = \int_0^t \frac{\sigma}{\eta(t,\sigma)}dt \quad \text{and not} \quad \varepsilon = \frac{1}{\eta(t)}\int_0^t \sigma\,dt \tag{14}$$

hence in this instance also variation of K, expressed as E_τ^β, will be accounted for by expressing Equations (1) as

$$\sigma = E\frac{d^\beta}{d(t/\tau)^\beta}\varepsilon \quad \text{or} \quad \varepsilon = \frac{1}{E}\frac{d^{-\beta}}{d(t/\tau)^{-\beta}}\sigma \quad \text{and not} \quad \varepsilon = \frac{1}{E\tau^\beta}\frac{d^{-\beta}}{dt^{-\beta}}\sigma \tag{15}$$

where τ depends on σ, ε and/or θ. Introduction of this form into the SSM leads to an implicit fractional differential equation to which an analytical solution is not readily available. In this work, numerical integration is carried out by treating the viscoelastic element individually, and then obtaining global stress or strain from the node and branch compatibility conditions.

Two methods of integration have been used. One is based on the Grünwald definition, Equation (2), where $f(t - jt/N)$ is replaced by $f(t - (j - \beta/2)t/N)$ to improve convergence, and the latter expression is evaluated by three-point Lagrange interpolation as $f_j + (\beta/4)(f_{j-1} - f_{j+1}) + (\beta^2/8)(f_{j-1} - 2f_j + f_{j+1})$. (G2 algorithm, [1], Section 3.4 and 8.2). If τ is not constant, the integration variable is t/τ rather than t. In principle, this algorithm requires knowledge of the integrand for the whole of previous history, and also at the present time t and at $t + \Delta t$ (f_0 and f_{-1}). However, this difficulty can be circumvented by extrapolating from earlier times. At each time step, the current value of stress is obtained from strain history for the viscoelastic element. Then the current strain, and stresses and strains on the other elements, are obtained from branch and node compatibility conditions.

The second method of integration is based on Boltzmann superposition. The relaxation modulus and the creep compliance of a viscoelastic element can be expressed as

$$E(t) = \frac{E}{\Gamma(1-\beta)}\left(\frac{\tau}{t}\right)^{\beta} \quad \text{and} \quad D(t) = \frac{1}{E\Gamma(1+\beta)}\left(\frac{t}{\tau}\right)^{\beta} \tag{16}$$

The current strain can be calculated as

$$\varepsilon_\beta = \sum_{1}^{n-1} [(\sigma_{\beta,i} - \sigma_{\beta,i-1})/(E\Gamma(1+\beta))] t_i^{*\beta} \tag{17}$$

where the reduced time is

$$t_i^* = \sum_{j=i+1}^{n} (t_j - t_{j-1})/\tau_j \tag{18}$$

Clearly, whichever method of integration is used, stability is superior when obtaining strain from stress history at short times , and when obtaining stress from strain history at long times.

3. Tensile Behaviour of Polycarbonate

From the standpoint of linear viscoelasticity, polycarbonate is expected to be a particularly simple case, as there is an exceptionally wide temperature range between the glass transition at about 150 °C and the first secondary (or β) transition centred at −100 °C. It is well established that within this temperature range, the dependence of yield stress on temperature and strain rate is described by the Ree–Eyring model involving a single deformation process [26, 27]. Therefore, it is expected that a generalized Zener model containing a single viscoelastic element should be appropriate. The characteristic time τ of the viscoelastic element is assumed to be stress activated, Equation (9), and also to depend on the structural temperature θ through Equation (10). The structural temperature itself depends on the anelastic component of deformation through Equation (11), and relaxes towards the temperature bath according to the annealing Equation (12). The response of the restraining spring is assumed to follow the inverse Langevin law, Equation (13). For this simulation, the following parameters were used: $E_0 = 2.4$ GPa (room temperature Young's modulus), $\lambda_M = 2.1$ (maximum network draw ratio of PC), $\sigma_0 = 1.28$ MPa at room temperature [27] $k_\theta = 0.83$ K^{-1} [28, 29], $\theta_0 = 400$ K corresponding to a well-annealed sample (annealed to equilibrium at T_g-20 K). The linear viscoelastic relaxed modulus E_1 was adjusted at 40 MPa to obtain a reasonable yield drop. The value of $k_\varepsilon = 200\text{K}$ used here is lower than that inferred from the work of Othmezouri–Decerf [29]. However, higher values lead to exaggerated strain softening. The initial time constant $\tau_0 = 10^{14}$ s was calculated as η/E_0 assuming a viscosity of 10^{12} Pa.s at the glass transition (147 °C) and an activation energy of approximately 200 kJ/mol corresponding to low-strain processes in PC [28]. This gives an order of magnitude, but in fact this value has no effect on the shape of the stress-strain curves, but simply scales the corresponding strain rates. In combination with E_0, this allows the initial (linear viscoelastic) value of K_1 to be obtained as $E_0\tau_0^{\beta_1}$. The exponent $\beta_1 = 0.3$ is close to values commonly found from linear viscoelastic behaviour for the low-temperature side of the α relaxation in amorphous polymers. The exponent should ideally be obtained from dynamic mechanical spectroscopy using frequency sweeps over as wide a frequency range as possible; this is essential when β is temperature dependent [18] although in common practice temperature sweeps, which are less time-consuming, are the rule.

Although the number of parameters might appear to be large, many parameters are obtained from linear elastic behaviour, or from independent data such as the experimental dependence of yield stress on strain rate. In fact only k_ε, k_θ and the relaxed modulus E_1 were adjusted in this work.

A set of stress-strain curves calculated from this model are shown in Figure 2, using the $G2$ algorithm described above. Also shown are the corresponding curves representing the change in structural temperature during deformation. It should be pointed out that the model represents intrinsic material behaviour, and that localization of deformation such as necking is not accounted for.

A number of features that are characteristic of mechanical behaviour of ductile glassy polymers are well represented in the model, in particular the dependence of upper yield stress on strain rate and the slighter dependence of lower yield stress; the dependence of yield stress on the structural state; and the upward curvature of the post-yield rise in stress. However, it was expected that the progressive approach towards yield would be well represented by a model containing a fractional element, since this would be expected to spread out the response in time. This is not the case: practically no pre-yield anelastic deformation appears in the model behaviour, and the transition from linear elastic to plastic behaviour occurs abruptly over a very narrow stress span. This is clearly visible in Figure 3, which gives a comparison of the simulation with an experimental stress-strain curve in the pre-yield region.

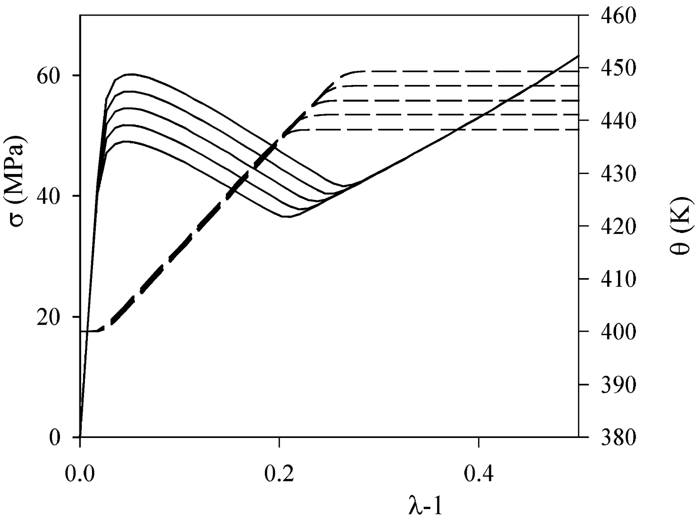


Figure 2. Calculated stress-strain curves (full lines, left scale) and change in structural temperature (dashed lines, right scale) for PC at room temperature. Strain rates (top to bottom): 0.5, 0.05, 0.005, 0.0005, 0.00005 s^{-1}.

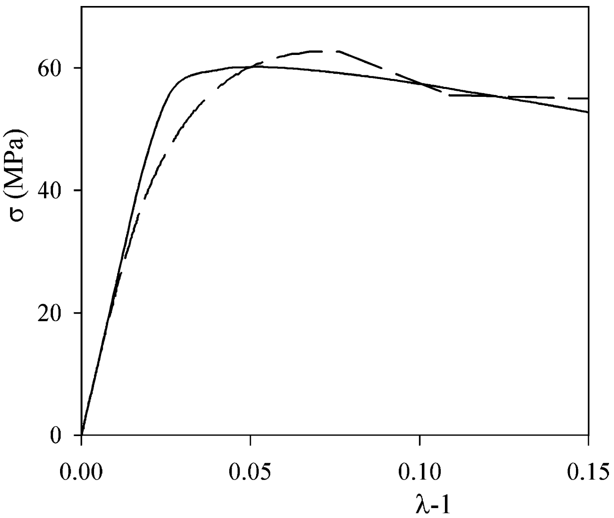


Figure 3. Comparison of model (full curve from Figure 2, 0.5 s^{-1}) with experimental behaviour (dashed curve) of PC at room temperature.

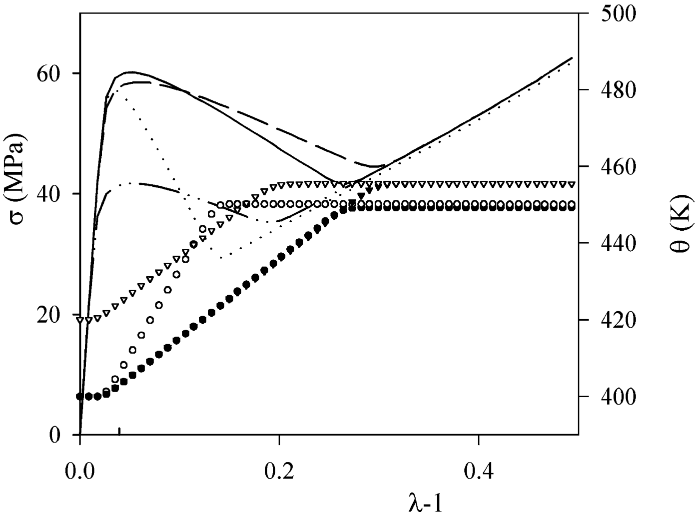


Figure 4. Model behaviour at 0.5 s^{-1} Lines: stress-strain curves, left scale; symbols: structural temperature, right scale. Full curve, black circles: as Figure 2; dotted curve, empty circles: $k_\varepsilon = 400$ K; dashed curve, black triangles: $k_\theta = 0.7$ K^{-1}; dashed-dotted curve, empty triangles: $k_\theta = 0.7$ K^{-1}, $\theta_0 = 420$ K.

Figure 4 shows the effect of various parameters on model behaviour. Increasing k_ε from 200 to 400 K decreases the yield stress slightly, and leads to a sharper and stronger yield drop. The structural temperature increases more rapidly, and the final structural temperature is marginally higher. Decreasing k_θ to 0.7 K^{-1} leads to a more gradual yield drop and a higher final structural temperature, since the condition for a stationary structural temperature is exact compensation of the strain-induced increase, Equation (11), by the relaxation-induced decrease, Equation (12). Increasing the initial structural temperature to 420 K, corresponding to a rapidly quenched sample, leads to a strong decrease of the upper yield stress, and a slighter change in the lower yield stress as observed experimentally. However, no set of parameters is able to produce the gradual approach to yield observed in the real material.

A similar problem has been encountered previously in many instances when attempting a unified description of various aspects of polymer behaviour. It has been shown that the gradual transition in yield behaviour at the onset of a secondary viscoelastic transition can only be modelled adequately if a distribution of activation energies is taken into account [30]. It has also been noted that activation energies for yield, annealing and ageing are different, and although this has been interpreted as an indication that these three phenomena involve different processes [28, 29], it has also been suggested that a single process is involved, but that one is looking at a different experimental window and hence a different subset of activation energies in the different kinds of experiments [31]. This matter is as yet unresolved. Also, the possibility that the linearised forms of the strain-softening effect, Equations (10) and (11), and the annealing Equation (12) are an oversimplification, cannot be ruled out.

A similar kind of discrepancy was observed when using a nested model as in Figure 1b to describe relaxation in polyethylene after strain reversal [20]. It was found that the effect of strain reversal was much stronger in the simulations than in the real material, implying that short-term relaxation was much stronger than in the model. Although it was expected that use of fractional models would adequately represent the spread in relaxation and deformation response that is observed in viscoelastic materials in the non-linear range, it turns out that this is not the case, and that anelastic behaviour must be accounted for separately. This could be carried out by taking account of a distribution of activation parameters. Specifically, any distribution of activation energies would lead to a distribution of time constants in the glassy state, even under the assumption of a single time constant in the melt. Such a distribution would also be linked with a distribution of activation volumes, hence of σ_0. Future work will attempt to introduce a treatment of these distributions into fractional order descriptions of polymer mechanical behaviour.

4. Conclusions

A simple standard solid model containing a spring-pot or fractional order element has been used in this work in an attempt to reproduce the tensile behaviour of a polymer in what was hoped to be a simple case, that of polycarbonate at room temperature, i.e. far from all viscoelastic transitions. The capability of such models to describe behaviour in the non-linear range of viscoelasticity and plasticity has been demonstrated. Although the general features of tensile behaviour are correctly reproduced, such as the presence of a yield drop and the change in yield behaviour with thermomechanical history, the shape of the stress-strain curve in the pre-yield region is not correctly reproduced. Future work will concentrate on incorporating an adequate treatment of anelasticity into the model, for instance by accounting for a distribution of activation energies and volumes of deformation processes.

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