Rheologica Acta Rheol Acta 33:210–219 (1994)

Fractal rheological models and fractional differential equations for viscoelastic behavior

N. Heymans and J.-C. Bauwens

Physique des Matériaux de Synthèse, Université Libre de Bruxelles, Bruxelles, Belgium

Abstract: A constitutive equation for viscoelastic behavior containing time derivatives of stress and strain to fractional order is obtained from a fractal rheological model. Equivalence between tree and ladder fractal models at long times is demonstrated. The fractional differential equation is shown to be equivalent to ordinary differential formulations in the case of a simple power-law response; the adequacy of such formulations to describe non-linearity has been demonstrated previously. The model gives a good description of viscoelastic behavior under all stress modes and will be extended in future to include aging effects.

Key words: Constitutive equation – fractional differintegral – fractal model – viscoelasticity – polymers

1. Introduction

Several authors (Tschoegl, 1989; Friedrich, 1991; Glöckle and Nonnenmacher, 1991) have recently suggested (or revived) use of differential or integral equations of fractional order to describe viscoelastic behavior intermediate between purely elastic and purely viscous. Such equations are usually introduced as a generalization of the differential equation related to the standard linear solid, or Zener model, obtained by replacing time derivatives of stress and strain by derivatives of fractional order. These descriptions lead asymptotically to power law behavior. (Similar generalizations of the diffusion equation have also been introduced and solved by Wyss (1986) and by Schneider and Wyss (1989).) Such formulations are concise in the sense that they give an adequate description of real viscoelastic behavior with a limited number of material parameters, with no need to use a relaxation (or retardation) spectrum. Tschoegl (1989) and Friedrich (1991 b) have stated, however, that these equations do not have any physical interpretation, although Bagley and Torvik (1983) obtained a fractional differential constitutive equation of order 1/2 from the Rouse model. The general differential equation given by Friedrich (1991 a)

$$\sigma + \tau^{\alpha} \frac{\partial^{\alpha} \sigma}{\partial t^{\alpha}} = \tau^{\beta} E_M \frac{\partial^{\beta} \varepsilon}{\partial t^{\beta}} + E_E \varepsilon \tag{1}$$

was shown to violate the thermodynamic condition for a monotonically decreasing energy function unless $\alpha = \beta$. Friedrich also showed that Eq. (1) can give a valid solution for $\alpha \leq \beta$ if a derivative of strain to order α is added to the righthand side, or if $E_E = 0$. Glöckle and Nonnenmacher (1991) used a description similar to Eq. (1) and showed that the relaxation function resulting from this equation can be expressed in terms of Fox functions, interpolating between stretched exponential short-time behavior and power-law behavior at long times. They were able to fit literature data on relaxation of polyisobutylene in the glass transition range using only four parameters (E_M, E_E, τ and $\beta = \alpha$) and showed that the same parameters could be used to describe literature data on storage and loss compliance in the same range; they were also able to fit dynamic data on natural rubber and galactomannan-borax gel using the four parameter model. Thus, this model adequately describes behavior in a variety of physical systems and strain histories. They found that β must be different from α to model the slope of the rubbery pseudoplateau, and that a difference between α and β leads to a limiting frequency restricting the range of validity of the treatment. They consider $\alpha = \beta$ as a special case. Also, Bagley and Torvik (1983) were able to fit dynamic data on butyl rubbers covering three decades of frequency to their fractional differential formulation of the Rouse model.

Independently, rheological models of viscoelastic behavior exhibiting self-similarity have been shown by Bauwens (1988, 1992a) to give an excellent description of the low-strain creep behavior of glassy polymers. These models also exhibit asymptotic power-law behavior. In certain cases, they can be described by ordinary differential equations; such equations have independently been shown to describe diffusion of deformation by a random walk along a linear structure and thus have physical meaning. Simultaneously, it has been shown by Schiessel and Blumen (1993) that a special kind of ladder model can be described by a fractional differential equation.

It is the purpose of this paper to show the connection among such fractal rheological models, and also the relationship between these models and the underlying deformation mechanism of a polymer chain. It will be shown that fractal rheological models lead to an analytical description of the time-dependent behavior in terms of integro-differential equations of fractional order, and therefore that the rheological model, the fractional differential equation approach and, under certain restrictive conditions, the ordinary differential equation approach are equivalent. Consequently, the most convenient approach may be used in each specific problem. It will also be shown that fulfilment of Friedrich's or Glöckle and Nonnenmacher's conditions for thermodynamic compatibility arises naturally when the fractional differential equation is obtained from a fractal rheological model.

It is not the purpose of this paper to show that fractional differential formulations of viscoelastic behavior fit experimental data adequately, as this has been done previously and can be found in the literature (e.g., Bagley and Torvik, 1983; Glöckle and Nonnenmacher, 1991).

2. Rheological model

2.1 General fractal tree model

Classical rheological models of viscoelastic behavior have been fully discussed by Tschoegl (1989). It is well known that no single element adequately describes all deformation modes equally well (the Maxwell element is better suited for stress relaxation and the Voigt model for creep). Behavior of real polymers can be reproduced by a combination of Maxwell elements in parallel or of Voigt elements in series, resulting in a distribution of relaxation or retardation times. Although these two distributions can be interconverted using classical procedures, they are not identical, and cannot therefore be considered as a fundamental property of the material, i.e., use of such distributions is simply a curve-fitting procedure requiring a large number of empirical parameters.

An alternative model requiring a low number of parameters which are identical for all deformation modes has been suggested by Bauwens (1988) and is shown in Fig. 1. In the most elementary form of this model, the viscoelastic response, determined by the complex modulus X, is represented by an elastic element E deforming in a viscous medium represented by an element whose complex modulus is $i\omega\eta$, both elements being connected in series with the viscoelastic medium, i.e., with an element whose complex modulus is X. The self-similar and recursive nature of the model is immediately apparent, since any part of the model (from any branching point to "infinity") is identical to the whole model. (For a definition of self-similarity see Mandelbrot, 1982.) The model is thus a fractal model. The complex modulus of the whole model fulfils the equation:

$$X = \left(\frac{1}{E}+\frac{1}{X}\right)^{-1} + \left(\frac{1}{i\omega\eta}+\frac{1}{X}\right)^{-1}, \tag{2}$$

which on rearranging gives:

$$X = \sqrt{i\omega\eta E} = E\sqrt{i\omega\tau}, \tag{3}$$

where $\tau = \eta/E$ is the time constant of the basic element, which is also the shortest time constant of the model.

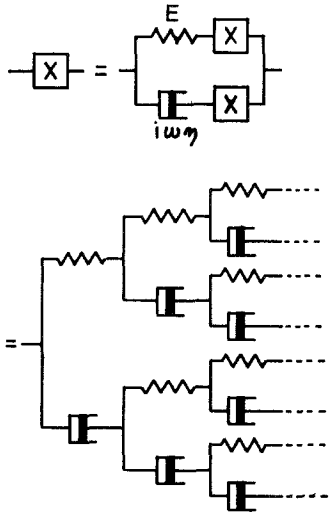

Fig. 1. Self-similar (fractal) tree model for viscoelastic behavior

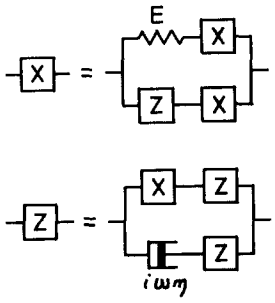

Fig. 2. Two-stage generalization of fractal tree model

If the viscous element is itself replaced by a fractal viscoelastic element composed as shown in Fig. 2, whose complex modulus is Z,

$$X = \sqrt{ZE} \tag{4}$$

and

$$Z = \sqrt{i\omega\eta X} \ , \tag{5}$$

giving

$$X = (i\omega\eta)^{1/4} E^{1/2} X^{1/4} \ , \tag{6}$$

or

$$X = (i\omega\eta)^{1/3} E^{2/3} \ . \tag{7}$$

By expressing X as $\sqrt{Z_1 Z_2}$ and iterating the process of decomposition of elements Z_i, Eq. (6) can be generalized to yield

$$X = (i\omega\eta)^{\Sigma(1/2^i)} E^{\Sigma(1/2^j)} X^{1-\Sigma(1/2^i)-\Sigma(1/2^j)} \ , \tag{8}$$

where the sums cover all values of i or j corresponding to the levels of decomposition where an element Z is a viscous or elastic element respectively. Thus, Eq. (7) becomes

$$X = (i\omega\eta)^{\beta} E^{1-\beta} \tag{9}$$

where

$$\beta = \frac{\Sigma(1/2)^i}{\Sigma(1/2)^i + \Sigma(1/2)^j} \ . \tag{10}$$

Since Eq. (10) is simply a binary representation of a number, an appropriate choice of the values of i and j allows any exponent β to be obtained to any desired precision. The model can thus be formally generalized to give any exponent β (although evidently ease of visualization of the structure of the model has become obscured in the process). It is thus legitimate to name the generalized model a "viscoelastic element of exponent β", expressing behavior intermediate between purely elastic behavior (obtained if $\beta = 0$) or linear viscous behavior (obtained if $\beta = 1$).

This model will be called the tree model hereafter to distinguish it from the ladder model to be investigated below, which is also a fractal model.

2.2 Ladder models

The ladder model, or Marvin-Oser model, has been extensively discussed by Tschoegl (1989). The classical ladder model can be depicted as in Fig. 3. The complex modulus X fulfills the equation:

$$\frac{1}{X} = \frac{1}{X + i\omega\eta} + \frac{1}{E} \tag{11}$$

or

$$X = -\frac{i\omega\eta}{2} + \sqrt{\frac{(i\omega\eta)^2}{4} + Ei\omega\eta} \ . \tag{12}$$

The ratio η/E is the time constant τ of the model. In terms of this time constant, Eq. (12) can be written:

$$X = -\frac{i\omega\eta}{2} + \sqrt{\frac{(i\omega\eta)^2}{4} + i\omega\tau E^2} \ . \tag{13}$$

Like the tree model, the ladder model is fractal. Differential operators of fractional order appear in its mathematical expression; although the model is conceptually simpler to visualize than the tree model, its analytical description is more complicated. The two models are equivalent in the continuous limit, since the viscous element then acts on an infinitely short segment; thus η becomes vanishingly small while E re-

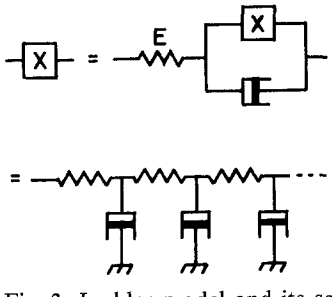

Fig. 3. Ladder model and its self-similar representation

mains constant. In this case, Eq. (13) relative to the ladder model reduces to Eq. (3) shown above to describe the fractal tree model. This equivalence will be discussed more fully below (4.1).

The ladder model with identical values of E and η for all elements can thus only yield $\beta = 1/2$; Schiessel and Blumen (1993) use a ladder model in which E and η of the k^{th} element depend on k as:

$$E_k = \frac{1}{2k-1}\frac{\Gamma(\beta)}{\Gamma(1-\beta)}\frac{\Gamma(k+1-\beta)}{\Gamma(k-1+\beta)}E_0 \ , \tag{14}$$

and

$$\eta_k = 2\frac{\Gamma(\beta)}{\Gamma(1-\beta)}\frac{\Gamma(k+1-\beta)}{\Gamma(k+\beta)}\eta_0 \ . \tag{15}$$

By expanding the Laplace transform of the constitutive equation of the model as a continued fraction, they showed that, to a first approximation, the behavior of the model can be described by a fractional differential with exponent β. Their model is thus hierarchical, but not self-similar.

2.3 Response of the model

The symbolic operator $(i\omega)^\beta$ represents the time-domain operator d^β/dt^β, so that differentiation to fractional order appears naturally as a consequence of the fractal nature of the rheological model. The differential equation

$$\sigma = E\tau^\beta \frac{d^\beta}{dt^\beta}\varepsilon \quad \text{or} \quad \varepsilon = \frac{1}{E\tau^\beta}\frac{d^{-\beta}}{dt^{-\beta}}\sigma \tag{16}$$

can easily be solved by classical methods. The solution can be found from the general relationship given by Oldham and Spanier (1974) (to whom the interested reader is referred for more information on fractional calculus than can be given here):

$$\frac{d^q t^p}{dt^q} = \frac{\Gamma(p+1)}{\Gamma(p-q+1)}t^{p-q} \ , \tag{17}$$

where q is positive for differentiation and negative for integration and the arguments of the gamma functions must be positive. Since, in fractional calculus, formally identical relationships are used for differentiation or integration, the term "differintegral" is applied to either operator.

It should be noted in passing that the two Eqs. (16) are not equivalent for a general function; they are, however, equivalent for functions which are expandable in terms of differintegrable units, in particular for functions which can be expressed as a series of powers of t^β and which are bounded for $t = 0$. As shown by Friedrich (1991 b), by Glöckle and Nonnenmacher (1991), and below, this is the case in creep and stress relaxation; an explicit solution of the fractional differential equation for periodic functions is given by Oldham and Spanier, and the dynamic response is not considered further in this paper.

In creep, strain is found by integration of the constant stress ($\sigma_0 t^p$ with $p = 0$) to order β, hence in Eq. (17) $p = 0$ and $q = -\beta$, and since $\Gamma(1) = 1$, the strain response is:

$$\varepsilon = \frac{\sigma_0}{E}\frac{1}{\Gamma(1+\beta)}\left(\frac{t}{\tau}\right)^\beta \ . \tag{18}$$

The stress relaxation response is found by differentiation of constant strain ($\varepsilon_0 t^p$ with $p = 0$) to order $q = \beta$ as:

$$\sigma = \frac{E\varepsilon_0}{\Gamma(1-\beta)}\left(\frac{\tau}{t}\right)^\beta \ . \tag{19}$$

The model is thus a non-standard model, i.e., it has a vanishing instantaneous compliance or an infinite instantaneous modulus. It can be transformed into a standard model by adding a spring E_M in series. The model is then a generalized Maxwell model composed of an elastic element in series with a viscoelastic β element. The behavior is now described by:

$$E\tau^\beta \frac{d^\beta}{dt^\beta}\varepsilon = \left(1 + \frac{E\tau^\beta}{E_M}\frac{d^\beta}{dt^\beta}\right)\sigma \ , \tag{20}$$

i.e., Eq. (1) with $\alpha = \beta$. The creep response becomes simply:

$$\varepsilon = \frac{\sigma_0}{E_M} + \frac{\sigma_0}{E}\frac{1}{\Gamma(1+\beta)}\left(\frac{t}{\tau}\right)^\beta \ , \tag{21}$$

or, on replacing $1/E_M$ by J_0 and $E\Gamma(1+\beta)\tau^\beta/E_M$ by τ_0^β,

$$J = J_0\left(1 + \left(\frac{t}{\tau_0}\right)^\beta\right) \ . \tag{22}$$

As expected, the response of the standard model in creep is obtained simply by adding the instantaneous compliance J_0 to the retarded compliance. It can be

noted that, with no loss of generality, E can be taken equal to E_M by a suitable adjustment of the time constant, thus no distinction will be made below between the two moduli.

The relaxation response can be found either by Laplace transform or by expanding σ in powers of t^β as carried out by Friedrich (1991 b) as:

$$\sigma = \sum a_j \left(\frac{t}{\tau}\right)^{j\beta} . \tag{23}$$

Equation (20) becomes

$$\frac{E\varepsilon_0}{\Gamma(1-\beta)}\left(\frac{t}{\tau}\right)^{-\beta} = \sum \left(a_j + a_{j+1}\frac{\Gamma[1+(j+1)\beta]}{\Gamma[1+j\beta]}\right)\left(\frac{t}{\tau}\right)^{j\beta} . \tag{24}$$

Term-by-term identification between both sides of Eq. (24) gives the recurrence relationship for the coefficients of Eq. (23), for all $j \neq -1$:

$$a_{j+1} = -a_j \frac{\Gamma[1+j\beta]}{\Gamma[1+(j+1)\beta]} , \tag{25}$$

whereas for $j = -1$ the starting condition is obtained:

$$a_0 + a_{-1}\Gamma(1-\beta) = E_M\varepsilon_0 . \tag{26}$$

There remains one degree of freedom in the choice of the parameters of the expansion. The short-time response can be found by choosing $a_{-1} = 0$; giving

$$a_0 = E_M\varepsilon_0$$

$$a_j = (-1)^j \frac{E_M\varepsilon_0}{\Gamma[1+j\beta]} . \tag{27}$$

The instantaneous modulus is, of course, E_M and at short times the expansion is similar to that of the stretched exponential.

The long-time response is found by choosing $a_0 = 0$, giving

$$a_{-1} = \frac{E_M\varepsilon_0}{\Gamma(1-\beta)}$$

$$a_{-j} = (-1)^{j+1} \frac{E_M\varepsilon_0}{\Gamma[1-j\beta]} . \tag{28}$$

The expansion contains only terms of negative power and is necessarily limited to $j\beta < 1$, since the fractional differential is not defined for larger powers of $1/t$; for $t \gg \tau$ the response is asymptotically a power law of exponent β; Eq. (28) can therefore be considered as yielding an asymptotic expansion valid at long times, showing that the response is a simple power law only at times much longer than the time constant. In practice, the (theoretically) convergent series defined by Eq. (27) leads to problems with rounding-off errors for t/τ greater than 20 or 30; in this region the asymptotic long-term expansion is not yet sufficiently precise to be a valid continuation of the series. However, by extending the series to $j\beta < 2$, using Eq. (28) for the coefficients, a closer approximation can be obtained, as shown in Fig. 4, although there is no justification for extending the expansion to powers lower than -1.

It should be noted that the response of the standard model can be retrieved from Eq. (16) by replacing ε by $\varepsilon - \sigma/E$; Eq. (16) thus gives the retarded deformation under the relaxing stress $\sigma(t)$. This equation can also be considered as describing a single viscoelastic element with behavior intermediate between linear elasticity ($\beta = 0$) and linear viscosity ($\beta = 1$). Thus, a combination of linear elastic and linearly viscous elements described by ordinary differential equations yields a model exhibiting intermediate viscoelasticity described by a fractional differential equation.

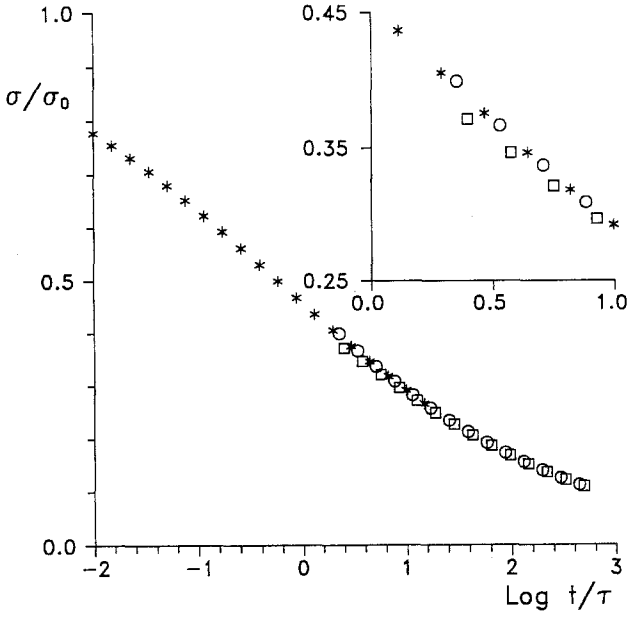

Fig. 4. Relaxation function of fractional Maxwell element with $\beta = 0.3$. * Power series, Eq. (27). Asymptotic expansion, Eq. (28): □ limited to $j\beta < 1$; ○ limited to $j\beta < 2$. Inset: enlargement of overlap region

3. Fractional differential formulation for solid models

3.1 Generalized Maxwell model

The Maxwell model can be generalized by replacing the elastic element and the viscous element by viscoelastic elements with exponents respectively equal to γ and β; with no loss of generality, one may assume $\gamma \leq \beta$. The constitutive equation of the generalized model in symbolic notation is:

$$\varepsilon = \sigma \left(\frac{1}{X_1} + \frac{1}{X_2} \right) \tag{29}$$

or

$$X_2 \varepsilon = \left(1 + \frac{X_2}{X_1} \right) \sigma \ , \tag{30}$$

or in fractional differential formulation:

$$\tau^\beta E \frac{\partial^\beta \varepsilon}{\partial t^\beta} = \sigma + \tau^\alpha \frac{\partial^\alpha \sigma}{\partial t^\alpha} \quad \text{with} \quad 0 < \alpha \leq \beta < 1 \ , \tag{31}$$

where α has been substituted for $\beta - \gamma$. Friedrich's condition for thermodynamic compatibility of Eq. (1) when $E_E = 0$ is thus obtained automatically when the fractional differential equation for the generalized Maxwell model is derived from a rheological model.

If $\gamma = 0$, one of the viscoelastic elements becomes purely elastic and $\alpha = \beta$ is obtained. On the other hand, if one of the elements becomes purely viscous $\beta = 1$.

3.2 Generalized Zener model

The constitutive equation for the standard three-element solid model (or Zener model, Fig. 5) is found from the system:

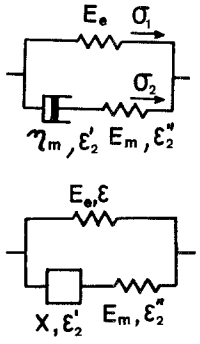

Fig. 5. Zener model and its extension including a fractal viscoelastic element

$$\sigma = \sigma_1 + \sigma_2$$

$$\varepsilon = \varepsilon_2' + \varepsilon_2''$$

$$\sigma_1 = E_E \varepsilon$$

$$\sigma_2 = E_M \varepsilon_2'' \ , \tag{32}$$

where subscripts M and E refer to the Maxwell element and the restraining elastic element respectively, and from the response of the viscous element:

$$\sigma_2 = \eta_M \frac{d\varepsilon_2'}{dt} \ . \tag{33}$$

Equations (32) allow the deformation of the viscous element to be expressed as

$$\varepsilon_2' = \varepsilon \left(1 + \frac{E_E}{E_M} \right) - \frac{\sigma}{E_M} \ . \tag{34}$$

Introducing Eq. (33) into Eq. (34):

$$\sigma_2 = \eta_M \frac{d\varepsilon}{dt} \left(1 + \frac{E_E}{E_M} \right) - \frac{d\sigma}{dt} \frac{\eta_M}{E_M} \ , \tag{35}$$

and since

$$\sigma_2 = \sigma - \sigma_1 = \sigma - E_E \varepsilon \tag{36}$$

$$\sigma - E_E \varepsilon = \frac{\eta_M}{E_M} \left[\frac{d\varepsilon}{dt} (E_M + E_E) - \frac{d\sigma}{dt} \right] \ , \tag{37}$$

η_M / E_M is the time constant τ_0 of the Maxwell element. The constitutive equation of the Zener model is therefore:

$$\sigma + \tau_0 \frac{d\sigma}{dt} = (E_M + E_E) \tau_0 \frac{d\varepsilon}{dt} + E_E \varepsilon \ . \tag{38}$$

Friedrich (1991a) and Glöckle and Nonnenmacher (1991) generalized Eq. (38) by replacing the time derivatives of stress and strain with fractional derivatives of order α and β, respectively, and showed that the compliance is a monotonically non-decreasing function of time only if $\alpha = \beta$. Friedrich (1991b) also stated that "The good flexibility of this model with fractional derivatives is unfortunately balanced by bad physical interpretability". Tschoegl (1989) discusses fractional differentiation in Chap. 6, devoted to mathematical models, with no reference to rheological models.

In fact, Friedrich's equation can be obtained from the Zener model itself: if the viscous element in the Zener model is replaced by a fractal viscoelastic element such as that in Figs. 1 or 2, its viscoelastic response is expressed by a fractional derivative according to Eq. (16), which replaces Eq. (33). Equation (34) expressing continuity of deformation remains valid, and on differentiating this equation to order β, we obtain:

$$\sigma - E_E\varepsilon = \tau_0^\beta \left[\frac{d^\beta \varepsilon}{dt^\beta}(E_M + E_E) - \frac{d^\beta \sigma}{dt^\beta} \right] , \tag{39}$$

or on rearranging:

$$\sigma + \tau_0^\beta \frac{d^\beta \sigma}{dt^\beta} = (E_M + E_E)\tau_0^\beta \frac{d^\beta \varepsilon}{dt^\beta} + E_E\varepsilon . \tag{40}$$

Thus, Friedrich's and Glöckle and Nonnenmacher's thermodynamic compatibility condition for the generalized Zener model is automatically fulfilled by replacing the viscous element by a fractal viscoelastic element.

Friedrich (1991a) noted that Eq. (1) could give a valid solution with $\alpha \leq \beta$ if a derivative of strain to order α is added. This corresponds to replacing the elastic element E_M by a viscoelastic element of order γ. Following the steps leading to Eqs. (31) and (40), the model is now described in symbolic notation by:

$$\varepsilon(E_E[X_1 + X_2] + X_1X_2) = \sigma(X_1 + X_2) , \tag{41}$$

or

$$\left(1 + \tau^\alpha \frac{\partial^\alpha}{\partial t^\alpha}\right)\sigma = \left[E_E(1 + \tau^\alpha)\left(\frac{\partial^\alpha}{\partial t^\alpha}\right) + E_M\tau^\beta \frac{\partial^\beta}{\partial t^\beta}\right]\varepsilon , \tag{42}$$

i.e., Eq. (1) with a derivative to order α added to the r.h.s.

4. Discussion

4.1 Equivalence between models in continuous limit

As shown above (2.2), the ladder model becomes equivalent to the tree model in the continuous limit. The physical interpretation of this equivalence is that, in the tree model, if the viscous elements become soft enough, the stress acting on any viscous element is transmitted directly to the "ground" through the elastic elements in series, which act as a rigid connection.

The two models are therefore equivalent in the continuous limit, that is as long as the time scale of the experiment is much longer than the shortest relaxation time, i.e., the relaxation time of the monomer. (The shortest relaxation time of the continuous model unphysically vanishes.) The tree model yields a more manageable constitutive equation if all elements are linear, and corresponds to a more realistic description of an entangled mass of polymer chains; however, it is not immediately clear how the constitutive equation can be generalized to account for non-linear behavior, e.g., non-Newtonian viscosity or rubber elasticity: should the constants τ and E appearing in the constitutive equation become dependent on the global stress and strain, or should the individual elements in the model obey laws depending on the "local" strains and stresses? The ladder model lends itself more readily to numerical calculations, since the behavior at each node can be expressed in terms of the local stress and strain rate, and the leading contribution shifts steadily along the structure during creep or stress relaxation. In the tree model, on the contrary, interest shifts from the bottom row of viscous elements to the top row of elastic elements (see Fig. 1) as deformation proceeds; at intermediate times many branches are required simultaneously and the region of interest is not clearly delimited. Also, implementation of the tree model becomes extremely laborious for $\beta < > 1/2$, whereas the ladder model can be implemented for all β using Schiessel and Blumen's (1993) expressions for E and η, Eqs. (14) and (15). Thus, the ladder model is better suited than the tree model for numerical simulations. Such simulations are currently in progress.

4.2 Equivalence between fractional differential and ordinary differential formulations

It has been shown by Bauwens (1992b) that, under creep conditions, diffusion of retarded strain by a random walk on a one-dimensional path, e.g., a polymer chain, is described by the equation:

$$\frac{d\varepsilon}{d(t/\tau)} = \left(\frac{\sigma_0}{E}\right)^3 \frac{1}{\varepsilon^2} , \tag{43}$$

which by integration gives the retarded creep compliance:

$$J = \frac{1}{E}\left(\frac{3t}{\tau}\right)^{1/3} . \tag{44}$$

This solution is formally identical to Eq. (18) which is the solution in creep of the fractional differential formulation of viscoelastic behavior, Eq. (16). Thus, in creep, i.e., for a constant stress step σ_0 applied suddenly at time $t = 0$, the fractional differential formulation, Eq. (16), appears to be equivalent to the ordinary differential, Eq. (43). Since most polymer scientists are more familiar with ordinary differential than with fractional differential calculus, it would be too tempting to extend the equivalence to a general deformation. It is shown below that this is not a valid generalization.

In the linear viscoelastic range, the response to a general stress can be found from the superposition principle:

$$\varepsilon(t) = \frac{1}{E}\left(\frac{3}{\tau}\right)^{1/3} \int_0^t (t-u)^{1/3} d\sigma(u)$$

$$= \frac{1}{E}\left(\frac{3}{\tau}\right)^{1/3} \int_0^t \frac{\sigma' du}{(t-u)^{1-4/3}} , \tag{45}$$

where σ' is the time derivative of stress. This integral is identical to the Riemann-Liouville definition of the fractional differintegral (Oldham and Spanier, 1974), so Eq. (45) can be rewritten:

$$\varepsilon(t) = \frac{1}{E}\left(\frac{3}{\tau}\right)^{1/3} \Gamma\left(\frac{4}{3}\right) \frac{d^{-4/3}(\sigma')}{dt^{-4/3}} , \tag{46}$$

or, on differentiating Eq. (46) to order 1/3,

$$\frac{d^{1/3}\varepsilon}{dt^{1/3}} = \frac{1}{E}\left(\frac{3}{\tau}\right)^{1/3} \Gamma\left(\frac{4}{3}\right) \sigma(t) , \tag{47}$$

which is identical to Eq. (16) except for a numerical factor which is close to 1 if $0<\beta<1$. If Eq. (43) is generalized by replacing ε^2 by ε^α, by following the steps leading from Eq. (43) to Eq. (47), $\beta = 1/(\alpha+1)$ is found; thus β is linked to the fractal dimension of a random walk on a polymeric structure. The fractional differential formulation is retrieved for a general stress history using Boltzmann's superposition principle, and is thus more general than Eq. (43), which is only valid in creep, or when the retarded response is a simple power law. This can be seen by attempting to retrieve the ordinary differential formulation, Eq. (43), from the fractional differential formulation, Eq. (16), as follows.

For a general deformation, the solution can be expanded as a power series:

$$\varepsilon = \sum a_j \left(\frac{t}{\tau}\right)^j , \tag{48}$$

where $j \geq 0$ since the initial deformation must remain finite.

Differentiation to order β gives

$$\frac{d^\beta \varepsilon}{d(t/\tau)^\beta} = \sum \frac{\Gamma(j+1)}{\Gamma(j-\beta+1)} a_j \left(\frac{t}{\tau}\right)^{j-\beta} , \tag{49}$$

whereas the first-order differential is:

$$\frac{d\varepsilon}{d(t/\tau)} = \sum a_j j \left(\frac{t}{\tau}\right)^{j-1} . \tag{50}$$

where $j \geq 0$ since the initial deformation must remain finite.

If the expansion contains more than one term, no simple relationship can be found between the fractional and ordinary differentials; in the case of simple power law behavior with exponent j, however, the following relationships are found:

$$\frac{d^\beta \varepsilon}{d(t/\tau)^\beta} = \frac{\Gamma(j+1)}{\Gamma(j-\beta+1)} \frac{\varepsilon}{(t/\tau)^\beta} \tag{51}$$

and

$$\frac{d\varepsilon}{d(t/\tau)} = j \frac{\varepsilon}{(t/\tau)} . \tag{52}$$

Raising Eq. (51) to power $1/\beta$, an equation similar to Eq. (43) is retrieved:

$$\frac{d\varepsilon}{d(t/\tau)} = j \left[\frac{\Gamma(j-\beta+1)}{\Gamma(j+1)}\right]^{1/\beta} \left(\frac{\sigma}{E}\right)^{1/\beta} \frac{1}{\varepsilon^{1/\beta-1}} . \tag{53}$$

The ordinary differential formulation is thus valid whenever the strain is a power law of any order j, corresponding to a stress which is a power $(j-\beta)$ of time. For example, the ordinary differential formulation is valid in stress relaxation for the generalized Maxwell element, but not for the generalized standard solid model.

Thus, the fractional differential formulation of viscoelastic behavior can be thought of as describing diffusion of deformation along a linear chain structure. Other interpretations have been given by Glöckle and Nonnenmacher (1993) in terms of continuous-time random walks in disordered three-dimensional

systems or by Le Mehauté and Crepy (1983) in terms of diffusion on fractal structures.

4.3 Physical meaning of the fractal Zener model

The fractal models depicted in Figs. 1 and 2 can be thought of as expressing the behavior of linear chains transmitting stress and deformation to neighboring chains through viscous drag. At times much longer than the relaxation time corresponding to local motions, the reference chain can be assumed as a first approximation to move in a rigid environment, leading to retrieval of the ladder model. The model leads to an identical formulation of viscoelastic behavior whatever the stress-strain history, and is thus internally consistent. This contrasts with classical approaches using a distribution of Maxwell elements (or relaxation times) in stress relaxation and a distribution of Voigt elements (or retardation times) in creep. As pointed out by Schiessel and Blumen (1993), "such an approach is arbitrary on the microscopic level and therefore, it does not explain the universality of the measured patterns".

The fractal decomposition of the viscoelastic behavior of a polymer is evidently valid only between a lower and an upper cut-off. The lower cut-off occurs at the level of the statistical segment which defines the smallest element that can be used in the fractal model. The basic elastic element E then describes the conformational elasticity of a statistical segment, and the viscosity η of the basic viscous element describes friction between statistical segments belonging to neighboring chains. The elastic element E_M in series with the viscoelastic element in the Maxwell element then describes low instantaneous deformability of the statistical segment, and the elastic element E_E in parallel describes the limiting deformation of the (entanglenent or permament) network. This idea paves the way to possible refinements in the model: in the case of a thermoplastic polymer, the temporary network will also flow at long times; this can be modeled by adding a slow viscoelastic element with an exponent $\alpha<\beta$ in series with E_E, or by replacing E_E by such an element. The exponents α and β express prevalence of viscous over elastic behavior or vice-versa: a low exponent expresses nearly elastic behavior, whereas an exponent close to 1 corresponds to nearly pure viscous behavior. Thus, these exponents can be expected to be temperature dependent, rising on going through the glass transition.

The conditions for thermodynamic compatibility of the response obtained from the model are automatically fulfilled, since the elements of the model can clearly only deform if deformation leads to release of energy. Thus, use of such models is justified by the simplicity of physical reasoning based on them.

One distinct advantage of the fractal models or the fractional differential formulation derived from them is their ability to describe real polymer behavior using only a small number of parameters. Although it is, of course, possible to derive relaxation and retardation spectra from the retardation and relaxation functions, as carried out by Glöckle and Nonnenmacher (1991), this represents an unnecessary mathematical complication, since the model itself requires only a single characteristic time. The underlying reason for the ability to describe real behavior using only one characteristic time is that the model itself incorporates complexity, as does its fractional differential description: for example, in stress relaxation, no single element can be found in the model on which the stress is an exponentially decreasing function of time. Since the formulation incorporates complexity, this is not required of the parameters.

5. Conclusions

It has been shown that constitutive equations for viscoelastic behavior involving fractional derivatives need not be considered as a mathematical artefact, but arise naturally when expressing the rheological behavior of a fractal model. The fractional differential formulation leads to power-law behavior in creep, and is readily solved for a general deformation in a linear viscoelastic solid. For extension to the nonlinear range of viscoelasticity, numerical treatment either of the rheological model or of the fractional differintegral is required; these approaches are fully equivalent in theory, however, numerical calculations on one of the rheological models are likely to be more tractable since the solution to the fractional differential equation is an alternating series containing large nearly compensating terms, rapidly leading to round-off errors. Such work is currently in progress.

If attention is restricted to the case of power-law behavior, the fractional differential formulation is also equivalent to ordinary differential equations describing diffusion of deformation by a random walk on a linear chain. This approach lends itself to generalizations taking aging effects into account; work in this direction is in progress and will be published shortly (Heymans et al., 1994).

References

Bagley RL, Torvik PJ (1983) A theoretical basis for the application of fractional calculus to viscoelasticity. J Rheol 27:201 – 210

Bauwens J-C (1988) Tentative de corrélation entre l'équation de Williams-Watts et la topologie viscoélastique. Deppos IX (Déformation plastique des polymères solides, 9th annual meeting), ENSAM, Paris, 18th – 19th October 1988

Bauwens J-C (1992a) Two nearly equivalent approaches for describing the non-linear creep behavior of glassy polymers. Colloid Polym Sci 270:537 – 542

Bauwens J-C (1992b) A deformation model of polycarbonate extended to the loss curve in the α transition range. Plastics, Rubber and Composites Processing and Applications 18:149 – 153

Friedrich Ch (1991a) Relaxation functions of rheological constitutive equations with fractional derivatives: thermodynamical constraints. In: Casas-Vázquez J, Jou D (eds) Lecture nodes in physics: vol 381, rheological modelling: thermodynamical and statistical approaches. Springer-Verlag, Berlin Heidelberg, 321 – 330

Friedrich Ch (1991b) Relaxation and retardation functions of the Maxwell model with fractional derivatives. Rheol Acta 30:151 – 158

Glöckle WG, Nonnenmacher TF (1991) Fractional integral operators and fox functions in the theory of viscoelasticity. Macromolecules 24:6426 – 6434

Glöckle WG, Nonnenmacher TF (1993) Fox function representation of non-Debye relaxation processes. J Stat Phys 71:741 – 757

Heymans N, Hellinckx S, Bauwens J-C, Analytical and fractal descriptions of non-linear mechanical behaviour of polymers. Accepted for publication in J Non-Crystalline Solids

Le Mehauté A, Crepy G (1983) Introduction to transfer and motion in fractal media: the geometry of kinetics. Solid State Ionics 9, 10:17 – 30

Mandelbrot BB (1982) The fractal geometry of nature. W.H. Freeman, New York, pp 34 – 41, 349 – 350

Oldham KB, Spanier J (1974) The fractional calculus. Academic Press, London

Schiessel H, Blumen A (1993) Hierarchical analogues to fractional relaxation equations. J Phys A: Math Gen 26:5057 – 5069

Schneider WR, Wyss W (1989) Fractional diffusion and wave equations. J Math Phys 30:134 – 144

Tschoegl NW (1989) The phenomenological theory of linear viscoelastic behaviour. Springer-Verlag, Berlin Heidelberg

Wyss W (1986) The fractional diffusion equation. J Math Phys 27:2782 – 2785

(Received July 21, 1993;
in revised form January 20, 1994)

Correspondence to:

Nicole Heymans
Physique des Matériaux de Synthèse 194/8
Université Libre de Bruxelles
1050 Bruxelles
Belgium