

PII: S0020-7683(96)00178-3

# A CONSTITUTIVE MODEL FOR NONLINEAR VISCOELASTIC MEDIA

#### ALEKSEY D. DROZDOV

Institute for Industrial Mathematics, Ben-Gurion University of the Negev, 22 Ha-Histadrut Street, Be'ersheba, 84213 Israel

#### (Received 3 November 1995; in revised form 28 July 1996)

Abstract—A new constitute model is derived for the nonlinear viscoelastic behavior of polymers under isothermal loading. The model extends the concept of adaptive links (entanglements) between polymeric molecules to aging viscoelastic solids. By using data for polypropylene and polyurethane in relaxation tests, material parameters are found. To verify the model, experimental data for loading/unloading with constant rates of strains are employed, which demonstrate fair agreement between measurements and their prediction.

The model is utilized to calculate stresses and displacements built-up in a conic pipe under the action of torques applied to its edges. An explicit solution to this problem is derived, where a time-dependent coefficient satisfies a nonlinear integral equation. The effect of geometrical parameters of the pipe and the loading history on stresses and displacements is studied numerically.

Two correspondence principles are derived which permit a solution to a viscoelastic problem to be found explicitly in terms of solutions to appropriate elastic problems. Some restrictions on the model nonlinearity are determined which imply these principles. © 1997 Elsevier Science Ltd.

### 1. INTRODUCTION

The paper is concerned with constitutive models for the nonlinear behavior of viscoelastic solids under isothermal loading with small strains. This problem has been in the focus of attention in the past three decades due to its numerous applications in polymer engineering. Despite a huge number of publications, see, e.g., their reviews by Findley *et al.* (1989) and Drozdov (1996a), it is rather difficult to mention a model which satisfies the following conditions : (i) the model is comparatively simple to be employed for the analysis of stresses and displacements in solids with an arbitrary geometry, (ii) its parameters can be determined experimentally by using the standard tests, and (iii) the model reflects adequately the material behavior under time-varying (in general, non-monotonic) loads.

These conditions impose rather strong restrictions on constitutive models. For example, in multiple-integral constitutive models, several functions of several variables should be found experimentally. This requires such a number of experimental data which is not available in the standard tests, see, e.g., Ward and Wolfe (1966). The number of variables increases if we deal with aging viscoelastic materials, see, e.g., Chai and McCrum (1984), McKenna (1989), Struik (1978), Waldron *et al.* (1995). Thus, conditions (i) and (ii) confine us to the so-called single-integral constitutive models. Several single-integral models demonstrate excellent fitting of experimental data which are used for determining material parameters, but fail to predict results in other experiments, see, e.g., Smart and Williams (1972), Fiegl *et al.* (1993). This implies that condition (iii) becomes extremely important for validating constitutive models.

The objective of the present paper is to derive a new model which is as simple as possible to be employed in engineering calculations, reflects some physical concept of interaction between macromolecules of solid polymers, and predicts adequately the material response under time-varying loads. Our model goes back to the concept of polymeric networks, see Green and Tobolsky (1946), Lodge (1989), Yamamoto (1956). According to the model, a viscoelastic medium is treated as a system of parallel elastic springs (links between polymeric molecules) which replace each other according to a special rule. This rule is described by a function X(t, s) which equals the number of links arisen before instant

s and existing at instant t. Up to Young's modulus E(s), the function X(t, s) coincides with the relaxation measure, see Drozdov (1993, 1996a) for details.

Our aim is to derive a constitutive model for aging media whose mechanical properties change in time due to some physical and chemical processes. For this purpose, the so-called physical and chemical agings are not necessarily to be distinguished, see, e.g., Struik (1978). For an aging viscoelastic material, the Young modulus E depends on time s, while the relaxation measure X depends on two variables t and s. For a non-aging medium, E is assumed to be constant, whereas the function X depends on the difference t-s only. These adjustable functions are found by fitting experimental data obtained in the standard relaxation tests. In the analysis of experimental data, we concentrate on experiments carried out for non-aging viscoelastic materials (polypropylene and polyurethane) by Smart and Williams (1972) and Partom and Schanin (1983). The study of the effect of stresses on the physical aging of polymers will be the subject of another work.

To determine a function of one variable E(s) and a function of two variables X(t, s), a large number of experimental data should be available. To reduce significantly this number, we suggest an approach based on the so-called multiplicative representation of the function X(t, s), see Drozdov and Kalamkarov (1995a). According to it, the function of two arguments X(t, s) is determined entirely by the rates of formation new links  $H^{(m)}(s)$  and the rates of breakage for existing links  $g_s^{(m)}(t-s)$  of mth type (m = 1, 2, ..., M). This concept has the following advantages: (i) the multiplicative representation implies positivity of the relaxation spectrum, see Pipkin (1972); (ii) it allows the processes of reformation and breakage of adaptive links to be described by a system of kinetic equations with constant coefficients.

The exposition will be as follows. In Section 2, we introduce the model of adaptive links and establish its equivalence to an integral constitutive equation in linear viscoelasticity. Section 3 is concerned with the multiplicative representation of the function X(t,s) determining the processes of formation and breakage for adaptive links. In Section 4, the material parameters of the model are determined, and the model is verified by a comparison of the results of numerical simulation with experimental data for loading/ unloading tests with constant strain rate. In Section 5, we extend the model to threedimensional loading. Section 6 deals with torsion of a conic pipe made of a nonlinear viscoelastic material. In Section 7, two correspondence principles in the nonlinear viscoelasticity are formulated and restrictions imposed by these principles on the material nonlinearity are analyzed. Finally, some concluding remarks are formulated in Section 8.

# 2. A MODEL OF AN AGING, VISCOELASTIC MATERIAL

We begin with uniaxial tension of a specimen made of an aging linear viscoelastic material whose behavior obeys the constitutive equation, see, e.g., Drozdov (1996a),

$$\sigma(t) = E(t)\varepsilon(t) - \int_0^t \frac{\partial X}{\partial s}(t,s)\varepsilon(s) \,\mathrm{d}s. \tag{1}$$

Here  $\sigma$  is the stress,  $\varepsilon$  is the strain, E(t) is Young's modulus, and

$$X(t,s) = E(s) - Q(t,s).$$
 (2)

The relaxation measure Q(t, s) satisfies the condition

$$Q(t,t) = 0$$

which implies that

$$X(t,t) = E(t). \tag{3}$$

It follows from eqns (1)-(3) that

$$\sigma(t) = E(0) \{ X_*(t,0)\varepsilon(t) + \int_0^t \frac{\partial X_*}{\partial s}(t,s)[\varepsilon(t) - \varepsilon(s)] \, \mathrm{d}s \}, \tag{4}$$

where

$$X_*(t,s) = E_*(s) - Q_*(t,s), \quad E_*(s) = \frac{E(s)}{E(0)}, \quad Q_*(t,s) = \frac{Q(t,s)}{E(0)}.$$
 (5)

Equation (4) allows the following mechanical interpretation.

Let us consider a system of parallel springs (links between polymeric molecules). The rigidity of each spring equals E(0). The springs of the system arise and collapse. At instant s, the system consists of  $X_*(s, s)$  springs, within the interval [s, s+ds],

$$\frac{\partial X_*}{\partial s}(s,s)\,\mathrm{d}s\tag{6}$$

new springs merge with the system. At the instant of 'birth', all the springs are stress-free. This means that the natural configuration of springs arising at instant s coincides with the actual configuration of the system at that instant. Thus, the strain at instant t in springs arisen at instant s equals

$$\varepsilon_s(t) = \varepsilon(t) - \varepsilon(s).$$

To describe the breakage of springs, the function  $X_*(t,s)$  is employed as well. The amount

 $X_{*}(t, 0)$ 

equals the number of initial springs existing at instant t, while the value

$$\frac{\partial X_*}{\partial s}(t,s)\,\mathrm{d}s\tag{7}$$

determines the number of springs arisen within the interval [s, s+ds] and existing at instant t.

For a system of parallel springs, the stress  $\sigma(t)$  equals the sum of stresses in separate springs

$$\sigma(t) = \sigma_0(t) + \int_0^t \mathrm{d}\sigma_s(t), \tag{8}$$

where  $\sigma_0(t)$  is the stress in the initial springs, and  $d\sigma_s(t)$  is the stress in the springs arisen in the interval [s, s+ds]. By assuming the Hooke law to be valid, we find that

$$\sigma_0(t) = E(0)X_*(t,0)\varepsilon(t),$$
  

$$d\sigma_s(t) = E(0)\frac{\partial X_*}{\partial s}(t,s)\varepsilon_s(t) ds = E(0)\frac{\partial X_*}{\partial s}(t,s)[\varepsilon(t)-\varepsilon(s)] ds.$$
(9)

Substituting expressions (9) into eqn (8), we obtain the constitutive eqn (4). The latter means that eqn (4) is equivalent to the above model of elastic links replacing each other.

To extend the constitutive eqn (4) to nonlinear materials, it is natural to replace the Hooke law for a separate spring by the nonlinear dependence

$$\sigma = \Phi(\varepsilon), \tag{10}$$

where  $\Phi(\varepsilon)$  is a given function, which is assumed to be odd and piece-wise continuously differentiable. As common practice, the power-law approximation is employed

$$\Phi(\varepsilon) = A |\varepsilon|^{\alpha} \operatorname{sign} \varepsilon, \tag{11}$$

where A and  $\alpha$  are positive material parameters.

According to eqn (10), the response of nonlinear elastic links is determined by the equalities similar to eqn (9)

$$\sigma_{0}(t) = X_{*}(t,0)\Phi(\varepsilon(t)),$$
  
$$d\sigma_{s}(t) = \frac{\partial X_{*}}{\partial s}(t,s)\Phi(\varepsilon_{s}(t)) ds = \frac{\partial X_{*}}{\partial s}(t,s)\Phi(\varepsilon(t)-\varepsilon(s)) ds.$$
(12)

Combining eqns (8) and (12), we arrive at the constitutive relation

$$\sigma(t) = X_*(t,0)\Phi(\varepsilon(t)) + \int_0^t \frac{\partial X_*}{\partial s}(t,s)\Phi(\varepsilon(t) - \varepsilon(s)) \,\mathrm{d}s, \tag{13}$$

which will be the subject of our analysis. For a non-aging medium, eqn (13) is simplified as follows:

$$\sigma(t) = [1 - Q_{*}(t)]\Phi(\varepsilon(t)) + \int_{0}^{t} \dot{Q}_{*}(t-s)\Phi(\varepsilon(t) - \varepsilon(s)) \,\mathrm{d}s, \tag{14}$$

where the superscript dot denotes the differentiation with respect to time.

A linear elastic spring with the constitutive eqn (9) is characterized by the strain energy density

$$\widetilde{W}(\varepsilon) = \int_0^{\varepsilon} E(0)\xi \,\mathrm{d}\xi = \frac{1}{2}E(0)\varepsilon^2. \tag{15}$$

By analogy with eqn (15), we write for a nonlinear elastic spring (10)

$$\widetilde{W}(\varepsilon) = \int_0^{\varepsilon} \Phi(\xi) \, \mathrm{d}\xi. \tag{16}$$

Since the function  $\Phi(\varepsilon)$  is odd, the function  $\tilde{W}(\varepsilon)$  is even, and we set

$$\widetilde{W}(\varepsilon) = \widetilde{W}(|\varepsilon|).$$

The strain energy density (per unit volume) of a system of parallel springs equals the sum of strain energy densities of separate springs. This assertion together with eqns (15) and (16) implies that for a linear viscoelastic medium

$$W(t) = \frac{1}{2}E(0)\{X_{*}(t,0)\varepsilon^{2}(t) + \int_{0}^{t} \frac{\partial X_{*}}{\partial s}(t,s)[\varepsilon(t) - \varepsilon(s)]^{2} ds\},$$
(17)

and for a nonlinear viscoelastic medium

$$W(t) = X_{*}(t,0)\tilde{W}(\varepsilon(t)) + \int_{0}^{t} \frac{\partial X_{*}}{\partial s}(t,s)\tilde{W}(\varepsilon(t) - \varepsilon(s)) ds$$
$$= X_{*}(t,0)\tilde{W}(|\varepsilon_{0}(t)|) + \int_{0}^{t} \frac{\partial X_{*}}{\partial s}(t,s)\tilde{W}(|\varepsilon_{s}(t)|) ds.$$
(18)

For a viscoelastic medium, the function W(t) depends on the strain  $\varepsilon(t)$  at the current instant t and on the entire history before that instant. Equation (17) was suggested as a strain energy density (the Lyapunov functional) for an aging linear viscoelastic solid by Dafermos (1970), while expression (18) is new.

It is easy to show that the stress  $\sigma(t)$  is expressed in terms of the strain energy density W(t) as

$$\sigma(t) = \frac{\partial W(t)}{\partial \varepsilon(t)},\tag{19}$$

see Truesdell (1975).

We do not intend to discuss thermodynamic restrictions imposed on the function  $X_*(t,s)$  referring, e.g., to Day (1972) and Drozdov and Kolmanovskii (1994), where this question has been already discussed. Nevertheless, it is of interest to present expressions for the rate of energy dissipation in a viscoelastic medium. According to the concept of adaptive links, the energy dissipated per unit volume and per unit time equals the energy of links located in the unit volume which break within the unit interval of time. Since the number of initial links collapsed during the interval [t, t+dt] equals

$$\frac{\partial X_*}{\partial t}(t,0)\,\mathrm{d}t,$$

and the number of links arisen within the interval [s, s+ds] and broken during the interval [t, t+dt] equals

$$\frac{\partial^2 X_*}{\partial t \partial s}(t,s) \,\mathrm{d}t \,\mathrm{d}s,$$

the rate of energy dissipation D for a nonlinear viscoelastic medium is calculated as follows :

$$D(t) = \frac{\partial X_*}{\partial t}(t,0)\tilde{W}(|\varepsilon_0(t)|) + \int_0^t \frac{\partial^2 X_*}{\partial t \partial s}(t,s)\tilde{W}(|\varepsilon_s(t)|) \,\mathrm{d}s.$$
(20)

For a linear viscoelastic medium, expression (20) is transformed into the formula

$$D(t) = \frac{1}{2} E(0) \left\{ \frac{\partial X_*}{\partial t}(t, 0) \varepsilon^2(t) + \int_0^t \frac{\partial^2 X_*}{\partial t \partial s}(t, s) [\varepsilon(t) - \varepsilon(s)]^2 \, \mathrm{d}s \right\},\tag{21}$$

which was discussed in detail by Arutyunyan and Drozdov (1992).

It is worth noting that eqn (13) is similar to the Leaderman model, see Leaderman (1943), to the Guth model, see Guth *et al.* (1946) and Rabotnov (1969), to the Schapery model, see Schapery (1964), and to the Findely model, see Findely *et al.* (1989). The above mentioned models and the model (13) are distinguished by the argument of the nonlinear function in the integrand: while those models require the nonlinear function  $\Phi$  to depend on  $\varepsilon(s)$  only, in our model  $\Phi$  depends on  $\varepsilon(t) - \varepsilon(s)$ . For the linear constitutive eqn (4) this difference is not significant, but for the nonlinear eqn (13) it becomes essential.

To the best of our knowledge, model (13) is the first constitutive model which employs the difference  $\varepsilon(t) - \varepsilon(s)$  in order to account for the effect of the strain history on stresses in 'physically nonlinear' media with small deformations. A similar variable, the so-called differential strain history, has been used in finite viscoelasticity from the 50s, see Green and Rivlin (1957), Coleman and Noll (1961), Bernstein (1966). In these works (and many others) the Weierstrass theorem was used to derive constitutive models at finite strains in the form of truncated Taylor series in multiple integrals. Despite their generality, these models cannot be reduced to the model (13), since our model contains a nonlinear function (11) with a weak singularity at zero.

In the general case, two different ways exist to account for the nonlinearity in constitutive relations. According to the first, a nonlinear behavior of adaptive links is introduced, while the reformation and breakage processes are assumed to be independent of stresses, see eqn (13). Such a hypothesis is called the separability principle for elastic and viscous effects.

According to the other approach, the process of replacing new links is assumed to depend on stress intensity in the medium, while the links can be linear or nonlinear. This implies a model, where the function X depends on variables t and s, as well as on the stress (or strain) intensity at some intermediate instant.

Phenomenological models for the effect of stresses (strains) on the function X for polymeric melts with finite deformations are suggested by Kaye and Kennett (1974), Wagner (1976), Wagner *et al.* (1979), Winter (1978).

Similar dependencies are employed in models based on the Doolittle concept of the free (freezed-in) volume. According to the free volume theory, the relaxation spectrum depends significantly on a scalar parameter (free volume), which, in turn, is a function of strains, temperature, and humidity at the current instant, see, e.g., Chengalva *et al.* (1995), Knauss and Emri (1987), Losi and Knauss (1992), Schapery (1964) for details.

Another way to describe the effect of stresses on the function X goes back to Eyring (1936), who proposed to treat inelastic deformation of a solid as a kinetic process. The processes of formation and destruction of links between polymeric molecules are assumed to be characterized by some activation (deactivation) energies and initiation times, which determine the relaxation spectrum of a viscoelastic material. This concept is discussed in detail by Drozdov and Kalamkarov (1995b), where the Eyring concept is applied to describe the viscoelasto-plastic behavior of polypropylene. For this purpose, a system of ordinary differential equations (typical of chemical kinetics) is developed for the numbers of links of different classes, and coefficients of these equations (the corresponding activation energies) are found by using the standard creep tests.

The present work is concerned with a constitutive model which obeys the separability principle. This model requires the minimal number of adjustable parameters to be found to fit experimental data compared with models, where the relaxation measure depends on stresses. Experimental data presented in Section 4 demonstrate that despite its simplicity, the constitutive model (13) describes adequately the mechanical response in a number of polymeric materials.

# 3. PRESENTATION OF THE FUNCTION X(t, s)

Let us now assume that the springs can be divided into two groups: the springs of the first group are not involved in the process of replacement, whilst the springs of the other group take part in this process. We denote by  $\chi \in [0, 1]$  concentration of springs of the first type, and by  $1 - \chi$  concentration of springs of the other type.

Let  $g_s(t-s)$  be the relative number of springs which have arisen at instant s and have collapsed before instant t. Since we set  $X_*(0,0) = 1$  for definiteness, we can write

$$X_{*}(t,0) = \chi + (1-\chi)[1-g_{0}(t)], \quad \frac{\partial X_{*}}{\partial s}(t,s) = H(s)[1-g_{s}(t-s)], \quad (22)$$

where

$$H(s) = \frac{\partial X_*}{\partial s}(s, s) \tag{23}$$

2691

is the rate of formation for new links. According to eqn (7), H(s)ds new springs join the system within the interval [s, s+ds].

The total number of springs at instant t can be calculated by the formula

$$X_{*}(t,t) = X_{*}(t,0) + \int_{0}^{t} \frac{\partial X_{*}}{\partial s}(t,s) \,\mathrm{d}s.$$
(24)

Substitution of expressions (22) and (23) into eqn (24) with the use of eqn (3) implies that

$$E_{*}(t) = \chi + (1-\chi)[1-g_{0}(t)] + \int_{0}^{t} H(s)[1-g_{s}(t-s)] \,\mathrm{d}s.$$
 (25)

For a given function  $E_*(t)$ , eqn (25) imposes restrictions on both H(t) and  $g_s(t-s)$ . In the general case, they are not sufficient for these functions to be found. However, for non-aging media, explicit expressions for H(s) and  $g_s(t-s)$  can be developed from eqn (25). Indeed, for a non-aging material,

$$E_{*}(t) = 1, \quad H(s) = \text{const.}, \quad g_{s}(t-s) = g_{0}(t-s).$$
 (26)

Substitution of expressions (26) into eqn (25) yields

$$(1-\chi)g_0(t) = H \int_0^t [1-g_0(t-s)] \,\mathrm{d}s.$$
 (27)

It follows from eqn (27) that

$$\frac{\mathrm{d}g_0}{\mathrm{d}t}(t) = \frac{H}{1-\chi} [1-g_0(t)], \quad g_0(0) = 0.$$
<sup>(28)</sup>

The solution of eqn (28) reads

$$g_0(t) = 1 - \exp(-\frac{H}{1-\chi}t).$$
 (29)

To find the function  $X_*(t, s)$ , we write

$$X_*(t,s) = X_*(t,t) - \int_s^t \frac{\partial X_*}{\partial \tau}(t,\tau) \,\mathrm{d}\tau.$$
(30)

Substitution of expressions (3), (22), (26), and (29) into eqn (30) yields

$$X_{*}(t,s) = E_{*}(t) - \int_{s}^{t} H(\tau) [1 - g_{\tau}(t - \tau)] d\tau$$
  
=  $1 - H \int_{s}^{t} \exp\left[-\frac{H}{1 - \chi}(t - \tau)\right] d\tau$   
=  $1 - (1 - \chi) \left[1 - \exp\left(-\frac{H}{1 - \chi}(t - s)\right)\right].$  (31)

Equation (31) provides the requested presentation of the relaxation kernel for a non-aging viscoelastic medium in terms of the rate of reformation H for adaptive links and the concentration  $\chi$  of non-replacing links.

It follows from eqns (2) and (31) that the only relaxation measure for a non-aging viscoelastic material coincides with the relaxation measure of the standard viscoelastic solid, see Christensen (1982),

$$Q_{*}(t,s) = (1-\chi) \left\{ 1 - \exp\left[ -\frac{H}{1-\chi}(t-s) \right] \right\}.$$
 (32)

To account for more complicated relaxation measures, we should assume that M different classes of links exist between polymeric molecules. This hypothesis is in fair agreement with experimental observations, where 'elastically active long chains', 'elastically active slide and entanglement chains', 'elastically active short chains', etc. are distinguished, see, e.g., He and Song (1993).

Denote by  $\eta^{(m)}$  concentration of the *m*th class of links (the ratio of the number of links in the *m*th class to the total number of links), by  $\chi^{(m)}$  concentration of non-replacing links, and by  $H^{(m)}(s)$  and  $g_s^{(m)}(t-s)$  the rates of reformation and breakage (m = 1, ..., M). The parameters  $\eta^{(m)}$  are assumed to be independent of time. To derive the balance law for *m*th class of links, similar to eqn (24), we state that the total number of links of *m*th class at instant t

$$\eta^{(m)}X_{*}(t,t) = \eta^{(m)}E_{*}(t)$$

equals the sum of the number of the initial links existing at instant t

$$\eta^{(m)}\chi^{(m)} + \eta^{(m)}(1-\chi^{(m)})[1-g_0^{(m)}(t)] = \eta^{(m)}\{\chi^{(m)} + (1-\chi^{(m)})[1-g_0^{(m)}(t)]\}$$

and the number of links arisen within the interval (0, t] and existing at instant t. The latter value can be calculated as follows. Within the interval [s, s+ds],

$$\eta^{(m)}H^{(m)}(s)\,\mathrm{d}s$$

new links of mth class arise. At instant t, their number reduces to

$$\eta^{(m)}H^{(m)}(s)[1-g_s^{(m)}(t-s)]\,\mathrm{d}s. \tag{33}$$

Summing up these amounts for various intervals, we obtain

$$\int_0^t \eta^{(m)} H^{(m)}(s) [1 - g_s^{(m)}(t-s)] \,\mathrm{d}s.$$

As a result, we arrive at the integral equations

$$E_{*}(t) = \chi^{(m)} + (1 - \chi^{(m)})[1 - g_{0}^{(m)}(t)] + \int_{0}^{t} H^{(m)}(s)[1 - g_{s}^{(m)}(t - s)] \,\mathrm{d}s, \tag{34}$$

which should be fulfilled for m = 1, ..., M.

It follows from eqns (7) and (33) that

$$\frac{\partial X_*}{\partial s}(t,s) = \sum_{m=1}^M \eta^{(m)} H^{(m)}(s) [1 - g_s^{(m)}(t-s)].$$
(35)

2693

Substitution of expressions (3) and (35) into eqn (30) implies that

$$X_{*}(t,s) = E_{*}(t) - \sum_{m=1}^{M} \eta^{(m)} \int_{s}^{t} H^{(m)}(\tau) [1 - g_{\tau}(t - \tau)] d\tau.$$
(36)

For a non-aging material (26), eqn (34) are solved explicity, and we obtain

$$g_0^{(m)}(t) = 1 - \exp\left(-\frac{H^{(m)}}{1 - \chi^{(m)}}t\right).$$
(37)

Substitution of expressions (26) and (37) into eqn (36) yields

$$X_{*}(t,s) = 1 - \sum_{m=1}^{M} \eta^{(m)} (1 - \chi^{(m)}) \left[ 1 - \exp\left(-\frac{H^{(m)}}{1 - \chi^{(m)}}(t - s)\right) \right].$$
(38)

It follows from eqns (2) and (38) that

$$Q_{*}(t,s) = \sum_{m=1}^{M} \mu^{(m)} \left[ 1 - \exp\left(-\frac{t-s}{T^{(m)}}\right) \right] = \sum_{m=1}^{M} \mu^{(m)} [1 - \exp(-\gamma^{(m)}(t-s))], \quad (39)$$

where

$$\mu^{(m)} = \eta^{(m)}(1 - \chi^{(m)}), \quad T^{(m)} = \frac{1 - \chi^{(m)}}{H^{(m)}}, \quad \gamma^{(m)} = \frac{H^{(m)}}{1 - \chi^{(m)}}.$$
(40)

Equation (39) implies that the relaxation measure of an arbitrary non-aging viscoelastic material can be presented as a sum of exponential functions with positive coefficients.

The relaxation measure (39) is determined by the number M of different classes of links, by the characteristic times of relaxation  $T^{(m)}$ , and by the characteristic viscosities  $\mu^{(m)}$ .

There are two ways to find the integer M. The first requires an adequate information regarding the chemistry of curing. According to it, M equals the number of (chemically) different kinds of entanglements and crosslinks between long polymeric molecules, see, e.g., He and Song (1993). According to the other (phenomenological) approach, the parameter M equals the number of terms in the truncated Prony series (39), which are necessary to ensure an adequate accuracy in fitting experimental data. As common practice, this number is not very large (2–3) for short-term relaxation tests, and it reaches 10–15 for long-term relaxation tests, see, e.g., Drozdov (1996a) for a discussion of this issue.

For given  $\mu^{(m)}$  and  $T^{(m)}$ , eqns (40) do not permit  $\eta^{(m)}$ ,  $\chi^{(m)}$ , and  $H^{(m)}$  to be calculated uniquely. For isothermal processes, knowledge of the parameters  $\eta^{(m)}$ ,  $\chi^{(m)}$ , and  $H^{(m)}$  in separate is not necessary at all, since only their combinations  $\mu^{(m)}$  and  $T^{(m)}$  determine the constitutive equations on the macro-scale. Another situation arises when non-isothermal loading is analyzed. Relaxation curves obtained at various temperatures show that the concentrations  $\chi^{(m)}$  of non-collapsing links (i) coincide for different classes of links, (ii) depend significantly on the temperature  $\Theta$ , and (iii) vanish at the rubber-glass transition temperature. On the other hand, the parameters  $\eta^{(m)}$  are found to be temperature-independent. Based on these hypotheses, all the parameters  $\eta^{(m)}$ ,  $\chi^{(m)}$ , and  $H^{(m)}$  may be calculated with the use of experimental data obtained in the standard relaxation tests at various temperatures. We do not dwell on this issue, referring to Drozdov (1996b), where this approach is discussed in detail for constitutive equations in linear thermoviscoelasticity.

Differentiation of eqn (39) with respect to s yields

$$R(t,s) = E(0) \sum_{m=1}^{M} \frac{\mu^{(m)}}{T^{(m)}} \exp\left(-\frac{t-s}{T^{(m)}}\right),$$
(41)

where R(t, s) is the relaxation kernel. Finally, by assuming that  $\mu^{(m)} \approx \mu(T^{(m)})(T^{(m+1)} - T^{(m)})$ and approaching the limit as  $M \to \infty$  in eqn (41), we arrive at the following presentation of the relaxation kernel for a non-aging medium:

$$R(t,s) = E(0) \int_0^\infty \frac{\mu(T)}{T} \exp\left(-\frac{t-s}{T}\right) dT,$$
(42)

where  $\mu(T)$  is a non-negative relaxation spectrum. The mechanical meaning of the positivity condition for the relaxation spectrum  $\mu(T)$  was discussed by Beris and Edwards (1993).

# 4. DETERMINATION OF THE MODEL PARAMETERS

Let us consider the standard relaxation test

$$\varepsilon(t) = \begin{cases} 0 & t < 0, \\ \varepsilon & t \ge 0. \end{cases}$$
(43)

Substitution of expression (43) into the constitutive eqn (13) yields

$$\sigma_{\varepsilon}(t) = [1 - Q_{*}(t)]\Phi(\varepsilon).$$
(44)

Bearing in mind the equality

$$Q_*(0) = 0, (45)$$

we present eqn (44) as follows:

$$\sigma_{\varepsilon}(t) = [1 - Q_{*}(t)]\sigma_{\varepsilon}(0),$$

which implies that

$$Q_*(t) = 1 - \frac{\sigma_{\varepsilon}(t)}{\sigma_{\varepsilon}(0)}.$$
(46)

We consider experimental data obtained by Smart and Williams (1972) for polypropylene specimens and by Partom and Schanin (1983) for polyurethane specimens. First, we calculated the ratios  $r_{\varepsilon_1,\varepsilon_2}(t)$  of stresses corresponding to different strains  $\varepsilon_1$  and  $\varepsilon_2$ . According to eqn (44), these ratios should be independent of time t, provided the function



Fig. 1. The ratios of stresses r vs time t (min) in relaxation tests at various strains  $\varepsilon$ . Circles and asterisks correspond to experimental data for a polypropylene specimen (A) and for a polyurethane specimen (B). Polypropylene-unfilled circles:  $r_{0.01,0.02}$ , filled circles:  $r_{0.01,0.03}$ , asterisks:  $r_{0.01,0.04}$ ; poly-urethane-unfilled circles:  $r_{0.02,0.03}$ , filled circles:  $r_{0.02,0.04}$ .

 $Q_*(t)$  is independent of strains. The dependencies plotted in Fig. 1 demonstrate that the process of replacing adaptive links is independent of strains. This is a significant advantage of our model, since other nonlinear constitutive models imply that the strain intensity affects significantly the reformation and breakage processes.

Since the relaxation measure  $Q_*(t)$  is independent of strains, it may be determined with the use of eqn (46) for an arbitrary strain  $\varepsilon$ . For convenience, we choose  $\varepsilon = 0.01$  for polypropylene specimens and  $\varepsilon = 0.02$  for polyurethane specimens (the lowest level of strains in appropriate tests). For these strains, we set  $\sigma_{0.01}(0) = 12.4$  (MPa) for polypropylene and  $\sigma_{0.02}(0) = 4.24$  (MPa) for polyurethane. These data are consistent with the Young moduli obtained in creep tests for a polypropylene monofilament, see Ward and Wolfe (1966), and for solid polyurethane, see Partom and Schanin (1983).

Since the number of experimental data in any relaxation test is comparatively small (about 10), we confine ourselves to M = 2 in eqn (39). Experimental data and their approximations by the exponential function (39) are plotted in Fig. 2.

To find the function  $\Phi(\varepsilon)$ , we use the equality

$$\sigma_{\varepsilon}(0) = \Phi(\varepsilon), \tag{47}$$

which follows from eqns (44) and (45). The corresponding dependencies are plotted in Fig. 3.

The relaxation curves for polypropylene and polyurethane together with their prediction by the model (13) are presented in Figs 4 and 5. The curves demonstrate fair agreement between experimental data and results of the numerical simulation.

To validate the model in experiments where both stresses and strains depend on time, we consider a loading/unloading test with a piece-wise constant rate of strain  $\dot{\varepsilon}$ 

$$\dot{\varepsilon}(t) = \begin{cases} \dot{\varepsilon}_0 & 0 \le t < T_0, \\ -\dot{\varepsilon}_0 & T_0 \le t \le 2T_0, \end{cases}$$
(48)

where  $\dot{\epsilon}_0$  and  $T_0$  are constants. Experimental data and results of numerical simulation with the use of eqn (13) are plotted in Fig. 6. According to this figure, our model ensures fair



Fig. 2. The dimensionless relaxation measure  $Q_{*}$  vs time t (min). Circles: experimental data for a polypropylene specimen (A) and for a polyurethane specimen (B). Solid lines: their approximation by the exponential function (39) with  $\mu_{1} = 0.210$ ,  $\mu_{2} = 0.210$ ,  $\gamma_{1} = 0.06$  (min<sup>-1</sup>),  $\gamma_{2} = 1.90$  (min<sup>-1</sup>) for polypropylene and  $\mu_{1} = 0.258$ ,  $\mu_{2} = 0.312$ ,  $\gamma_{1} = 0.03$  (min<sup>-1</sup>),  $\gamma_{2} = 1.70$  (min<sup>-1</sup>) for polyurethane.



Fig. 3. The function  $\Phi(\varepsilon)$  (MPa). Circles: experimental data, solid lines: their approximation by the power-law function (11). Curve 1: a polypropylene specimen with A = 157.48 (MPa) and  $\alpha = 0.5519$ ; curve 2: a polyurethane specimen with A = 16.88 (MPa) and  $\alpha = 0.3525$ .

prediction of experimental data under time-dependent loading without any additional fitting of adjustable parameters.

Two sources of small deviations between experimental data and results of numerical simulation may be distinguished. The first may explain discrepancies between experimental data and their prediction in the region of small strains (less than 0.5 per cent). As is well-known, majority of polymeric materials demonstrate the linear response at very small strains. Since the power function (11) is not reduced to the linear dependence in the vicinity of the point  $\varepsilon = 0$ , the use of this function can cause a bias to larger stresses which is demonstrated in Fig. 6. To avoid these discrepancies, a more sophisticated function  $\Phi(\varepsilon)$ 



Fig. 4. The stress  $\sigma$  (MPa) vs time t (min) in relaxation test. Large circles: experimental data for polypropylene specimens; small circles: prediction of the model. Curve 1:  $\varepsilon = 0.01$ , curve 2:  $\varepsilon = 0.03$ .



Fig. 5. The stress  $\sigma$  (MPa) vs time t (min) in relaxation tests. Large circles : experimental data for polyurethane specimens ; small circles : prediction of the model. Curve 1 :  $\varepsilon = 0.02$ , curve 2 :  $\varepsilon = 0.03$ , curve 3 :  $\varepsilon = 0.04$ .

should be chosen, whose derivative with respect to  $\varepsilon$  (Young's modulus) is finite at the point  $\varepsilon = 0$ .

The discrepancies may be also caused by an insufficient number of terms (M = 2) in the truncated Prony series (39). To make the numerical prediction more accurate, the number of different classes of links should be increased, which permits the material viscosities  $\mu^{(m)}$  and the relaxation times  $T^{(m)}$  to be calculated more precisely.

The above refinements lead to an essential increase in the number of material parameters to be found by fitting experimental data, and we do not dwell on them in the present study.



Fig. 6. The stress  $\sigma$  (MPa) vs strain  $\varepsilon$  in loading/unloading tests with  $\dot{\varepsilon}_0 = 0.0033$  (min<sup>-1</sup>) and  $T_0 = 6$  (min). Large circles : experimental data ; small circles : prediction of the model.

# 5. THE CONSTITUTIVE EQUATIONS FOR THREE-DIMENSIONAL LOADING

In this section we generalize the model to three-dimensional loading using an approach suggested by Drozdov (1993). For simplicity we confine ourselves to incompressible media.

Let us consider uniaxial tension of a viscoelastic rod as a three-dimensional deformation. Points of the rod refer to Cartesian coordinates  $\{x_i\}$ , where the axis  $x_1$  coincides with the longitudinal axis of the rod, while the axes  $x_2$  and  $x_3$  are located in the crosssectional plane. In an incompressible material, the strain tensor  $\hat{\varepsilon}(t)$  has the following nonzero components:

$$\varepsilon_{11}(t) = \varepsilon(t), \quad \varepsilon_{22}(t) = \varepsilon_{33}(t) = -\frac{1}{2}\varepsilon(t).$$

It follows from these equalities that the deviatoric part  $\hat{e}(t)$  of the strain tensor coincides with  $\hat{e}(t)$  and that the strain intensity

$$\Gamma_{s}(t) = \sqrt{\frac{2}{3}I_{1}(\hat{e}_{s}^{2}(t))}$$
(49)

is calculated as

$$\Gamma_s(t) = |\varepsilon_s(t)| = |\varepsilon(t) - \varepsilon(s)|.$$
(50)

Here  $I_1$  stands for the first invariant of a tensor. Substituting expression (50) into eqn (18), we find the strain energy density (per unit volume) W(t) in the form

$$W(t) = X_*(t,0)\tilde{W}(\Gamma_0(t)) + \int_0^t \frac{\partial X_*}{\partial s}(t,s)\tilde{W}(\Gamma_s(t)) \,\mathrm{d}s.$$
(51)

By analogy with eqn (20), the rate of energy dissipation (per unit volume) is calculated as

$$D(t) = \frac{\partial X_*}{\partial t}(t,0) \, \widetilde{W}(\Gamma_0(t)) + \int_0^t \frac{\partial^2 X_*}{\partial t \partial s}(t,s) \, \widetilde{W}(\Gamma_s(t)) \, \mathrm{d}s.$$

In an incompressible viscoelastic medium, the stress tensor  $\hat{\sigma}(t)$  is presented as the sum

$$\hat{\sigma}(t) = -p(t)\hat{I} + \hat{S}(t), \qquad (52)$$

2699

where p is pressure,  $\hat{I}$  is the unit tensor, and the deviatoric part  $\hat{S}(t)$  of the stress tensor is calculated by the formula similar to eqn (19)

$$\hat{S}(t) = \frac{\partial W(t)}{\partial \hat{e}(t)}.$$
(53)

According to Lurie (1990), we write

$$\frac{\partial\Gamma_s(t)}{\partial\hat{e}(t)} = \frac{1}{3\Gamma_s(t)} \frac{\partial I_1(\hat{e}_s^2(t))}{\partial\hat{e}_s(t)} = \frac{2}{3\Gamma_s(t)} \hat{e}_s(t) = \frac{2}{3\Gamma_s(t)} [\hat{e}(t) - \hat{e}(s)].$$
(54)

It follows from eqns (51), (53), and (54) that

$$\hat{S}(t) = \frac{2}{3} \bigg\{ X_{*}(t,0) \frac{W'(\Gamma_{0}(t))}{\Gamma_{0}(t)} \hat{e}(t) + \int_{0}^{t} \frac{\partial X_{*}}{\partial s}(t,s) \frac{W'(\Gamma_{s}(t))}{\Gamma_{s}(t)} [\hat{e}(t) - \hat{e}(s)] \, \mathrm{d}s \bigg\},$$
(55)

where the prime denotes differentiation. Finally, substituting expression (55) into eqn (52) and bearing in mind eqn (16), we obtain the constitutive equation of an aging incompressible nonlinear viscoelastic medium

$$\hat{\sigma}(t) = -p(t)\hat{I} + \frac{2}{3} \bigg\{ X_*(t,0)\Psi(\Gamma_0(t))\hat{e}(t) + \int_0^t \frac{\partial X_*}{\partial s}(t,s)\Psi(\Gamma_s(t))[\hat{e}(t) - \hat{e}(s)] \,\mathrm{d}s \bigg\}, \quad (56)$$

where

$$\Psi(\Gamma) = \frac{W'(\Gamma)}{\Gamma} = \frac{\Phi(\Gamma)}{\Gamma}.$$
(57)

In particular, for the nonlinear function (11), eqn (57) implies that

$$\Psi(\Gamma) = A\Gamma^{\alpha-1}.$$
 (58)

# 6. TORSION OF A CONIC PIPE

As an example of application of the constitutive model (56), we consider torsion of a conic pipe with angles  $\vartheta_1$  and  $\vartheta_2$ . The pipe is deformed under the action of torques M = M(t) applied to its edges which are located at distances  $b_1$  and  $b_2$  from the apex, see Fig. 7. The



Fig. 7. A conic pipe.

lateral surfaces of the pipe are stress-free, body forces are absent. The pipe obeys the constitutive eqn (56) with the nonlinearity (58). The problem is of interest for designers of pipelines, where conic members are employed to connect pipes with different cross-sections.

Introduce a cylindrical coordinate frame  $\{r, \phi, z\}$  with the origin at the apex and unit vectors  $\bar{e}_r$ ,  $\bar{e}_{\phi}$ ,  $\bar{e}_z$ . We assume that components  $u_r$ ,  $u_{\phi}$ ,  $u_z$  of the displacement vector  $\bar{u}$  are presented in the form

$$u_r = 0, \quad u_{\phi} = a(t)rF(Y), \quad u_z = 0.$$
 (59)

Here a(t) is an unknown function of time, F(Y) is an unknown function of Y, where  $Y = r^2 + z^2$ . It follows from eqn (59) that the non-zero components of the strain tensor  $\hat{\varepsilon}$  equal

$$\varepsilon_{\phi r} = a(t)r^2 F'(Y), \quad \varepsilon_{\phi z} = a(t)rzF'(Y). \tag{60}$$

Equation (60) imply that torsion of a conic pipe is an isochoric deformation. Therefore, the non-zero components of the deviatoric part  $\hat{e}$  of the strain tensor coincide with the non-zero components of the strain tensor  $\hat{e}$ , and pressure p vanishes.

Combining eqns (49) and (60), we find that

$$\Gamma^{2}(t) = \frac{4}{3} [a(t) - a(s)]^{2} r^{2} Y [F'(Y)]^{2}.$$

We assume the derivative of F(Y) to be positive (this assertion will be checked below) and obtain

$$\Gamma(t) = \sqrt{\frac{4Y}{3}} |a(t) - a(s)| rF'(Y).$$
(61)

Substitution of expressions (60) and (61) into the constitutive equations (56) and (58) yields the following non-zero components of the stress tensor  $\hat{\sigma}$ :

$$\sigma_{\phi r} = \frac{1}{2} (\frac{4}{3})^{(\alpha+1)/2} A \Lambda_{\alpha}(t) r^{\alpha+1} Y^{(\alpha-1)/2} [F'(Y)]^{\alpha},$$
  
$$\sigma_{\phi z} = \frac{1}{2} (\frac{4}{3})^{(\alpha+1)/2} A \Lambda_{\alpha}(t) r^{\alpha} z Y^{(\alpha-1)/2} [F'(Y)]^{\alpha},$$
 (62)

where

$$\Lambda_{\alpha}(t) = X_{*}(t,0) |a(t)|^{\alpha} \operatorname{sign} [a(t)] + \int_{0}^{t} \frac{\partial X_{*}}{\partial s}(t,s) |a(t) - a(s)|^{\alpha} \operatorname{sign} [a(t) - a(s)] \, \mathrm{d}s.$$
(63)

The only equilibrium equation

$$\frac{\partial \sigma_{\phi r}}{\partial r} + \frac{\partial \sigma_{\phi z}}{\partial z} + 2\frac{\sigma_{\phi r}}{r} = 0$$

can be rewritten as

$$\frac{\partial}{\partial r}(r^2\sigma_{\phi r}) + \frac{\partial}{\partial z}(r^2\sigma_{\phi z}) = 0.$$
(64)

We substitute expressions (62) into eqn (64) and transform the obtained equality. After simple algebra, we find that

$$2\alpha YF'' + (3+2\alpha)F' = 0.$$
 (65)

2701

The general solution of eqn (65) is

$$F(Y) = C_1 - \frac{\alpha}{3} C_2 Y^{-3/2\alpha},$$
 (66)

where  $C_1$  and  $C_2$  are arbitrary constants.

In eqn (59), the function F(Y) is defined up to an arbitrary multiplier (because the function a(t) is unknown as well). Thus, without loss of generality we may set  $C_2 = b_2^{3/\alpha}$ . The constant  $C_1$  is found by assuming additionally that some points of the pipe are fixed. For example, if the points of circumference BB' remain motionless, see Fig. 7, eqn (59) and (66) imply that

$$C_1 = \frac{\alpha}{3} \cos^{3/\alpha} \vartheta_1. \tag{67}$$

It follows from eqn (66) that the derivative of the function F(Y) is positive (which confirms the above assumption) and

$$[F'(Y)]^{\alpha} = 2^{-\alpha} b_2^3 Y^{-(\alpha+3/2)}.$$

Substitutive of this expression into eqn (62) implies that

$$\sigma_{\phi r} = 3^{-(\alpha+1)/2} A b_2^3 \Lambda_{\alpha}(t) r^{\alpha+1} (r^2 + z^2)^{-(\alpha+4)/2},$$
  

$$\sigma_{\phi z} = 3^{-(\alpha+1)/2} A b_2^3 \Lambda_{\alpha}(t) r^{\alpha} z (r^2 + z^2)^{-(\alpha+4)/2}.$$
(68)

Expression (68) satisfies the boundary conditions on the lateral surfaces of the pipe

$$(\sigma_{\phi r}\cos\vartheta - \sigma_{\phi z}\sin\vartheta)|_{\vartheta=\vartheta_1} = 0, \quad (\sigma_{\phi r}\cos\vartheta - \sigma_{\phi z}\sin\vartheta)|_{\vartheta=\vartheta_2} = 0.$$

The boundary conditions on the edges of the pipe are written in the integral form

$$M(t) = 2\pi \int_{b_1 \tan \theta_1}^{b_1 \tan \theta_2} \sigma_{\phi z}(t, r, b_1) r^2 \, \mathrm{d}r = 2\pi \int_{b_2 \tan \theta_1}^{b_2 \tan \theta_2} \sigma_{\phi z}(t, r, b_2) r^2 \, \mathrm{d}r.$$
(69)

We substitute expression (68) into eqn (69) and introduce the new variables  $r = b_1 \tan \theta$  in the first integral and  $r = b_2 \tan \theta$  in the other integral. After simple algebra, we find that

$$M(t) = 2 \cdot 3^{-(\alpha+1)/2} \pi A b_2^3 J_{\alpha}(\vartheta_1, \vartheta_2) \Lambda_{\alpha}(t),$$

$$\tag{70}$$

where

$$J_{\alpha}(\vartheta_1,\vartheta_2)=\int_{\vartheta_1}^{\vartheta_2}\sin^{\alpha+2}\theta\,\mathrm{d}\theta.$$

Combining eqn (63) and (70), we arrive at the nonlinear integral equation

$$X_{*}(t,0)|a(t)|^{\alpha} \operatorname{sign}[a(t)] + \int_{0}^{t} \frac{\partial X_{*}}{\partial s}(t,s)|a(t) - a(s)|^{\alpha} \operatorname{sign}[a(t) - a(s)] \,\mathrm{d}s = m(t) \quad (71)$$

with



Fig. 8. Level curves for the stress  $\sigma_{\phi r}$  in a polyurethane pipe with  $b_1 = 0.03$  (m),  $b_2 = 0.08$  (m),  $\vartheta_1 = 30^\circ$ ,  $\vartheta_2 = 60^\circ$  under the action of torque M = 2000 (N·m). The curve with number *n* corresponds to  $\sigma_{\phi r} = 0.5n$  (MPa).

$$m(t) = \frac{3^{(\alpha+1)/2} M(t)}{2\pi A b_2^3 J_{\alpha}}$$

For a non-aging viscoelastic material, eqn (71) is simplified, and we obtain

$$[1 - Q_*(t)] |a(t)|^{\alpha} \operatorname{sign} [a(t)] + \int_0^t \dot{Q}_*(t-s) |a(t) - a(s)|^{\alpha} \operatorname{sign} [a(t) - a(s)] \, \mathrm{d}s = m(t).$$
(72)

It follows from eqns (68) and (70) that

$$\sigma_{\phi r} = \frac{M}{2\pi J_{\alpha}} \frac{r^{\alpha+1}}{(r^2+z^2)^{(\alpha+4)/2}}, \quad \sigma_{\phi z} = \frac{M}{2\pi J_{\alpha}} \frac{r^{\alpha} z}{(r^2+z^2)^{(\alpha+4)/2}}.$$
(73)

According to eqn (73), stress distribution in a non-linear viscoelastic pipe coincides with stress distribution in an appropriate elastic pipe. For a fixed geometry of the pipe, the stress distribution is determined by the only material parameter  $\alpha$ . Stresses calculated by formula (73) are plotted in Figs 8 and 9. We draw the following conclusions:

- the stresses  $\sigma_{\phi r}$  and  $\sigma_{\phi z}$  are very close to each other in the entire pipe except for a narrow region near the upper edge;
- these stresses change rather slowly for large z values. With a decrease in z values, the gradient of stresses increases rapidly.

To analyze the effect of torque M and the geometrical parameters  $\vartheta_1$  and  $\vartheta_2$  on displacements in the pipe, the Volterra integral equation (72) is solved numerically. The function a(t) is plotted in Figs 10–12.



Fig. 9. Level curves for the stress  $\sigma_{\phi_2}$  in a polyurethane pipe with  $b_1 = 0.03$  (m),  $b_2 = 0.08$  (m),  $\vartheta_1 = 30^\circ$ ,  $\vartheta_2 = 60^\circ$  under the action of torque M = 2000 (N·m). The curve with number *n* corresponds to  $\sigma_{\phi_2} = 0.5n$  (MPa).



Fig. 10. The dimensionless function a vs time t (min) for a polyurethane pipe with  $\vartheta_1 = 30^\circ$  and  $\vartheta_2 = 60^\circ$  under the torque  $M(t) = M_0 + M_1 t$  with  $M_0 = 2560$  (N·m) and various  $M_1$  (N·m/min). Curve 1:  $M_1 = 0.0$ , curve 2:  $M_1 = 2.56$ , curve 3:  $M_1 = 5.12$ , curve 4:  $M_1 = 25.6$ , curve 5:  $M_1 = 51.2$ , curve 6:  $M_1 = 102.4$ .

Figure 10 shows that for small torques M, the dependence of the displacement vector  $\bar{u}$  on M is practically linear: any increase in the derivative  $M_1$  of the torque leads to a proportional increase in a for any instant t after some transition period. Curve 6 in this figure shows that such a proportionality is limited to comparatively small torques M: for relatively large loads, the function a grows essentially in time.

Figures 11 and 12 demonstrate creep in the pipe under the action of a fixed torque. We plot results of numerical calculations for a hollow truncated cone in Fig. 11 and for a monolithic truncated cone in Fig. 12. The geometrical parameters affect significantly the displacement field. For any instant t, the displacements decrease rapidly with the growth of the angle  $\vartheta_2$ . For example, for  $\vartheta_1 = 30^\circ$ , the growth of  $\vartheta_2$  within the interval from  $40^\circ$  to  $50^\circ$  leads to a decrease of displacements by more than 15 times.



Fig. 11. The dimensionless function a vs time t (min) for a polyurethane pipe with  $\vartheta_1 = 30^\circ$  and  $b_2 = 0.08$  (m) under the constant torque M = 1024 (N·m). Curve 1:  $\vartheta_2 = 40^\circ$ , curve 2:  $\vartheta_2 = 45^\circ$ , curve 3:  $\vartheta_2 = 50^\circ$ .



Fig. 12. The dimensionless function a vs time t (min) for a polyurethane truncated cone  $(\vartheta_1 = 0)$ with  $b_2 = 0.08$  (m) under the constant torque M = 1024 (N·m). Curve 1:  $\vartheta_2 = 40^\circ$ , curve 2:  $\vartheta_2 = 45^\circ$ , curve 3:  $\vartheta_2 = 50^\circ$ , curve 4:  $\vartheta_2 = 60^\circ$ .

# 7. THE CORRESPONDENCE PRINCIPLE IN NONLINEAR VISCOELASTICITY

Torsion of a conic pipe demonstrate that stresses in a viscoelastic medium coincide with stresses in an appropriate elastic solid, while displacements in a viscoelastic medium are proportional to displacements in an elastic solid with a time-dependent coefficient of proportionality, provided the surface tension is given on the entire boundary of the body and is time-independent. Such an assertion is called the correspondence principle (the Alfrey theorem). Our objective now is to formulate and prove two correspondence principles for viscoelastic media obeying the constitutive model (56) and to analyze restrictions on the nonlinearity (57) imposed by these principles.

Theorem 1. Let continuously differentiable functions  $\psi$  and  $\Xi$  exist such that for any  $\beta$  and  $\Gamma$ 

$$\Psi(\beta\Gamma) = \psi(\beta)\Xi(\Gamma). \tag{74}$$

Suppose that inertia forces can be neglected, a body force  $\overline{B}$  is given, a surface traction  $\overline{b}$  is prescribed on the entire surface of a solid, and the vectors  $\overline{B}$  and  $\overline{b}$  are independent of time. Then the stress tensor in the aging nonlinear viscoelastic body with constitutive equation (56) coincides with the stress tensor in a nonlinear elastic medium with the constitutive law

$$\hat{\sigma}(t) = -p(t)\hat{I} + \frac{2}{3}\Psi(\Gamma_0(t))\hat{e}(t).$$
(75)

The displacement vector  $\tilde{u}_v(t)$  in the aging viscoelastic solid is proportional to the displacement vector  $\tilde{u}_e$  in the elastic medium

$$\bar{u}_v(t) = \kappa(t)\bar{u}_e,$$

where the function  $\kappa(t)$  satisfies the nonlinear integral equation

$$X_{*}(t,0)\psi(|\kappa(t)|)\kappa(t) + \int_{0}^{t} \frac{\partial X_{*}}{\partial s}(t,s)\psi(|\kappa(t)-\kappa(s)|)[\kappa(t)-\kappa(s)] \,\mathrm{d}s = 1.$$
(76)

Theorem 2. Let eqn (74) be satisfied. Suppose that inertia forces can be neglected, body

forces vanish, displacements  $\overline{U}$  are given on the entire surface of a body and are timeindependent. Then the displacement vector  $\overline{u}_v$  in the viscoelastic medium (56) coincides with the displacement vector  $\overline{u}_e$  in the elastic solid (75), whereas the stress tensor  $\sigma_v(t)$  in the viscoelastic solid is proportional to the stress tensor  $\sigma_e$  in the elastic medium

$$\sigma_v(t) = X_*(t,0)\sigma_e. \tag{77}$$

To prove these assertions, it suffices to substitute expressions (76) and (77) into the governing equations and boundary conditions for a viscoelastic medium and check that these equalities turn into identities provided the elastic displacements and stresses satisfy the same governing equations.

We do not dwell on this issue and instead concentrate on the description of functions which satisfy eqn (74). The most surprising result is that despite the presence of two arbitrary functions in the right-hand side of this functional relationship, the power-law function (58) provides the only solution of eqn (74).

*Proposition.* Any continuously differentiable function  $\Psi(\Gamma)$  satisfying eqn (74) has the form

$$\Psi(\Gamma) = D\Gamma^{\delta},\tag{78}$$

where D and  $\delta$  are arbitrary constants.

To prove this assertion, we first set  $\beta = 1$  in eqn (74) and find that

$$\Xi(\Gamma) = \frac{\Psi(\Gamma)}{\psi(1)}.$$

Substitution of this expression into eqn (74) implies that

$$\Psi(\beta\Gamma) = \frac{\psi(\beta)}{\psi(1)}\Psi(\Gamma).$$
(79)

Afterwards we set  $\Gamma = 1$  in eqn (79) and obtain

$$\psi(\beta) = \frac{\Psi(\beta)}{\Psi(1)}\psi(1).$$

Combining this equality with eqn (79), we arrive at the formula

$$\Psi(\beta\Gamma) = \frac{\Psi(\beta)}{\Psi(1)}\Psi(\Gamma).$$
(80)

We differentiate eqn (80) with respect to  $\beta$ , set  $\beta = 1$ , and find that

$$\Psi'(\Gamma)\Gamma = \delta\Psi(\Gamma),\tag{81}$$

where

$$\delta = \frac{\Psi'(1)}{\Psi(1)}.$$

By integrating eqn (81), we arrive at the required formula (78), which completes the proof.

This assertion serves as an additional source of justification for the model developed, since it shows that the nonlinearity (58) is the only nonlinearity which implies the correspondence principles.

#### 8. CONCLUDING REMARKS

A new model for the nonlinear viscoelastic behavior of aging polymers is suggested and verified by comparison with experimental data for polypropylene and polyurethane. The model generalizes the Green–Tobolsky approach by introducing additional hypotheses regarding the rates of reformation and breakage for adaptive links of various types at isothermal loading.

For an arbitrary number of types of adaptive links, the model provides the general presentation for the relaxation measure of a viscoelastic medium which satisfies natural assumptions regarding the energy dissipation, see eqn (39).

Assuming a limited number of different types of links, the model ensures fair agreement with experimental relaxation curves and predicts correctly the material response under time-dependent loading without any additional fitting of adjustable parameters, see Fig. 6.

To demonstrate advantages of the model developed, an explicit solution is derived for torsion of a conic pipe made of a non-linear viscoelastic material. This applied problem is of special interest for pipeline industry. The stress distribution in the pipe is found analytically. To calculate strains and displacements, a nonlinear Volterra equation is solved. The effect of the loading history and the pipe geometry on the displacement field is analyzed numerically.

Two correspondence principles in viscoelasticity are formulated for the nonlinear model, and explicit restrictions of the nonlinearity are found which imply these principles to be valid.

# REFERENCES

- Arytyunyan, N. K. and Drozdov, A. D. (1992) Phase transitions in nonhomogeneous aging, viscoelastic bodies. International Journal of Solids and Structures 29, 783-797.
- Beris, A. N. and Edwards, B. J. (1993) On the admissibility criteria for linear viscoelasticity kernels. *Rheologica* Acta 32, 505-510.
- Bernstein, B. (1966) Time-dependent behavior of an incompressible elastic fluid. Some homogeneous deformation histories. Acta Mechanica 2, 329-354.
- Chai, C. K. and McCrum, N. G. (1984) The freezing-in of non-equilibrium values of the limiting compliances as a mechanism of physical ageing. *Polymer* 25, 291–298.
- Chengalva, M. K., Kenner, V. H. and Popelar, C. H. (1995) An evaluation of a free volume representation for viscoelastic properties. *International Journal of Solids and Structures* **32**, 847-856.

Christensen, R. M. (1982) Theory of Viscoelasticity. An Introduction. Academic Press, New York,

Coleman, B. D. and Noll, W. (1961) Foundations of linear viscoelasticity. *Review of Modern Physics* 33, 239–249.

- Dafermos, C. M. (1970) Asymptotic stability in viscoelasticity. Archives of Rational Mechanical Analysis 37, 297–308.
- Day, W. A. (1972) Thermodynamics of Simple Materials with Fading Memory. Springer-Verlag, Berlin.
- Drozdov, A. D. (1993) On constitutive laws for aging viscoelastic materials at finite strains. European Journal of Mechanics A/Solids 12, 305–324.
- Drozdov, A. D. (1996a) Finite Elasticity and Viscoelasticity. World Scientific, Singapore.
- Drozdov, A. D. (1996b) A constitutive model in thermoviscoelasticity. *Mechanical Research Communications* 23 (in press).
- Drozdov, A. D. and Kalamkarov, A. L. (1995a) A new model for an aging thermoviscoelastic material. Mechanical Research Communications 22, 441–446.
- Drozdov, A. D. and Kalamkarov, A. L. (1995b) A constitutive model of adaptive links in viscoelastoplasticity. In 1995 ASME Int. Mech. Engng Congress. Proc. ASME Materials Division. San-Francisco, ASME, MD69-1, pp. 469-483.
- Drozdov, A. D. and Kolmanovskii, V. B. (1994) Stability in Viscoelasticity. North-Holland, Amsterdam.
- Eyring, H. (1936). Viscosity, plasticity, and diffusion as examples of absolute reaction rates. Journal of Chemistry Physics 4, 283-291.
- Feigl, K., Ottinger, H. C. and Meissner, J. (1993) A failure of a class of K-BKZ equations based on principal stretches. *Rheologica Acta* 32, 438–446.
- Findley, W. N., Lai, J. S. and Onaran, K. (1989) Creep and Relaxation of Nonlinear Viscoelastic Materials. Dover Publications, New York.
- Green, A. E. and Rivlin, R. S. (1957) The mechanics of nonlinear materials with memory. 1. Archives of Rational Mechanical Analysis 1, 1–21.
- Green, M. S. and Tobolsky, A. V. (1946) A new approach to the theory of relaxing polymeric media. Journal of Chemistry and Physics 14, 80-92.
- Guth, E., Wack, P. E. and Anthony, R. L. (1946) Significance of the equation for state for rubber. Journal of Applied Physics 17, 347-351.
- He, Z. R. and Song, M. S. (1993) Elastic behaviors of swollen multiphase networks of SBS and SIS copolymers. *Rheologica Acta* **32**, 254–262.
- Kaye, A. and Kennett, A. J. (1974) Constrained elastic recovery of a polymeric liquid after various shear flow histories. *Rheologica Acta* 13, 916–923.

- Knauss, W. G. and Emri, I. J. (1987) Volume change and the nonlinearly thermoviscoelastic constitution of polymers. *Polymer Engineering Science* 27, 86–100.
- Leaderman, H. (1943) Elastic and Creep Properties of Filamentous Materials. Textile Foundation, Washington. DC.
- Lodge, A. S. (1989) Elastic recovery and polymer-polymer interactions. *Rheologica Acta* 28, 351-362.
- Losi, G. U. and Knauss, W. G. (1992) Free volume theory and nonlinear thermoviscoelasticity. *Polymer Engineering Science* 32, 542–557.

Lurie, A. I. (1990) Non-Linear Theory of Elasticity. North-Holland, Amsterdam.

- McKenna, G. B. (1989) Glass formation and glassy behavior. In Comprehensive Polymer Science, Vol. 2: Polymer Properties, (eds C. Booth and C. Price), pp. 311–362. Pergamon Press, Oxford.
- Partom, Y. and Schanin, I. (1983) Modelling nonlinear viscoelastic response. *Polymer. Engineering Science* 23, 849–859.

Pipkin, A. C. (1972) Lectures on Viscoelasticity Theory. Springer-Verlag, New York.

Rabotnov, Ju. N. (1969) Creep Problems in Structural Members. North-Holland, Amsterdam.

- Schapery, R. A. (1964) Application of thermodynamics to thermomechanical, fracture, and birefringent phenomena in viscoelastic media. *Journal of Applied Physics* **35**, 1451–1465.
- Smart, J. and Williams, J. G. (1972) A comparison of single-integral non-linear viscoelasticity theories. Journal of Mechanics, Physics and Solids 20, 313–324.
- Struik, L. C. E. (1978) Physical Ageing of Amorphous Polymers and Other Materials. Elsevier, Amsterdam.

Truesdell, C. (1975) A First Course in Rational Continuum Mechanics. Academic Press, New-York.

- Wagner, M. H. (1976) Analysis of time-dependent non-linear stress-growth data for shear and elongation flow of a low-density branched polyethylene melt. *Rheologica Acta* 15, 136-142.
- Wagner, M. H., Riable, T. and Meissner, J. (1979) Tensile stress overshoot in uniaxial extension of a LDPE melt. *Rheologica Acta* 18, 427–428.
- Waldron, W. K., McKenna, G. B. and Santore, M. M. (1995) The nonlinear viscoelastic response and apparent rejuvenation of an epoxy glass. *Journal of Rheology* **39**, 471–497.

Ward, I. M. (1971) Mechanical Properties of Solid Polymers. Wiley-Interscience, London.

- Ward, I. M. and Wolfe, J. M. (1966) The non-linear mechanical behaviour of polypropylene fibers under complex loading programmes. *Journal of Mechanics, Physics and Solids* 14, 131-140.
- Winter, H. H. (1978) On network models of molten polymers: loss of junctions due to stretching of material planes. *Rheologica Acta* 17, 589-594.
- Yamamoto, M. (1956) The visco-elastic properties of network structure. 1. General formalism. Journal of the Physics Society of Japan 11, 413–421.