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A multi-mode approach to finite, three-dimensional, nonlinear viscoelastic behavior of polymer glasses

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Synopsis

In this study a phenomenological constitutive model is proposed to describe the finite, nonlinear, viscoelastic behavior of glassy polymers up to the yield point. It is assumed that the deformation behavior of a glassy polymer up to the yield point is completely determined by the linear relaxation time spectrum and that the nonlinear effect of stress is to alter the intrinsic time scale of the material. A quantitative three-dimensional constitutive equation for polycarbonate as a model polymer was obtained by approximating the linear relaxation time spectrum by eighteen Leonov modes, all exhibiting the same stress dependence. A single Leonov mode is a Maxwell model employing a relaxation time that is dependent on an equivalent stress proportional to the Von Mises stress. Furthermore, a Leonov mode separates the (elastic) hydrostatic and (viscoelastic) deviatoric stress response and accounts for the geometrical complexities associated with simultaneous elastic and plastic deformation. Using a single set of parameters, the multi-mode Leonov model is capable of describing realistic constant strain rate experiments, including the strain rate dependent yield behavior. It is also capable of giving a quantitative description of nonlinear stress-relaxation experiments. © *1996 Society of Rheology.*

I. INTRODUCTION

In the description of the deformation behavior of solid polymers, usually a distinction is made between the linear viscoelastic regime at low stress, the nonlinear viscoelastic response at moderate stress, and the yield behavior at high stress (Ward, 1990). The linear viscoelastic deformation is adequately described using linear response theory, which results in the well known Boltzmann single integral representation. The nonlinear regime has been, and still is, an active field of research, and a large number of theories have been put forward. Most of these theories aim at a one-dimensional description of the nonlinear behavior at moderate strain, often for a special deformation mode like, for example,

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creep. An extensive survey of these theories can be found in the monograph by Ward (1990). Yield of polymer materials is classically described by using yield criteria, of which the pressure and rate-dependent Von Mises criterion seems to be most successful. After yielding, strain hardening sets in, sometimes preceded by intrinsic strain softening.

Recently, several attempts have been made to come to a more unified approach to the deformation behavior of polymer materials. The ''BPA model'' by Boyce *et al.* (1988) and the related ''full-chain model'' by Wu and van der Giessen (1993) combine the elasto-viscoplastic response at small strain and the strain hardening behavior during plastic deformation, into a single three-dimensional constitutive equation. The BPA model was later refined by Arruda (1992) with respect to the strain-hardening response and by Hasan *et al.* (1993) to include the effect of aging and rejuvenation. In all these models no explicit use is made of a yield criterion. Instead, the deformation behavior is determined by a single relaxation time that is dependent on an equivalent stress (proportional to the Von Mises stress). This results in a sharp transition from solidlike to fluidlike behavior, similar to an elasto-plastic response employing a rate-dependent Von Mises criterion.

The principle to describe yieldlike behavior by use of a stress-dependent relaxation time dates back to Tobolsky and Eyring (1943). It was used later by Haward and Thackray (1968) who added a Langevin spring to account for the finite extensibility of the entanglement network. However, the use of a single stress-dependent relaxation time cannot account for the (non)linear viscoelastic response at small and moderate strains. Moreover, using a single relaxation time results in an abrupt transition from elastic to viscous behavior that is rarely seen in practice. Therefore, a description employing a spectrum of relaxation times would be more appropriate. If the additional assumption is made that all relaxation times depend in the same way on the total stress, one arrives at the principle of time-stress superposition, equivalent to time-temperature superposition, where it is assumed that all relaxation times depend in the same way on temperature. Time-stress superposition implies that the nonlinear effect of stress is to alter the intrinsic time scale of the material, hence it is sometimes referred to as a ''stress clock'' (Bernstein and Shokooh, 1980).

Other choices are possible as well. Valanis (1971) assumed that strain instead of stress accelerates relaxation processes in a material. However, using the total strain as a variable implies that the material under consideration is a solid and since all materials ultimately flow, it is better to use a fluid point of view (Bernstein and Shokooh, 1980). Shay and Caruthers (1986) considered a volume clock to describe nonlinear viscoelastic behavior and yielding. However, in this way, they were unable to recover Von Mises like yield behavior that is observed experimentally. Hasan and Boyce (1995) used a spectrum of activation energies to describe the distributed nature of local plastic transformations. However, using a spectrum of activation energies results in thermorheological complex behavior which is not always observed in practice.

The concept of time-stress superposition has been used frequently to describe nonlinear viscoelastic behavior. It was incorporated in the Boltzmann integral by Schapery (1969) using the concept of a reduced time (Leaderman, 1943). Bernstein and Shokooh (1980) showed that the introduction of special stress-clock functions can transform a viscoelastic relation [in their case, the class BKZ equations (Larson, 1988)] into an elastic-perfectly plastic constitutive equation. In this paper, time-stress superposition is used to obtain a three-dimensional constitutive equation, which provides a unified description of compressible, finite, nonlinear viscoelastic behavior and yield. The constitutive relation will be verified experimentally using polycarbonate as a model polymer.

It is well known, that the viscoelastic behavior of polymers changes with time, a thermo-reversible process called ''physical aging'' (Struik, 1978). In the present investigation, all experiments were performed on separate samples of identical thermal history, their age exceeding by far the longest time in the experiments. It is, therefore, assumed that the all samples are equally affected by physical aging at the start of the experiment, and, moreover, that aging during the experiments can be neglected. Therefore, to a first approximation, aging will not be taken into account.

II. THEORY

A. Single mode approach

In a previous paper (Tervoort *et al.*, 1994) an elasto-viscoplastic equation for polymer glasses (and other materials) was introduced, the so-called "compressible Leonov model" (Leonov, 1976). In this theory, a decoupling of the volume response and isochoric "shape" response was achieved, by assuming that the free energy of the system is determined by two state variables: the relative volume deformation, $J = \det(\mathbf{F})$, where $\mathbf{F}$ is the deformation gradient and the isochoric Cauchy–Green strain tensor, $\tilde{\mathbf{B}}_e[\det(\tilde{\mathbf{B}}_e) = 1$, in case of elastic behavior $\tilde{\mathbf{B}}_e = J^{-2/3}\mathbf{F}\cdot\mathbf{F}^T$, see also Rubin (1994) and Baaijens (1991)]. Using a formalism developed to derive thermodynamically consistent constitutive equations (Jongschaap *et al.*, 1994), it was shown that the hydrostatic stress is coupled to the volume deformation, whereas the deviatoric stress is determined by the isochoric (constant volume) elastic strain $\tilde{\mathbf{B}}_e$. Furthermore, it was assumed that the volume deformation remained elastic, whereas the accumulation of isochoric-elastic strain was reduced because of a plastic strain rate $\mathbf{D}_p$. At small volume deformations ($J \approx 1$) the compressible Leonov model reduces to

$$\left[\begin{array}{l} \mathbf{T} = K(J-1)\mathbf{I} + G\tilde{\mathbf{B}}_e^d, \\ \overset{\circ}{\tilde{\mathbf{B}}}_e = (\mathbf{D}-\mathbf{D}_p)\cdot\tilde{\mathbf{B}}_e + \tilde{\mathbf{B}}_e\cdot(\mathbf{D}-\mathbf{D}_p), \\ \dot{J} = J\ \mathrm{tr}(\mathbf{D}). \end{array}\right. \tag{1}$$

Here, K is the bulk modulus, G the shear modulus, the superscript "d" denotes the deviatoric part, and $\overset{\circ}{\tilde{\mathbf{B}}}_e$ is the Jaumann or corotational derivative of $\tilde{\mathbf{B}}_e$

$$\overset{\circ}{\tilde{\mathbf{B}}}_e = \dot{\tilde{\mathbf{B}}}_e - \mathbf{W}\cdot\tilde{\mathbf{B}}_e - \tilde{\mathbf{B}}_e\cdot\mathbf{W} \tag{2}$$

with the vorticity tensor $\mathbf{W}$. The plastic strain rate $\mathbf{D}_p$, which reduces the accumulation of isochoric-elastic strain, was constitutively described by the Eyring equation. The Eyring equation for plastic flow is a semiempirical relation which describes stress-activated flow of structural units in a material, like segments in case of a polymer. It is depicted three dimensionally as (Tervoort *et al.*, 1994)

$$\left[\begin{array}{l} \mathbf{D}_p = \dfrac{\mathbf{T}^d}{2\,\eta(\tau_{\mathrm{eq}})}, \\ \eta(\tau_{\mathrm{eq}}) = A\tau_0\dfrac{(\tau_{\mathrm{eq}}/\tau_0)}{\sinh(\tau_{\mathrm{eq}}/\tau_0)} = \eta_0 a_0(\tau_{\mathrm{eq}}), \\ \tau_{\mathrm{eq}} = \sqrt{\tfrac{1}{2}\,\mathrm{tr}(\mathbf{T}^d\cdot\mathbf{T}^d)}. \end{array}\right. \tag{3}$$

Here, τ_{eq} is an equivalent stress, proportional to the Von Mises stress. The material constants (at constant temperature), A and τ_0, are related to, respectively, the activation energy ΔH, and the activation volume V^*

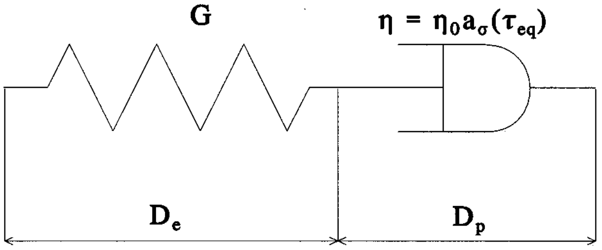

FIG. 1. Graphical representation of the deviatoric stress response of a single Leonov mode.

$$A = A_0 \exp\left(\frac{\Delta H}{RT}\right), \quad \tau_0 = \frac{RT}{V^*} \tag{4}$$

with A_0 a pre-exponential factor involving the fundamental vibration frequency, R the gas constant, and T the absolute temperature. The product $A\tau_0$ is the zero-shear viscosity η_0. The shift function $a_\sigma(\tau_{eq})$ is in fact a dimensionless viscosity, which is equal to one when $\tau_{eq} < \tau_0$ and rapidly decreases to zero when $\tau_{eq} \geqslant \tau_0$.

From Eqs. (1) and (3) it can be seen that the deviatoric stress response as described by the compressible Leonov model (to be called: "a single Leonov mode") can be depicted as a single Maxwell model employing a nonlinear relaxation time $\lambda = \eta/G$ (see Fig. 1).

In the Eyring approach, it is assumed that deformation processes are essentially always present and that stress, like temperature, merely changes the rate of deformation. This is reflected by the functional dependence of the relaxation time on stress [Eqs. (1) and (3)]. At low equivalent stress ($\tau_{eq} \ll \tau_0$) there is a linear region where the relaxation time is constant, $\lambda = \lambda_0 = \eta_0 = \eta_0/G$. At higher stress ($\tau_{eq} \geqslant \tau_0$) the relaxation time decreases rapidly as described by the shift function $a_\sigma(\tau_{eq})$. Thus, the intrinsic time scale of the material ("the internal clock") is changed by the application of stress, hence the name "stress-clock" material (Bernstein and Shokooh, 1980). The nonlinear effect of stress can be observed most clearly in a constant stress experiment, like the creep test. For a creep experiment at a very low (equivalent-) stress level ($\tau_{eq} < \tau_0$), the compliance curve of a single Leonov mode is determined by the linear relaxation time λ_0 as can be seen in Fig. 2.

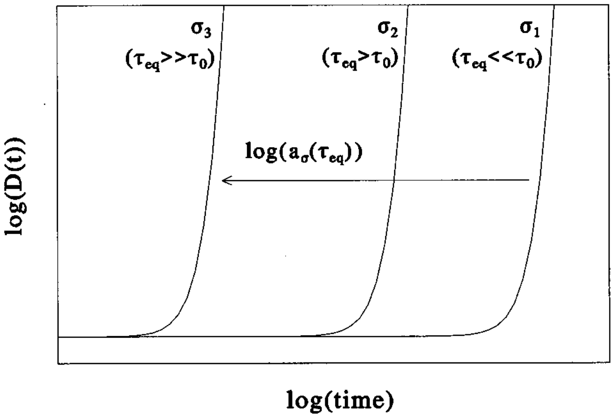

FIG. 2. Compliance curves for a single Leonov mode at various stress levels.

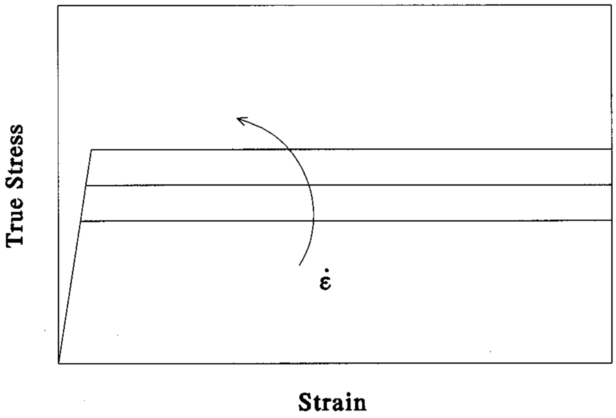

FIG. 3. Calculated tensile curves for a single Leonov mode at various rates of strain.

For creep tests performed at higher stress levels ($\tau_{eq} \geqslant \tau_0$), the relaxation time is reduced by a factor $a_\sigma(\tau_{eq})$. On a logarithmic time axis, this results in a horizontal shift of the compliance curve (hence the name "shift function"). A single Leonov mode is not capable of predicting a realistic compliance curve, since it is dominated by a single relaxation time.

A typical set of tensile curves calculated from a single Leonov mode is depicted in Fig. 3. As with the creep test, a single Leonov mode is not able to offer a realistic description of the experimental curve. Comparing an experimental tensile curve with the model predictions, a single Leonov mode only accounts correctly for the initial modulus and the (strain-rate dependent) "yield stress". This is not surprising, since these are essentially the material parameters which are supplied to the model. However, there is a serious discrepancy between the calculated and experimental curve before and after the experimental yield point (maximum in the tensile curve). An experimental curve has a more gradual transition from elastic to yield behavior, and the yield point is, therefore, found at a higher strain. Inhomogeneous deformation and possible strain softening account for the discrepancy after the "yield point." In contrast, before the yield point the deformation is fairly homogeneous and the deviation between model prediction and the experimental curve must be due to something else. In this article it will be shown that a quantitative description of the tensile test and in fact the complete three-dimensional nonlinear viscoelastic behavior of polymer glasses can be obtained by using a spectrum of stress-dependent relaxation times rather than one.

It is to be noted that the inability of a single Leonov mode to describe accurately the nonlinear viscoelastic response of a polymer glass is inherent to all models which employ only one stress-dependent relaxation time (Boyce *et al.*, 1988; Wu and van der Giessen, 1993).

B. Multi-mode approach

From polymer physics it is well known that time-dependent behavior of amorphous polymers can result from a wide variety of molecular transitions. The most important of these is the glass transition (α transition) which is associated with main chain segmental motion. Many polymers also exhibit so-called secondary transitions (β transitions) originating from the motions of side groups, end groups, or restricted motion of the main chain (Ward, 1990).

The time dependence resulting from a specific molecular transition is mathematically represented by a spectrum of relaxation times. In contrast, it is normally assumed that the activation of a molecular transition by temperature is determined by a single parameter, the activation energy ΔH. This implies that all the relaxation times due to a specific molecular transition dependent in the same way on temperature, resulting in the well known time-temperature superposition principle (thermo-rheological simple behavior). According to this principle, the influence of temperature on viscoelastic properties, whose time dependence is determined by (a set of) relaxation time(s), can be described by a so-called reduced time t^* (Leaderman, 1943):

$$\tau^* = \int_0^t \frac{dt'}{a_T}. \tag{5}$$

On a logarithmic time axis, dividing the real time t by a shift factor a_T, results in a horizontal shift by a factor $\log(a_T)$, where a_T is the ratio of the relaxation times at temperatures T and T_0.

In practice, experimental verification of the applicability of time-temperature superposition consists of two parts (Ferry, 1980): first it is attempted to construct a smooth master curve of a viscoelastic quantity like the creep compliance at a certain reference temperature. This is done by shifting curves measured at different temperatures horizontally along the logarithmic time axis. Secondly, if a smooth master curve is obtained, a plot of the resulting shift factors as a function of temperature must obey a ‘‘familiar’’ relation, e.g., the Arrhenius equation or the WLF equation.

According to the Eyring approach, besides activation by temperature, a molecular transition can also be activated by stress (to be more precise: by the equivalent stress τ_{eq}). Again, it is normally assumed that stress activation is described by a single parameter, the activation volume V^*. Indeed, determination of the activation energy and volume is often used for the identification of certain molecular transitions (Ward, 1990). It is therefore logical to assume that, as in the case of activation by temperature, all relaxation times are the same function of the *total equivalent stress.* This leads to the principle of time-stress superposition, which states that the nonlinear effect of stress can be described by using a reduced time, as in the case of temperature. It implies that, if a discrete spectrum of Leonov modes is used as an approximation of the relaxation time spectrum, all the modes will be shifted by the same factor $a_\sigma(\tau_{\mathrm{eq}})$, where τ_{eq} is the *total equivalent stress.* Furthermore, it implies that the experimental verification of the applicability of time-temperature superposition, as described above, could also be used to justify time-stress superposition. Data obtained for constant stress levels must shifts to a smooth master curve, and the resulting shift factors as a function of equivalent stress must obey a familiar relation, like the Eyring Eq. (3). In essence, for polymer glasses, time-stress superposition implies that yielding can be regarded as a stress induced glass transition.

III. EXPERIMENT

Experiments were carried out on test specimens produced according to ASTM D 638 from extruded sheets of Makrolon (bisphenol A polycarbonate, Bayer) 2 mm thick. Polycarbonate was selected as a model polymer since, at room temperature, it exhibits only

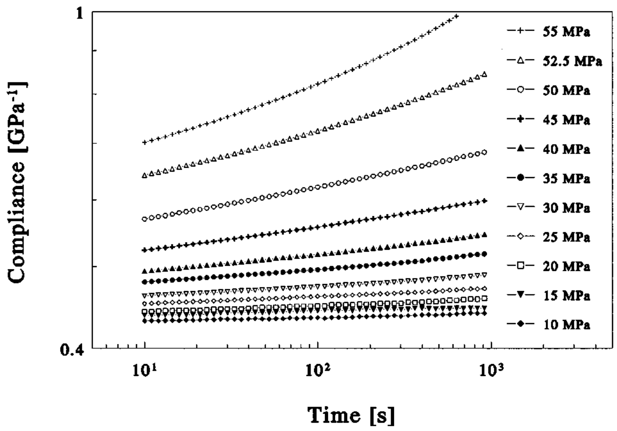

FIG. 4. Creep compliance of polycarbonate at various loads at 20 °C.

one active relaxation mechanism of interest—the glass transition. At room temperature the β transition, which is situated at -100 to -50 °C, is only relevant for very fast processes.

Stress relaxation experiments were performed on a Frank 81565 tensile tester, whereas creep and constant strain rate experiments were performed on a Zwick Rel servo hydraulic tensile tester (20 kN). In all cases the extension was measured using an Instron (2020-602) strain gauge extensometer with a measure length of 50 mm and a range of ±2.5 mm. The radial strain was measured using an Instron (2640-008) transverse extensometer. The relative accuracy in the force and strain measurements was 1%.

Stress relaxation experiments with loading times not exceeding 10^4 s were performed at strains of 0.5%–3%. Creep experiments with loading times not exceeding 10^3 s were performed in dead weight loading at loads of 10–55 MPa. The strains and loads in the stress relaxation and creep experiments were applied within 1 s. Tensile test experiments were performed at constant strain rates up to 10^{-2} s^{-1}. Each experiment was performed on a new sample at room temperature. All test samples had the same age, which exceeded by far the longest time in the experiments.

IV. RESULTS

In Sec. II it was argued that the deformation behavior of a glassy polymer is determined by the linear relaxation time spectrum, which is shifted to shorter times when stress is applied. In this section, the admissibility of this time-stress superposition principle will be verified experimentally, using polycarbonate as a model polymer. Subsequently, the linear relaxation time spectrum will be determined in order to complete the multi-mode Leonov model for polycarbonate. Finally, the model will be verified using constant strain rate experiments and stress relaxation experiments (in tensile deformation).

A. Admissibility of time-stress superposition

In order to verify experimentally the admissibility of time-stress superposition for polycarbonate, it was first attempted to construct a smooth master curve from a number of creep tests at different stress levels, as described in Sec. II B. The results of the creep tests are depicted in Fig. 4.

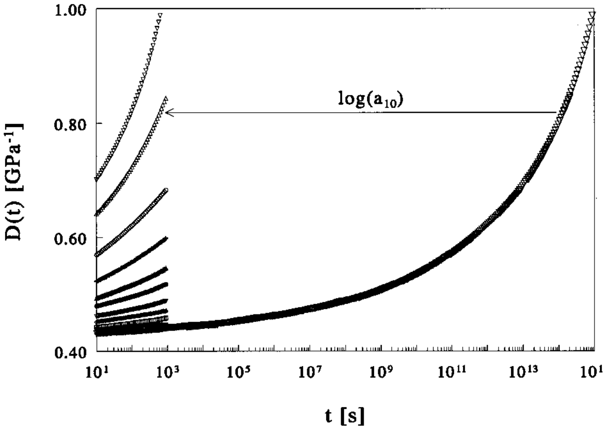

FIG. 5. Construction of the master curve of the creep compliance at a reference stress of 10 MPa.

These creep curves were shifted horizontally along the logarithmic time axis with respect to the 10 MPa reference curve. The resulting master curve is depicted in Fig. 5.

From Fig. 5, it is clear that a smooth compliance master curve can be constructed by horizontal shifting of the creep tests at different stresses. It must be emphasized that the compliance master curve at 10 MPa is a "virtual" curve that will strongly deviate from an experimental creep test on the same time scale, due to aging effects.

The logarithm of the shift factors $\log(a_{10})$ necessary to construct the master compliance curve at 10 MPa (see Fig. 5), are tabulated in Table I as a function of the creep load.

The second part of the experimental verification of time-stress superposition consists of fitting the shift data from Table I with the Eyring Eq. (3). A plot of all the shift factors with respect to the 10 MPa creep curve is depicted in Fig. 6.

The solid line is a fit using the Eyring expression for the shift function (3). It is clear that the creep data are determined by one Eyring shift function. Therefore, the second condition is also met, and we may assume that time-stress superposition may be applied.

B. Material parameters

In the previous section it was verified experimentally that time-stress superposition applies to polycarbonate. To complete the multi-mode Leonov model for polycarbonate, the material parameters have to be determined.

1. The Eyring parameters

The Eyring viscosity function (3) which describes the nonlinearity in the stress response is determined by two parameters, the zero-shear viscosity η_0 and the nonlinearity parameter τ_0. These material constants may be determined by fitting a plot of the viscosity as a function of equivalent stress. Therefore, we need to extract viscosity data from the creep tests at different stress levels (Fig. 4). In principle, this should be done by measuring the plateau-creep rate ($\dot{\varepsilon}_{\mathrm{pl}}$) of each creep experiment. The plateau-creep rate is

TABLE I. Shift factors resulting from the construction of the 10 MPa master compliance curve.

σ_0 [MPa]	10	15	20	25	30	35	40	45	50	52.5	55
$\log(a_{\sigma\,10})$ [−]	0	−1.5	−2.6	−3.9	−5	−6.5	−7.4	−8.6	−10	−11.4	−12.2

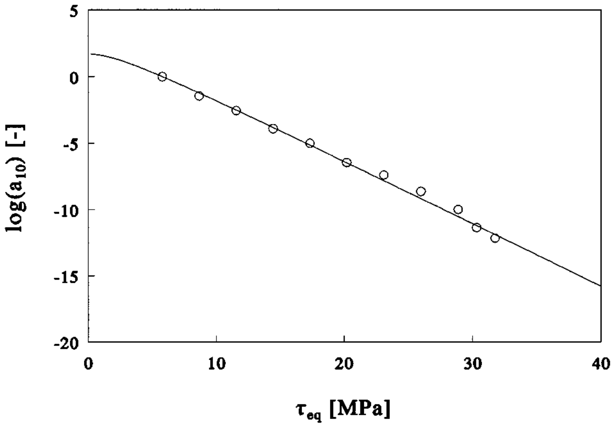

FIG. 6. Logarithm of the shift factors with respect to 10 MPa, obtained from the creep tests, as a function of equivalent stress.

determined by constancy of the creep rate at an imposed (constant) creep load σ_0 and therefore defines a viscosity $\eta_{\mathrm{pl}}^e = \sigma_0/\dot{\varepsilon}_{\mathrm{pl}}$. Note that this is an extensional viscosity (as denoted by the superscript "*e*"), since the creep data were obtained from tensile experiments. In terms of the Leonov model, the plateau-creep viscosity η_{pl}^e is equal to the sum of the viscosity $\eta_i^e = \eta_{0i}^e a_\sigma$ of all the Leonov modes separately

$$\eta_{\mathrm{pl}}^e = \frac{\sigma_0}{\dot{\varepsilon}_{\mathrm{pl}}} = \sum_i \eta_{0i}^e a_\sigma(\tau_{\mathrm{eq}}^{\mathrm{pl}}), \tag{6}$$

where $\tau_{\mathrm{eq}}^{\mathrm{pl}}$ is the equivalent stress associated with the creep load σ_0. The plateau-creep rate is normally obtained from a *Sherby–Dorn plot,* which is a graph of the creep rate versus creep strain.

Due to the limited experimental time window, a plateau-creep rate was observed only at the highest creep load of 55 MPa. From a Sherby–Dorn plot the value of the plateau-creep rate was estimated to be $\dot{\varepsilon}_{\mathrm{pl}} = 10^{-5}\ \mathrm{s}^{-1}$ leading to a plateau-creep viscosity of: $\eta_{\mathrm{pl}}^e = 55 \times 10^5$ MPa s (see Fig. 7). For all the other creep tests, a constant creep rate could not be established experimentally. However, according to Eq. (6), the ratio of the plateau-creep viscosities at two different stress levels τ_{eq}^1 and τ_{eq}^2, is equal to the ratio of the shift factors at these stress levels

$$\frac{\eta_{\mathrm{pl}}^e(\tau_{\mathrm{eq}}^1)}{\eta_{\mathrm{pl}}^e(\tau_{\mathrm{eq}}^2)} = \frac{a_\sigma(\tau_{\mathrm{eq}}^1)}{a_\sigma(\tau_{\mathrm{eq}}^2)}. \tag{7}$$

Therefore, the value of the plateau-creep viscosity at 55 MPa may be used to convert the plot of shift factors (Fig. 6) to a graph of viscosity as a function of equivalent stress (Fig. 8).

In order to obtain an accurate estimation of both the activation volume (τ_0) and the zero-shear viscosity η_0, it is necessary to have viscosity data up to the (equivalent) yield stress. Therefore, yield data obtained by tensile testing at different strain rates were included in Fig. 8. Note that a yield point also defines a viscosity since it is determined by the moment the stress becomes constant at an imposed constant strain rate. Since it is

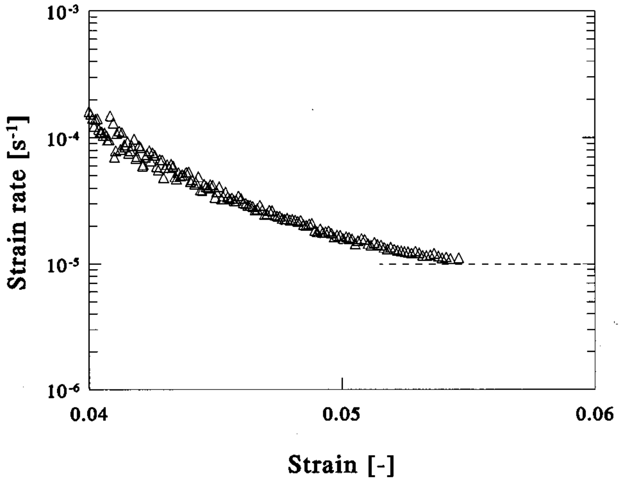

FIG. 7. Sherby–Dorn plot for the determination of the plateau-creep rate at 55 MPa.

irrelevant whether this steady-state situation is achieved at imposed stress or imposed strain rate, the "yield viscosity" is also equal to the sum of the viscosities of all the Leonov modes separately

$$\eta_y^e = \sum_i \eta_{0i}^e a_\sigma(\tau_{\text{eq}}^y), \tag{8}$$

where τ_{eq}^y is the equivalent yield stress.

The results of the tensile tests at different strain rates are tabulated in Table II. A plot of all the viscosity data is depicted in Fig. 8. In contrast to Fig. 6, a logarithmic stress axis is used to show more clearly the linear region characterized by the zero-shear viscosity η_0. The solid line is a best fit using a single Eyring viscosity function. From Fig. 8 it is

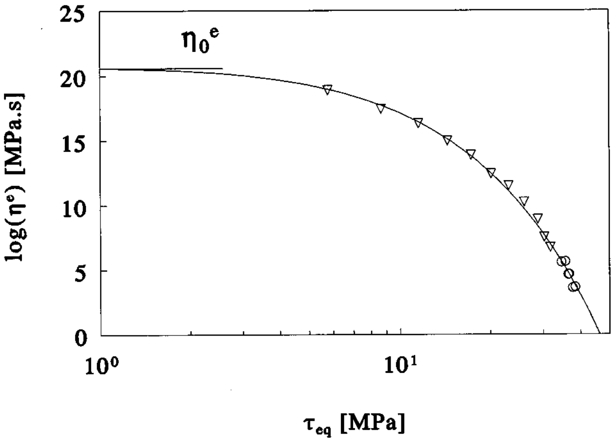

FIG. 8. A plot of the elongational viscosity as a function of equivalent stress, obtained from creep data (▽) and yield data (○). The solid line is a fit using a single Eyring function.

TABLE II. Viscosities from yield points at different rates of strain as a function of equivalent stress.

$\dot{\varepsilon}$ [s^{-1}]	1.4×10^{-4}	1.5×10^{-4}	1.4×10^{-3}	1.4×10^{-3}	1.4×10^{-3}	1.6×10^{-2}	1.4×10^{-2}
σ_{yield} [MPa]	61.7	59.9	63.6	63.1	63.1	65.3	66.6
η_{yield} [MPa s]	4.5×10^{5}	4.1×10^{5}	4.6×10^{4}	4.5×10^{4}	4.5×10^{4}	4.2×10^{3}	4.7×10^{3}
$\tau_{\mathrm{eq}}^{\mathrm{yield}}$	35.6	34.6	36.7	36.4	36.4	37.7	38.5

clear that both yield and creep are determined by the same Eyring process. The best fit resulted in a value for $\tau_0 = 0.89$ MPa and for $\eta_0 = 4.6561\times10^{20}$ MPa s.

2. Linear viscoelastic parameters

In the limit of small stress and strain, the multi-mode Leonov model reduces to a generalized Maxwell model (in shear). Therefore, in order to find the linear Leonov parameters, the linear relaxation time spectrum needs to be determined. In Sec. IV A the 10 MPa compliance master curve was obtained through application of the time-stress superposition principle. This compliance curve is complete towards the long time limit, since the plateau-creep regime was estimated. However, the 10 MPa compliance master curve does not constitute the linear compliance curve. The value of the nonlinearity parameter τ_0 indicates that above an equivalent stress of 0.89 MPa polycarbonate already behaves in a nonlinear way. Therefore, the linear compliance curve could only be obtained indirectly by shifting the 10 MPa master curve horizontally by a factor $a_\sigma(\tau_{\mathrm{eq}}^{10\ \mathrm{MPa}})$. The resulting linear compliance curve is depicted in Fig. 9. Again, this is a virtual curve, since aging has not been taken into account. Only the first part of this virtual curve is equal to the experimental linear compliance curve for polycarbonate of this particular age and grade. At longer times, the experimental curve will deviate from the virtual linear compliance curve (Fig. 9) due to aging.

Also plotted in Fig. 9 is the single model approximation of the linear compliance curve, which is obtained by only taking into account the initial "glassy" response and the final "fluid" response (characterized by the glassy compliance D_g and the total zero-shear viscosity η_0^e).

The solid line in Fig. 9 is a fit using a generalized Kelvin–Voigt model

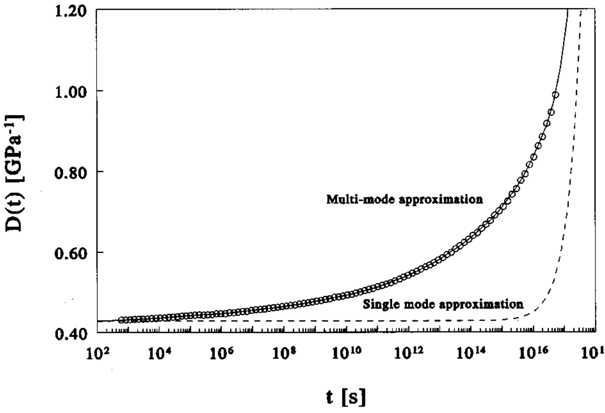

FIG. 9. The linear compliance curve $D(t)$ (○). The solid line is a fit using a generalized Kelvin–Voigt model; for comparison the single mode approximation is added (dashed line).

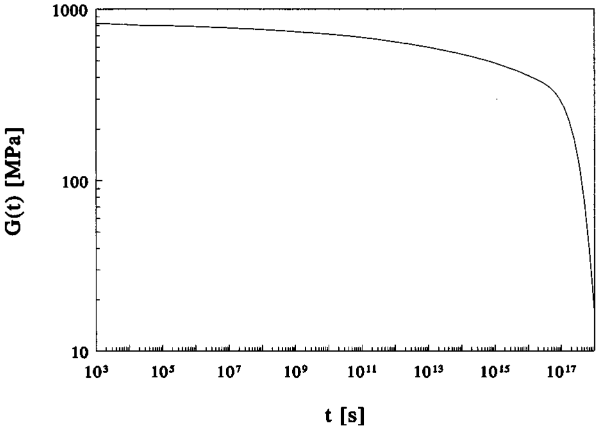

FIG. 10. The linear shear relaxation modulus $G(t)$ calculated from the linear tensile compliance curve $D(t)$ as described in the appendix.

$$D(t) = D_g + \sum_{i=1}^{n} D_i(1 - e^{-t/\lambda_i}) + \frac{t}{\eta_0^e} \tag{9}$$

with $D_g = 1/E_g$, where the initial (glassy) Young's modulus was measured to be $E_g = 2335$ MPa. The fit was obtained using CONTIN, a constrained regularization program developed to invert ill-posed linear integral equations (Provencher, 1982a, 1982b) (see appendix). Using an equidistant grid of relaxation times, eighteen modes were necessary to obtain an accurate description of the linear compliance curve. At this stage of the research, no further attempts were made to reduce the number of modes.

In order to obtain the linear Leonov parameters, the linear tensile compliance curve $D(t)$ must be converted to the linear shear relaxation modulus curve $G(t)$. This was done by invoking the correspondence principle (Tschoegl, 1989), assuming a constant bulk modulus $K = 4300$ MPa (which corresponds to the experimentally determined initial Poisson ratio of polycarbonate $\nu = 0.41$ [−], see appendix). The resulting shear relaxation modulus is depicted in Fig. 10; the eighteen shear moduli and relaxation times are tabulated in Table III. It must be emphasized that these linear parameters bear no physical meaning, only the relaxation modulus $G(t)$ itself is a material function.

C. Model verification

In Sec. II B it was argued that the finite nonlinear viscoelastic behavior of polymer glasses is determined by the linear relaxation time spectrum which is shifted to shorter times when stress is applied. In the previous Sec. IV B, the linear relaxation time spectrum for a model polymer, polycarbonate, was approximated using eighteen Leonov modes, all subdued to the same stress dependence. In this section, this multi-mode Leonov constitutive equation of polycarbonate will be verified by constant strain rate experiments (homogeneous uniaxial tensile tests) and stress-relaxation experiments.

1. Uniaxial tensile test

The first verification experiment considered is a standard uniaxial tensile test at various constant strain rates (constant cross head speed). Figure 11 shows a comparison between the experimental data (open symbols) and the numerical predictions (solid line).

TABLE III. Linear Leonov parameters obtained by fitting the linear relaxation modulus.

i	λ_i [s]	G_i [MPa]	$\eta_i = \lambda_i \cdot E_i$ [MPa s]
1	0.7080e+04	0.2254e+02	0.1596e+06
2	0.3548e+06	0.9810e+01	0.3481e+07
3	0.2512e+07	0.1096e+02	0.2753e+08
4	0.1778e+08	0.1354e+02	0.2407e+09
5	0.1259e+09	0.1633e+02	0.2056e+10
6	0.8913e+09	0.1687e+02	0.1503e+11
7	0.6310e+10	0.2125e+02	0.1341e+12
8	0.4467e+11	0.2331e+02	0.1041e+13
9	0.3162e+12	0.3336e+02	0.1055e+14
10	0.2239e+13	0.3642e+02	0.8153e+14
11	0.1585e+14	0.4226e+02	0.6698e+15
12	0.1122e+15	0.4532e+02	0.5085e+16
13	0.7943e+15	0.5148e+02	0.4089e+17
14	0.5623e+16	0.7140e+02	0.4015e+18
15	0.3981e+17	0.5088e+01	0.2026e+18
16	0.2818e+18	0.3992e+03	0.1125e+21
17	0.1995e+19	0.6563e+01	0.1310e+20
18	0.1413e+20	0.2049e+01	0.2894e+20

It is clear that, in contrast to a single mode Leonov model (see Fig. 3), the multi-mode Leonov model provides an quantitative description of the strain rate dependent "yield behavior" of polycarbonate.

In the multi-mode Leonov model, polycarbonate is essentially regarded as a highly nonlinear fluid. It is, therefore, instructive to divide both stress and strain data in Fig. 12 by the constant applied strain rates and make a plot of the extensional viscosity versus time, as is common practice in rheology.

During the tensile test the lateral contraction was also measured. Figure 13 shows a comparison between the experimental data (open symbols) and the numerical predictions (solid line). The dashed line is the prediction for an elastic solid with a (constant) Poisson ratio equal to the initial Poisson ratio of polycarbonate $\nu = 0.41$.

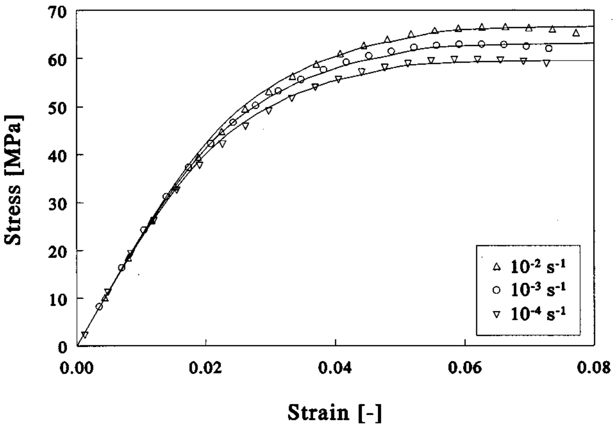

FIG. 11. Standard uniaxial tensile experiments at various strain rates (open symbols), compared to model predictions (solid lines).

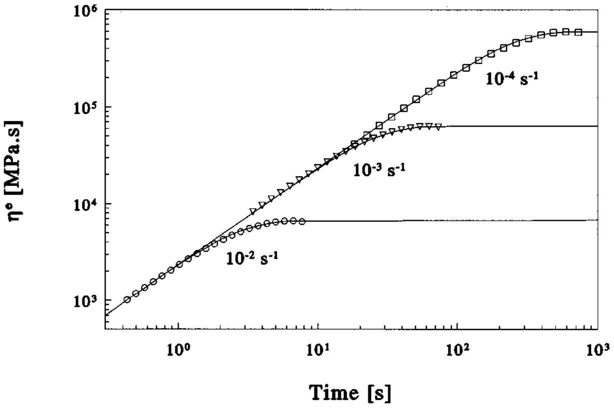

FIG. 12. Extensional viscosity buildup measured at various (Hencky) strain rates (symbols), compared to model predictions (solid lines).

From Fig. 13 it is clear that the multi-mode Leonov model also provides a quantitative description of the strain-rate dependent volume behavior during tensile testing of polycarbonate up to the yield point.

2. Stress relaxation

In order to verify the description of the nonlinear viscoelastic behavior of polycarbonate offered by the multi-mode Leonov model, nonlinear relaxation experiments were considered. The results of experimental data and numerical calculations at various strain levels are depicted in Fig. 14.

Note that all the stress relaxation experiments displayed in Fig. 14 are essentially nonlinear, since the equivalent stress levels are well above the value of the nonlinearity parameter $\tau_0 = 0.89$ MPa. In contrast, visually, the response up to 1% strain appears to be quite linear, which illustrates that conclusions about true linear behavior can only be drawn with great precaution. This becomes evident when describing these nonlinear

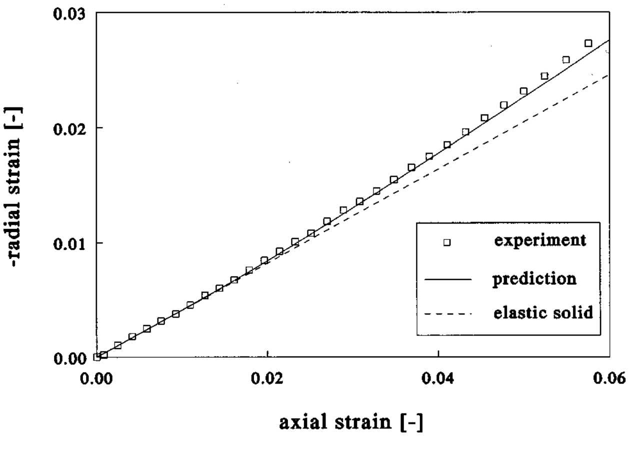

FIG. 13. Calculated radial strain during a constant strain rate tensile test (solid line, $\dot{\varepsilon} = 10^{-3}$ s^{-1}), compared to experimental data.

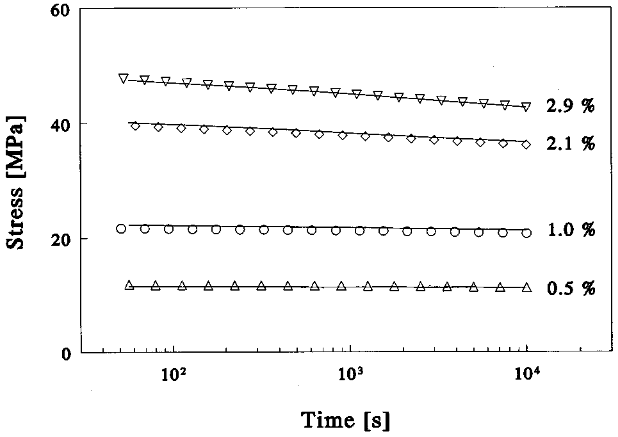

FIG. 14. Stress-relaxation experiments measured at various strain levels (open symbols), compared to model predictions (solid lines).

stress-relaxation experiments. In an ideal stress relaxation experiment, it is assumed that loading takes place instantaneously. In practice, however, loading always occurs over a finite time. In case of true linear behavior, the difference in response between instantaneous and ramplike loading is negligible after ten times the loading time (Struik, 1978). In contrast, due to the nonlinear behavior, it was found that, in order to obtain a good agreement between experimental data and calculations as displayed in Fig. 15, it was necessary to take into account the exact loading program as used in the experiment. Assuming an instantaneous loading program in the calculations resulted in differences with the experiments which persisted much longer than ten times the experimental loading time. This kind of "hidden" nonlinear behavior could be of importance when considering the influence of a short stress pulse on creep behavior (Struik, 1978), as was also mentioned by McKenna *et al.* (1994).

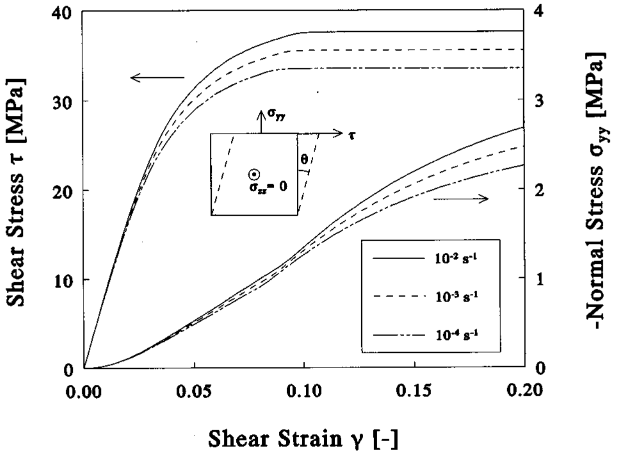

FIG. 15. Calculated plane-stress shear test experiments, at various shear strain rates. The left axis is the shear stress and the right axis is the normal stress in the y direction.

3. Shear test

Another possible verification experiment would be a plane-stress shear test also called ''laboratory shear'' [see Fig. 14, the shear strain $\gamma = \tan(\phi)$]. The predicted shear stress τ versus shear strain γ data is depicted in Fig. 15. Note that the yield points in tensile and in shear deformation compare very well to a (strain rate dependent) Von Mises criterion. This is due to the fact that the equivalent stress τ_{eq}, which determines the nonlinear response, is proportional to the Von Mises equivalent stress. Unfortunately, at the moment we are not able to measure the shear stress response experimentally, nor could we find accurate data in literature having the same thermal history as our samples.

D. CONCLUSIONS

A phenomenological constitutive model has been developed to describe the finite, nonlinear viscoelastic behavior of polycarbonate, including yielding. The model is based on stress-clock models used in the past, and seems a promising approach, within the range of experiments performed. The basic model assumption is that the finite, three-dimensional, nonlinear viscoelastic behavior (including yielding) of polycarbonate is determined by the (in good approximation constant) bulk modulus, the linear shear relaxation time spectrum, and one nonlinearity parameter, which describes how the spectrum is shifted to shorter times upon loading. The nonlinearity parameter (related to the activation volume) and the linear relaxation time spectrum can be determined on the basis of creep experiments and constant strain rate experiments using time-stress superposition. Polycarbonate was selected as a model system, since it exhibits only one relaxation mechanism of interest at room temperature (the glass transition). A quantitative three-dimensional constitutive equation for polycarbonate as a model polymer was obtained by approximating the relaxation time spectrum by eighteen Leonov modes. A single Leonov mode is a Maxwell model, employing a relaxation time which is dependent on an equivalent stress proportional to the Von Mises equivalent stress. Furthermore, a Leonov mode separates the hydrostatic and deviatoric stress response, and accounts for the geometrical complexities associated with simultaneous (large) elastic and plastic deformations.

The present research establishes the linear shear relaxation time spectrum as the key quantity determining the nonlinear viscoelastic behavior of glassy polymers. Deviatoric stress (and temperature) merely distort the time scale. It should be noted that mechanical properties in general and viscoelastic behavior especially are also profoundly influenced by physical aging (Struik, 1978). It is now well established that under the influence of aging the creep compliance curve shifts toward longer times, which can be quantified by an aging-time shift factor as defined by Struik (1978). However, all samples used in this study had the same age, which by far exceeded the longest time in the experiment. Therefore, to a first approximation, aging was not taken into account (which will cause the model to be less accurate for differently aged samples). As opposed to aging, it has also been observed that plastic deformation beyond the yield point can result in a decrease of the viscosity, leading to intrinsic strain softening and a decrease of the yield stress. This phenomenon is called ''rejuvenation'' and is thought to be the result of mechanically ''de-aging'' the sample by plastic deformation (Hasan *et al.*, 1993; Struik, 1978). The good agreement between experiments and predictions for the stress-relaxation experiments, as well as the applicability of time-stress superposition, suggest that for monotone loading paths up to the yield stress, rejuvenation effects are not important.

It is also known that during plastic flow of a (glassy) polymer, the covalent bonded chains give rise to steric hindrance, resulting in a rubberlike strain hardening behavior (Arruda and Boyce, 1993). In this study, however, only the response up to the yield point is considered (relative small deformations) and strain hardening is not taken into account. Some aspects of strain hardening, like the state of deformation dependence and the issue of finite extensibility will be discussed in a forthcoming paper.

ACKNOWLEDGMENT

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APPENDIX: INTERCONVERSION OF LINEAR VISCOELASTIC RESPONSE FUNCTIONS

Interconversion of linear viscoelastic response functions in various modes of deformation is most readily done by invoking the correspondence principle. According to this principle, the appropriate Laplace transform of an elastic solution to a stress analysis problem corresponds to the viscoelastic solution in the transform plane. The time-dependent solution is then obtained by inverting the transform. The principle can only be applied if the boundaries themselves do not change with time (Tschoegl, 1989).

In case of step response functions the appropriate Laplace transform is the Carson transform (s-$\underline{m}$ultiple$\underline{d}$ Laplace transform). As an example, substitution of the Carson transforms sE and sD in the elastic relation $E = 1/D$ results in

$$\bar{E}(s)\bar{D}(s) = \frac{1}{s^2}.$$

Here, s is the transform variable and the overbar denotes the Laplace transform. Retransforming then yields the relation between the creep compliance and the relaxation modulus, Eq. (A1)

$$\int_0^t D(t-t')E(t')dt' = t. \tag{A1}$$

Conversion of the creep compliance in tensile mode to the shear relaxation modulus can be realized in a similar way. From Hooke's law for isotropic elastic materials the relation between the shear modulus G, the tensile compliance D, and the bulk modulus K reads

$$G = \frac{3K}{9KD-1}.$$

The Carson transform relation therefore becomes

$$s\bar{G}(s) = \frac{3s\bar{K}(s)}{9s\bar{K}(s)s\bar{D}(s)-1}.$$

Since it is assu$\underline{m}$ed that the volume response remains elastic, the Laplace transform of the bulk modulus K equals K_0/s and the transform equation becomes

$$s\bar{G}(s) = \frac{3K_0}{9K_0 s\bar{D}(s)-1}. \tag{A2}$$

This relation can be used to transform the experimental tensile compliance function $D(t)$ [Fig. 9] to the shear relaxation modulus $G(t)$ by collocation. To this extend, the experimental compliance function was first fitted to a generalized Kelvin–Voigt model

$$D(t) = D_g + \sum_{i=1}^{n} D_i (1 - e^{-t/\lambda_i}) + \frac{t}{\eta_0^e}$$

with the Carson transform

$$s\bar{D}(s) = D_g + \sum_{i=1}^{n} \frac{D_i}{1+\lambda_i s} + \frac{1}{s\eta_0^e}.$$

The fit was obtained using CONTIN, a constrained regularization program developed to invert ill-posed linear integral equations (Provencher, 1982a, 1982b). The key feature making CONTIN particularly suitable for fitting ill-posed problems is the ability to incorporate *a priori* knowledge of the solution structure, like non-negativity of the Kelvin–Voigt parameters, into the numerical algorithm (Mead, 1994). A satisfactory fit was obtained using a log-equidistant grid of eighteen relaxation times (see Fig. 9). The next step consisted of calculating for a range of s values the Carson transform of the shear relaxation modulus, $s\bar{G}(s)$, by substitution of the Carson transform of the Kelvin–Voigt representation of $D(t)$ into Eq. (A2). The resulting curve was fitted to a generalized Maxwell model

$$s\bar{G}(s) = \sum_{i=1}^{n} \frac{G_i \lambda_i s}{1+\lambda_i s}.$$

Again, the fit was obtained using CONTIN, imposing non-negativity of the Maxwell parameters and constraining the zeroth and the first moment of the distribution to the *a priori* known values of the glassy shear modulus G_g and the zero-shear viscosity η_0

$$G_g = \sum_{i=1}^{n} G_i = \frac{3K_0}{9K_0 D_g - 1},$$

$$\eta_0 = \sum_{i=1}^{n} \eta_i = \sum_{i=1}^{n} G_i \lambda_i = \frac{\eta_0^e}{3}.$$

The first relation follows from Hooke's law, whereas the second relation reflects the Trouton ratio between extensional and shear viscosity. An excellent fit was obtained using a log-equidistant grid of eighteen relaxation times. The resulting shear relaxation modulus is depicted in Fig. 10 and the eighteen shear moduli and relaxation times are tabulated in Table III. A check of the conversion procedure was provided by comparing the original fit of the Carson transform of $D(t)$ with the generalized Maxwell fit of (the Carson transform of) $G(t)$, again using Eq. (A2). A good agreement was obtained.

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