A simple model for non-linear stress relaxation

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A simple model for the prediction of non-linear stress relaxation following the cessation of steady shear flow is proposed. The model allows the calculation of the shear and first normal stress difference components of the stress. The mathematical flexibility of the model is reduced to a minimum with the result that no adjustable parameters are employed and only linear dynamic deformation data are required to calculate the non-linear behaviour. Verification of the model was carried out with data available for two viscoelastic fluids and good agreement between the predictions and the experimental results was obtained for the range of shear rates examined $(0.167 \leqslant \gamma \leqslant 16.7 \text{ sec}^{-1})$.

INTRODUCTION

Viscoelastic fluids which have been deformed to such an extent that their response is non-linear have proven difficult to model. The rheological attack on this problem area has generally resulted in constitutive equations designed to model all observed fluid phenomena. The equations thus obtained usually have a large number of parameters or a limited number of functionals. Of course, these equations must reduce considerably in the elementary situations such as steady simple shear flow. This axiomatic approach is described[1] as being 'developed in logical order from constitutive assumptions which are regarded as definitions of a certain class of materials—independent of the existence in nature of any materials satisfying the basic assumptions'. Much progress in the theory of viscoelasticity has been achieved through the axiomatic theories approach, however, the result is often inconvenient for engineering practice. This is a direct consequence of the 'high order memory function' required to model the non-linear viscoelastic behaviour and the resulting mathematical complexity.

The method proposed in this paper considerably reduces the mathematical flexibility of the model. The advantages that follow from this method are: (a) the calculation of the stress components during relaxation is simple and straightforward; (b) the model is directly testable by experimental data and errors do not accumulate in the calculation of a large number of parameters of functions; (c) the model can be interpreted qualitatively at the molecular level.

At the present state of development, the model is restricted to the stress relaxation occurring upon the cessation of steady shear flow. Rheologically, this restriction is severe but in practice there are a number of flows occurring in polymer processing (e.g. extrusion and injection moulding) where the method could be useful.

THEORY: REDUCTION OF THE NUMBER OF FREE PARAMETERS

The number of free parameters (moduli, viscosities or relaxation time constants) used in a rheological model is significant when the model is applied to real flow data. The problem associated with choosing the number of parameters has been discussed[2] for differential models, and for integral models[3]. The difficulty is essentially the same for both types of model and arises because the model incorporates either a series or spectral representation of the fluid properties. Stated briefly, the problem is that if the number of terms in the series (or the resolution of the spectrum) is increased then the accuracy of the parameter associated with each term (or the accuracy of the spectrum) is decreased[3,4]. Thus, for a given set of experimental data, we can either determine a large number of independent parameters with very large error or a small number of parameters with great precision but which are mutually interdependent. From a problem solving point of view both cases are equally bad. In addition, these models are computationally awkward even when solved numerically with the aid of a digital computer.

The difficulties outlined above can be avoided by a model based on an 'identity strategy'. This simple model reduces the number of parameters to a minimum yet allows the accurate calculation of non-linear stress relaxation. The model is developed by considering the fluid to be in steady state shear flow. This condition is described by the White—Metzner equation:

$$P + \theta \, \frac{\delta P}{\delta t} = 2\eta \mathbf{d} \tag{1}$$

where $\delta/\delta t$ = the Oldroyd derivative; θ = a characteristic time; P = the deviatoric stress tensor; η = fluid viscosity; $\mathbf{d}$ = the rate of deformation tensor.

We follow the interpretation of White and Metzner[5] and Seyer and Metzner[6] for θ and η and take:

$$\theta = \frac{P_{11} - P_{12}}{2P_{12}} \quad \text{and} \quad \eta = \frac{P_{12}}{\dot{\gamma}} \tag{2}$$

In this case, equation (1) is an identity and is satisfied by any viscoelastic fluid in steady shear flow provided only that the second normal stress difference, $P_{22}-P_{33}$ is zero. The idea of Truesdell[7] that a fluid in steady shear flow may

be characterized by only one relaxation time leads to the following equation at the instant of cessation of flow:

$$\frac{dP_{12}}{dt} = -\frac{1}{\theta} P_{12} \ ; \ t = 0 \tag{3}$$

Equation (3) serves to define the characteristic time, θ, and thus at the cessation of flow we have two characteristic times: θ, defined by the steady shear and $\bar{\theta}$. If the fluid is regarded as experiencing simultaneous stress build-up and relaxation in steady shear[8] and there is no large discontinuity in the relaxation properties at the instant of cessation of flow we may take the two characteristic times as equal, $\theta \cong \bar{\theta}$. Experimentally, it is known that the rapid relaxation rate occurring at the cessation of flow persists for a short time and equation (3) may be applied in the interval, $0 \leqslant t \leqslant 1/\dot{\gamma}$. This is justified by the molecular interpretation recently proposed by Hlaváček and Carreau[8] where the macromolecule retains some compact coiled structure which is responsible for the relaxation behaviour for $t \leqslant 1/\dot{\gamma}$. The model of simultaneous stressing and relaxation suggests a correspondence between the characteristic time in steady shear flow and an effective relaxation time, θ_l, obtained from dynamic (sinusoidal) deformation[9]. The characteristic time, θ_l, is obtained from:

$$\theta_l = \frac{G'(\omega)}{G''(\omega)\omega} \tag{4}$$

where G' and G'' are respectively the real and imaginary parts of the complex loss modulus and ω is the frequency of the sinusoidal excitations. Hlaváček et al.[9] noted that at the cessation of flow the relationship $(\theta - \Delta\theta)_{t=0} \simeq \theta_l$, where $\Delta \ll 1$, is valid and θ_l is thus the characteristic parameter governing the fluid's memory.

In this paper, we take directly, $\theta - \Delta\theta|_{t=0} = \theta_l$ and use the approximation:

$$\theta \approx \bar{\theta}|_{t=0} = \theta_l = \frac{G'(\omega)}{G''(\omega)\omega} \Bigg|_{\omega=\dot{\gamma}} \tag{5}$$

for the interval $0 \leqslant t \leqslant 1/\dot{\gamma}$.

For long times, $t \to \infty$, the component P_{12} relaxes according to the well-known function:

$$\frac{dP_{12}}{dt} = \frac{1}{\tau_{max}} P_{12} \ ; \quad t \to \infty \tag{6}$$

where τ_{max} is the largest relaxation time in the spectral sense. For the purposes of calculation, equation (6) can be applied for $t \geqslant \tau_{max}$ with negligible error. The characteristic time $\bar{\theta}$ is seen to be a function of time in the interval $\theta_l \leqslant \bar{\theta} \leqslant \tau_{max}$ as t varies between $1/\dot{\gamma}$ and τ_{max}. In the manner of Hlaváček et al.[9] we choose the following dependence for $\bar{\theta}(t)$:

$$\bar{\theta}(t) = \frac{G'(\omega)}{G''(\omega)\omega} \Bigg|_{\omega=1/t} \tag{7}$$

and note that the similarity between $\log\theta$ vs. $\log 1/t$ and $\log\theta_l$ vs. $\log\omega$ supports the use of equation (7).

The P_{12} component may thus be found at any time by use of the appropriate relaxation time, $\bar{\theta}$, for that instant:

$$\frac{dP_{12}}{dt} = -\frac{1}{\bar{\theta}} P_{12}, \text{ all } t \tag{8a}$$

where

$$\bar{\theta} = \frac{G'(\omega)}{G''(\omega)\omega} \Bigg|_{\omega=\dot{\gamma}} \qquad 0 \leqslant t \leqslant \frac{1}{\dot{\gamma}} \tag{8b}$$

$$= \frac{G'(\omega)}{G''(\omega)\omega} \Bigg|_{\omega=1/t} \qquad \frac{1}{\dot{\gamma}} \leqslant t \leqslant \tau_{max} \tag{8c}$$

$$= \tau_{max} \qquad\qquad t \geqslant \tau_{max} \tag{8d}$$

Similarly, the normal stress component, $P_{11}-P_{22}$, as determined from equations (2) and (3) is:

$$\frac{d(\tilde{P}_{11} - \tilde{P}_{22})}{dt} = -\frac{1}{\bar{\theta}} (\tilde{P}_{11} - \tilde{P}_{22}) - \tilde{P}_{12} \tag{9}$$

where $\bar{\theta}$ is given by equations (8b, 8c, 8d). The tilde, $\tilde{\ }$, indicates the normalized component, e.g. $\tilde{P}_{ij} = P_{ij}(t)/P_{ij}(t=0)$.

The model may be summarized as the approximation embodied in equation (8c) which interpolates between the points $t = 0$ and $t = \infty$ where equation (8a) is identically satisfied. The model has been tested with data of two viscoelastic fluids as described below. Equation (9) is the corresponding approximation for the first normal stress difference and has been verified (for a slightly different history of $\bar{\theta}$) recently by Hlaváček et al.[9].

CALCULATIONS AND EXAMPLES

The differential equations (8) and (9), valid in a small time interval, Δt, are written in finite difference form as:

$$\{P_{12}\}_{i+1} = \{P_{12}\}_i \exp - \left(\frac{\Delta t}{\bar{\theta}_i}\right) \tag{10}$$

$$\{\tilde{P}_{11} - \tilde{P}_{22}\}_{i+1} = - \{(\tilde{P}_{11} - \tilde{P}_{22}) - \tilde{P}_{12}\}_i \times$$

$$\exp - \left(\frac{\Delta t}{\bar{\theta}_i}\right) + \{\tilde{P}_{11} - \tilde{P}_{22}\}_i \tag{11}$$

The subscripts i and $i + 1$ refer to the values of the variables at the ith and $i + 1$ time intervals respectively. Two systems (1.5% polyacrylamide and 2% polyisobutene solutions) for which relaxation data were available[10] and whose properties are given in *Table 1* were used to verify the model. The results are presented in *Figures 1–4* as dimensionless stress *versus* time for both shear and normal components for a range of steady shear deformation rates. Generally, good agreement is obtained for the range of variables examined.

The small discontinuity evidenced by the dimensionless stress relaxation curves commencing at a value somewhat smaller than 100% at time, $t = 0$, is not explicitly accounted for at this stage of development of the model. Consequently, it was necessary to estimate the discontinuity by assuming different values for the magnitude of the discontinuity and choosing the value that gave the best fit of calculated results to the experimental data. It was found that the discontinuity was about 12% of the steady shear value (for

Table 1 Data for the two fluids used to test the proposed non-linear stress relaxation model

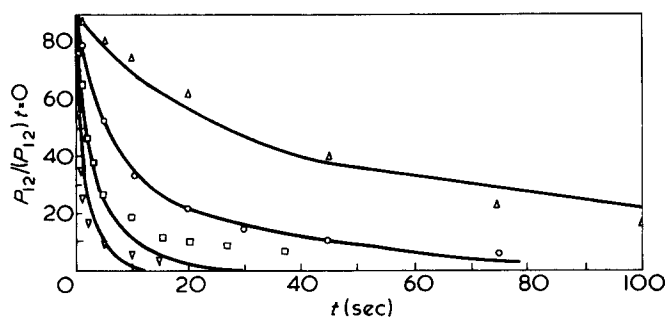| $\dot{\gamma}$ (sec^{-1})	2.0% Polyisobutylene in Primol 355				1.5% Polyacrylamide (Dow ET597) in 50/50 vol % water—glycerine			
	$\dfrac{P_{11}-P_{22}}{2P_{12}\dot{\gamma}}$	θ_I (sec)	$\eta(\dot{\gamma})$ (cp)	$\dfrac{\eta(\dot{\gamma})}{\eta'(\omega=\dot{\gamma})}$	$\dfrac{P_{11}-P_{22}}{2P_{12}\dot{\gamma}}$	θ_I (sec)	$\eta(\dot{\gamma})$ (cp)	$\dfrac{\eta(\dot{\gamma})}{\eta'(\omega=\dot{\gamma})}$
0.0167	61.7	58.4	4080	1.18	—	—	—	—
0.040	35.8	32.0	2370	1.32	30.8	24.3	1334	1.38
0.167	12.6	10.2	942	1.60	12.2	8.55	534	1.61
0.400	6.45	4.77	535	1.82	6.03	4.13	299	1.77
1.67	2.06	1.30	212	2.24	1.97	1.16	115	2.07
4.00	1.03	0.579	120	2.55	0.962	0.520	64.5	2.27
16.7	0.322	0.149	47.0	3.14	0.290	0.135	24.8	2.65
40.0	0.160	0.064	26.8	3.57	0.135	0.0580	13.9	2.92
167.0	—	—	—	—	0.0400	0.0147	5.33	3.41
400.0	—	—	—	—	0.0192	0.0630	2.97	3.76

Figure 1 Dimensionless shear stress relaxation for 2% polyisobutylene solution in Primol 355. Calculated values of $\dot{\gamma}$ (sec^{-1}): △, 0.0167; ○, 0.162; □, 0.527; ▽, 5.27. ——, Experimental data
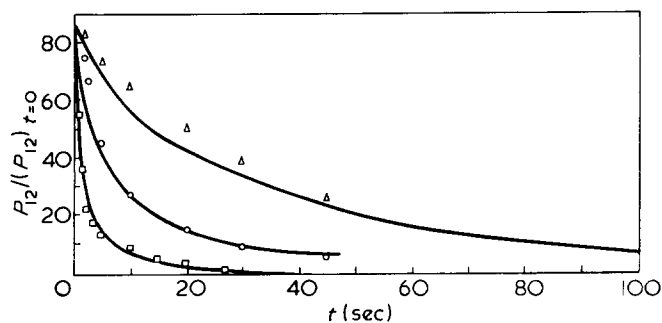

Figure 3 Dimensionless shear stress relaxation for 1.5% polyacrylamide (DOW ET-597) solution in 50/50 water/glycerine. Calculated values of $\dot{\gamma}$ (sec^{-1}): △, 0.0167; ○, 0.167; □, 1.67. ——, Experimental data
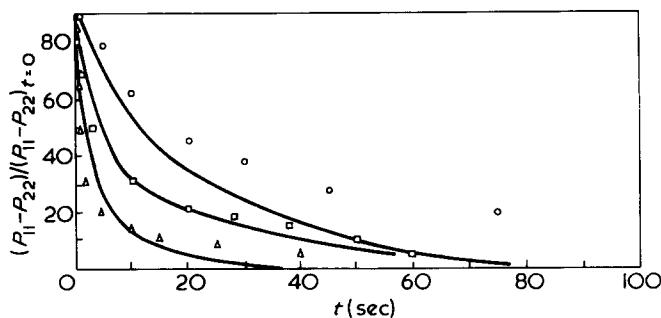

Figure 2 Dimensionless 1st normal stress difference relaxation for 2% polyisobutylene solution in Primol 355. Calculated values of $\dot{\gamma}$ (sec^{-1}):○, 0.167;□, 1.67; △, 16.7. ——, Experimental data
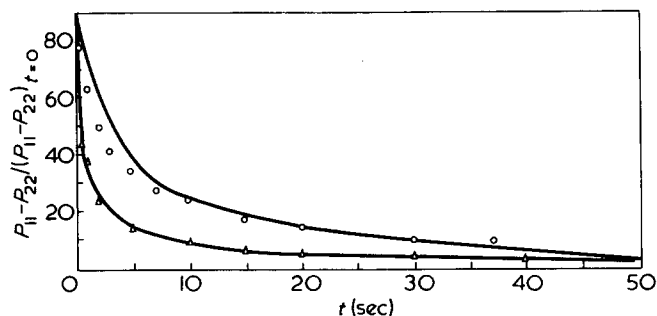

Figure 4 Dimensionless 1st normal stress difference relaxation for 1.5% polyacrylamide (DOW ET-597) solution in 50/50 water/glycerine. Calculated values of $\dot{\gamma}$ (sec^{-1}): ○, 1.67; △, 16.7. ——, Experimental data

each component) for the polyacrylamide solution and approximately 10% for the polyisobutylene solution.

The choice of Δt for the calculation is relatively non-critical and is easily established. Clearly, at small time, Δt has the limit $\Delta t \leqslant 1/\dot{\gamma}$. In practice it seems adequate to take $\Delta t \leqslant 1/10\dot{\gamma}$ for the region $t \leqslant 1/\dot{\gamma}$. At long times, $t \geqslant \tau_{max}$, the calculation is sufficiently accurate with $\Delta t = \tau_{max}$. In the interval between $t = 1/\dot{\gamma}$ and $t = \tau_{max}$, $\Delta t = 1/\dot{\gamma}$ is adequate although a logarithmic variation of Δt minimizes the number of iterations required at the expense of additional program complexity. It is remarked that, in general, reducing Δt leads to a more accurate solution and does not cause computational problems.

DISCUSSION

It is seen from *Figures 1–4* that agreement between the proposed method and experimental data is quite good. In general, the model tends to underestimate the speed of relaxation, particularly at slow rates of deformation. This may be due to either inaccuracies in the original data or it may reflect the difficulty of accurately determining the dynamic modulus at low frequencies. Since the relaxation curves are calculated directly from the value of $\overline{\theta}$ obtained from the dynamic moduli (equations 8b—d) the errors appear undiminished in the result. It appears that the model is sufficiently accurate to warrant further investiga-

tion and the proposal that the rate of stress relaxation is governed by an effective relaxation time obtained from dynamic data has validity.

The model completely avoids the problems, both computational and interpretive, associated with the extrapolation of 'higher order memory functions' into the regime of non-linear behaviour. In place of the multiparametric approach there is only one parameter, a variable relaxation time which is specified throughout its range in a simple manner and, at the extrema, by equations which are identically satisfied. This yields a model which is simple and straightforward.

The non-linearity is accounted for by the very short relaxation times which are dominant immediately after the cessation of flow. Thereafter the relaxation is governed by relaxation times determined from dynamic data. This is reasonable in view of the similarity between the curves of θ and θ_I[9] (*Table 1*) and the physical interpretation of this similarity recently proposed by Hlaváček and Carreau[8]. This interpretation is based on a proposal by Bueche[11] that a macromolecule in steady shear flow experiences an oscillating stress and is consistent with a greater rigidity $[G'(\omega)]$ and a faster non-linear stress relaxation at higher rates of deformation. This is in contrast to the network theories[12], where parameters of the theory have to be varied in order to obtain a satisfactory fit to the data. The problem in this situation is the interpretation of this variation since the parameter is not directly related to the physical model. In the proposed model the memory of the fluid at higher gradients is shorter because $\bar{\theta}$ is a sharply decreasing function of $\dot{\gamma}$ and not because a certain level of network deformation has been reached. Consequently, $\bar{\theta}$ is seen to be the parameter governing the memory of the fluid.

A difficulty with the proposed model (and others) is the apparent discontinuity of the stress at the cessation of flow. At the present time, there is no obvious way to include this discontinuity which may be due to purely viscous effects in the polymer solution. An alternative possibility is that it is an artifact of the method used to obtain the data. In either case, it is clear that additional data is required to give insight into the effect (instantaneous viscous 'relaxation' or an extremely fast non-linear relaxation) or to obtain accurate data with which to test or modify the existing model. Since the effect is small, about 10% of the steady state stress, it is not anticipated that the basic features of the model will be required to be changed.

CONCLUSIONS

A model based on the White—Metzner equation and the idea of Truesdell to characterize a steady shear flow by one characteristic time has been formulated to predict non-linear stress relaxation. The model is simple and has only one time varying parameter, $\bar{\theta}$, which is easily calculable from linear dynamic moduli data. The model thus avoids the difficulties inherent in the higher order memory func-

tion models because of the close relationship of $\bar{\theta}$ to experimental data and predicted results. Further, the correlation afforded by the use of the dynamic modulus is easily interpretated by ideas originally proposed by Philippoff[13] and Bueche[11] and recently refined and extended by Hlaváček and Carreau[8].

The model uses easily obtained linear dynamic data, and these data are used to predict the non-linear stress relaxation.

NOMENCLATURE

d	the rate of deformation tensor,
G'	real part of the complex modulus,
G''	imaginary part of the complex modulus,
P	deviatoric stress tensor,
t	time,
$\dot{\gamma}$	shear rate,
$\delta/\delta t$	Oldroyd derivative,
η	fluid viscosity,
θ	characteristic time, equation (1),
$\bar{\theta}$	characteristic time, equation (3),
θ_I	characteristic time, equation (4),
τ_{max}	largest relaxation time of the fluid,
ω	frequency of sinusoidal excitation.

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