Modifications to Non-linear Rheological Models of Viscoelastic Fluids

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ABSTRACT

Four constitutive equations have been used to describe the behaviour of viscoelastic fluids viz., (i) upper convected Maxwell, (ii) Oldroyd 4-constant, (iii) Bogue-White and (iv) Bird-Carreau. These were modified to improve their ability to predict the observed behaviour of viscoelastic fluids in viscometric and oscillatory shear flows. The fluids used during the experimental work are four different concentrations of polyacrylamide (Separan AP 30) solutions, i.e. 0.6, 0.8, 1.0, and 1.2%, in glycerine / water mixtures. The experimental data are obtained under simple shear and small-amplitude oscillatory shear flow conditions. The viscosity data, obtained from steady shear experiments, and the dynamic viscosity and storage modulus obtained from oscillatory shear experiments have been used to determine the model parameters. The performance of the original and modified models have been studied by comparing their predictions of the viscosities, in steady, and the dynamic viscosities, in oscillatory shear flows. The average root mean square has been used as a criterion for the comparison. Finally, the results of the predictions made by the modified models to the first normal stress coefficients are given to see how they can predict a material function other than those used to determine the model parameters. This may justify the application of these modified models in complex flows such as free coating.

Key Words: rheological models, viscoelastic fluids, shear flows, viscometric material functions, small-amplitude-oscillatory material function

INTRODUCTION

Practical processes such as free coating consist of complex flow fields that are combinations of simpler flows, e.g. steady simple shear. In applying a constitutive equation to these kinds of flows, one important point is how the model parameters should be determined so that they may be suitable to be used in the

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process. So far no single constitutive model capable of describing the fluid behaviour in all possible flow fields has been proposed. Therefore, any constitutive model has an area of performance within which the specified flow field may be explained satisfactory.

Standard constitutive equations in literature are usually applied to some simple kinds of flows. This motivated the authors to modify some constitutive equations to test their ability in characterizing the behaviour of viscoelastic materials undergoing tests in viscometric and oscillatory shear flows in predicting, e.g., the final film thickness in free coating.

Since it has been shown [1–3] that the upper convected Maxwell model, the Oldroyd 4-constant model, the Bogue-White model and the Bird-Carreau model give rather reasonable results in free coating, so they have been considered in this work.

MODIFIED MODELS

Modified Upper Convected Maxwell Model

Spearot and Metzner [4] put forward a modified upper convected Maxwell model as:

$$\tau + \lambda(\Pi_d)\tau_{(1)} = -\eta(\Pi_d)\gamma_{(1)} \tag{1}$$

$$\gamma_{(1)} = \dot{\gamma} = 2d = \nabla v + (\nabla v)^{\dagger} \tag{2}$$

where the first upper convected time derivative is:

$$\Lambda_{(1)} = \frac{D}{Dt}\Lambda - (\nabla v)^{\dagger}\cdot\Lambda - \Lambda\cdot(\nabla v) \tag{3}$$

for an arbitrary second-order tensor Λ, with the second invariant $\Pi_d = 1/2(d{:}d)$.

In applying this modified upper convected Maxwell model to spinning of polymer melts, they suggested the relations $\lambda = \lambda_0/(1+c\lambda_0^2\Pi_d)$, and $\eta = G\lambda$ where c and λ_0 are constants. They assumed that G is also a constant. This is clearly not so for many polymer solutions. The shear and elongational response of the model failed to agree with experimental data [5].

Baid and Metzner [5] in applying the modified upper convected Maxwell model in elongational flow used two different functional forms for λ, and η but the application of their model to elongational flow yielded poor agreement.

To obtain a more flexible modification, the following functional forms for λ, and η have been chosen in this work:

$$\eta(\Pi_d) = \eta_0/(1 + a\Pi_d^b)\ ;\ \lambda(\Pi_d) = \lambda_0/(1 + c\Pi_d^d) \tag{4}$$

where a, b, c, and d are material constants.

Modified Oldroyd 4-Constant Model

Oldroyd 8-constant model [6] and Oldroyd 3-constant model of Williams and Bird [7] are limited to small shear rates and frequencies. Adachi et al. [3] have empirically modified the 4-constant version of the Oldroyd model to predict the film thickness in free coating of viscoelastic materials, but their model did not agree with experimental data. The following constitutive equation is proposed to cover the experimental data more satisfactorily:

$$\pi + \lambda_1(\Pi_d)\tau_{(1)} + \frac{1}{2}\mu_0(\mathrm{tr}\tau)\lambda_{(1)} = -\eta_0(\lambda_{(1)} + \lambda_2(\Pi_d)\gamma_{(2)}) \tag{5}$$

where, $\gamma_{(2)} = (\gamma_{(1)})_{(1)} = \frac{D}{Dt}\gamma_{(1)} - (\nabla v)^{\dagger}\cdot\gamma_{(1)} - \gamma_{(1)}\cdot(\nabla v)$
and:

$$\lambda_1(\Pi_d) = \lambda_{10}/(1 + c_1\Pi_d^{c_2});\ \lambda_2(\Pi_d) = \lambda_{20}/(1 + c_3\Pi_d^{c_4}) \tag{6}$$

λ_{10}, λ_{20}, η_0, μ_0, c_1, c_2, c_3, and c_4 are material constants.

Modified Bogue-White Model

Spearot et al. [4] in studying the behaviour of a series of molten polymers undergoing an extensional flow, used the Bogue-White eqn [8]:

$$\tau = \int_{-\infty}^{t} M[(t-t'), \Pi_d(t-t')]\gamma_{[0]}(t, t')dt' \tag{7}$$

$$\gamma_{[0]ij}(x, t, t') = \delta_{ij} - \frac{\partial x_i(x', t', t)}{\partial x'_m}\cdot\frac{\partial x_j(x', t', t)}{\partial x'_n} \tag{8}$$

(see, e.g. Bird et al. [9]) where:

$$M[(t-t'), \Pi_d(t-t')] = \sum_k \frac{G_k}{\lambda_{\mathrm{eff},k}}\exp[-(t-t')/\lambda_{\mathrm{eff},k}] \tag{9}$$

$$\lambda_{eff,k} = \frac{\lambda_k}{1 + a(\lambda_k \langle \Pi_d^{1/2} \rangle)} \quad (10)$$

$$\langle \Pi_d^{1/2} \rangle = \frac{1}{s} \int_0^s [\Pi_d(s)]^{1/2} ds \quad (11)$$

and s = t − t′. They found that the two-term series of the above equations do not portray the shear and elongational data satisfactorily. The following modification to eqn (9) is used to overcome this drawback in this work:

$$\lambda_{eff,k} = \frac{\lambda_k}{1 + a(\lambda_k \langle \Pi_d^{1/2} \rangle)^{\alpha}} \quad (12)$$

α is a constant and a is an adjustable parameter.

Modified Bird-Carreau Model

As pointed out by Carreau [10], the Bird-Carreau model [11] has been found inadequate in fitting the stress growth, stress versus hysteresis loop, finite-amplitude sinusoidal and mainly transient data. Carreau argued that the dependency of memory function on the second invariant of Bird-Carreau model is not adequate. He then modified the latter. However, the Carreau model is too complicated and it has been shown by Macdonald [12] that this model fails to describe the large amplitude oscillatory data. To obtain a more adequate functional dependency on the second invariant of the rate-of-strain tensor, in this investigation the memory function of the Bird-Carreau model [11] is modified as:

$$M[(t-t'), \Pi_d(t-t')] = \sum_{n=1}^{\infty} \frac{\eta_n}{\lambda_2^{(n)2}} \frac{\exp[-(t-t')/\lambda_2^{(n)}]}{1 + b\lambda_2^{(n)2}[\sqrt{\Pi_d(t-t')}]^{\beta}} \quad (13)$$

with the same single integral of eqn (7).

Where β and b are constants and the following empricisms are assumed for parameters:

$$\eta_n = \eta_0 \lambda_1^{(n)} / \sum_{k=1}^{\infty} \lambda_1^{(k)} \quad (14)$$

$$\lambda_k^{(n)} = \left(\frac{2}{n+1}\right)^{\alpha_k} \lambda_k \quad \text{for } k = 1,2 \quad (15)$$

Considering the proposed modifications as a whole, it may be seen that they consist of improving the dependency of model parameters and memory functions on the second invariant of the rate-of-strain tensor which in turn describes how fast the fluid under consideration deforms with time. All the modifications are based on the nature of the corresponding material properties such as non-Newtonian viscosity and relaxation time. Therefore, the modifications put no unwanted influence on the physical nature of the original models. For example, the decreasing of the viscosity with increasing shear rate in steady shear flow, i.e. shear thinning, is known for normal non-Newtonian fluids such as CMC or polyacrylamide solutions. Therefore, the functional forms given here, e.g. eqn (4), are quite realistic.

MATERIAL FUNCTIONS

Steady Shear Flow

In a steady shear flow with a constant shear rate $\dot{\gamma} = |\partial v_1/\partial x_2|$, we have:

$$v_1 = v_1(x_2) = \dot{\gamma} x_2 \; ; \; v_2 = v_3 = 0$$

These kinds of kinematical relations may be used when the fluid motion is to be described by means of the velocity field $v(x, t)$ that is suitable for derivative-type constitutive models. Since, for integral-type models, finite strain tensors are to be considered, an alternative description of the fluid motion is needed. In this approach, a fluid particle is selected and then its trajectory through the three-dimensional space occupied by the fluid is considered. At some past time t′ the particle has position x_i', and at the present time t the particle has position x_i. The designation x_i, t (or x_i', t′) then uniquely specifies the particle and is referred to as a "particle label." The motion of the particle may then be described by the functions:

$$x_i' = x_i'(x, t, t')$$

which give the past position x_i' of the particle x_i, t as function of time t′, or by the functions:

$$x_i = x_i(x_i', t', t)$$

which give the present position x_i of the particle x_i', t' as a function of time t. The functions on the right sides of the two last equations are called the displacement functions. In these functions the first two arguments identify the particle and the last argument indicates the time dependence. The displacement functions for all particles and all times completely specify the motion of the fluid. For the present steady shear flow we have:

$$x_1' = x_1 - \dot{\gamma}(t - t')x_2$$
$$x_2' = x_2$$
$$x_3' = x_3$$

Steady-shear material functions are:

$$\tau_{12} = -\eta\dot{\gamma}$$
$$\tau_{11} - \tau_{22} = -\psi_1\dot{\gamma}^2$$

Material functions, as defined above, for modified models are:

(i) modified upper convected Maxwell model:

$$\eta(\dot{\gamma}) = \eta_0/(1 + a\Pi_d^b) \quad (16)$$

$$\psi_1(\dot{\gamma}) = 2\eta_0\lambda_0/(1 + a\Pi_d^b)(1 + c\Pi_d^d) \quad (17)$$

where $\Pi_d = \dot{\gamma}^2/4$

(ii) modified Oldroyd 4-constant model:

$$\eta(\dot{\gamma}) = \eta_0 \frac{(1 + c_3\Pi_d^{c_4}) + \eta_0\lambda_{20}\dot{\gamma}^2}{(1 + c_1\Pi_d^{c_2}) + \eta_0\lambda_{10}\dot{\gamma}^2} \times \frac{(1 + c_1\Pi_d^{c_2})}{(1 + c_3\Pi_d^{c_4})} \quad (18)$$

$$\psi_1(\dot{\gamma}) = 2\eta_0 \frac{\lambda_{10}(1 + c_3\Pi_d^{c_4}) - \lambda_{20}(1 + c_1\Pi_d^{c_2})}{[(1 + c_1\Pi_d^{c_2}) + \eta_0\lambda_{10}\dot{\gamma}^2](1 + c_3\Pi_d^{c_4})} \quad (19)$$

(iii) modified Bogue-White model:

$$\eta(\dot{\gamma}) = \textstyle\sum_i G_i\lambda_i/[1 + a\lambda_i(\dot{\gamma}/2)^{\alpha}] \quad (20)$$

$$\psi_1(\dot{\gamma}) = 2\textstyle\sum_i G_i\lambda_i^2/[1 + a\lambda_i(\dot{\gamma}/2)^{\alpha}]^2 \quad (21)$$

(iv) modified Bird-Carreau model:

$$\eta(\dot{\gamma}) = \frac{\eta_0}{\zeta(\alpha_1) - 1} \sum_{n=2}^{\infty} \frac{n^{\alpha_1}}{n^{2\alpha_1} + b2^{2\alpha_1}\lambda_1^2\dot{\gamma}^{\beta}} \quad (22)$$

$$\psi_1(\dot{\gamma}) = \frac{2^{\alpha_2+1}\lambda_2\eta_0}{\zeta(\alpha_1) - 1} \sum_{n=2}^{\infty} \frac{n^{\alpha_1-\alpha_2}}{n^{2\alpha_1} + b2^{2\alpha_1}\lambda_1^2\dot{\gamma}^{\beta}} \quad (23)$$

It should be noted that the infinite series in eqns (22 and 23) converge very rapidly, therefore, in the present investigation only five terms of the series are used in evaluation of $\eta(\dot{\gamma})$, and $\psi_1(\dot{\gamma})$ and rearrangements of these equations to more rapidly convergent series are avoided.

Oscillatory Shear Flow

For small-amplitude sinusoidal shear flow with frequency ω of:

$$v_1 = v_1(x_2, t)$$
$$v_2 = 0$$
$$v_3 = 0$$

the kinematics of the flow is described by:

$$x_1' = x_1 - \Re e\{\frac{v_1^{\circ}(x_2)}{i\omega}(e^{i\omega t} - e^{i\omega t'})\}$$
$$x_2' = x_2$$
$$x_3' = x_3$$

The superscript '°' shows complex amplitude. For small-amplitude oscillations, quantities oscillate as:

$$\dot{\gamma} = \Re e\{\dot{\gamma}^{\circ}e^{i\omega t}\}$$
$$\tau_{12} = \Re e\{\tau_{12}^{\circ}e^{i\omega t}\}$$

Using the definition of linear viscoelasticity in the limit of small-amplitude oscillations, we have:

$$\tau_{12}^{\circ} = -\eta^{*}|\dot{\gamma}^{\circ}|$$

$$\eta^{*} = \eta' - i\frac{G'}{\omega}$$

It can be shown that the real strain-amplitude $\dot{\gamma}^{\circ}$ is given by [13]:

$$\dot{\gamma}^{\circ} = (\omega\phi_1/\theta_c)\left((\phi_2/\phi_1)^2 - 2(\phi_2/\phi_1)\cos\varepsilon + 1\right)^{1/2} \quad (24)$$

where ϕ_1 and ϕ_2 are angular amplitude of the motion of the plate and cone, respectively, ε is the phase shift and θ_c is the gap angle. In this work the second invariant of strain tensor is taken as $\Pi_d(\omega) = \dot{\gamma}^{\circ 2}/4$.

Material functions for modified models are:

(i) modified upper convected Maxwell model:

$$\eta'(\omega) = \eta_0 \frac{(1 + c\Pi_d^d)^2}{(1 + c_1\Pi_d^d)^2 + (\lambda_0\omega)^2} \tag{25}$$

$$\frac{G'(\omega)}{\omega^2} = \eta_0\lambda_0 \frac{(1 + c\Pi_d^d)}{(1 + c\Pi_d^d)^2 + (\lambda_0\omega)^2} \tag{26}$$

(ii) modified Oldroyd 4-constant model:

$$\eta'(\omega) = \eta_0[(1 + c_1\Pi_d^{c2})(1 + c_3\Pi_d^{c4}) + \lambda_{10}\lambda_{20}\omega^2](1 + c_1\Pi_d^{c2})/[(1 + c_1\Pi_d^{c2}) + (\lambda_{10}\omega)^2](1 + c_3\Pi_d^{c4}) \tag{27}$$

$$\frac{G'(\omega)}{\omega^2} = \eta_0[\lambda_{10}(1 + c_3\Pi_d^{c4}) - \lambda_{20}(1 + c_1\Pi_d^{c2})] (1 + c_1\Pi_d^{c2})/[(1 + c_1\Pi_d^{c2}) + (\lambda_{10}\omega)^2](1 + c_3\Pi_d^{c4}) \tag{28}$$

(iii) modified Bogue-White model:

$$\eta'(\omega) = \Sigma_i \frac{G_i\lambda_i}{1 + \lambda_i^2(\omega/2)^\alpha} \tag{29}$$

$$\frac{G'(\omega)}{\omega^2} = \Sigma_i \frac{G_i\lambda_i^2}{1 + \lambda_i^2(\omega/2)^\alpha} \tag{30}$$

(iv) modified Bird-Carreau model:

$$\eta'(\omega) = \frac{\eta_0}{\zeta(\alpha_1) - 1} \sum_{n=2}^{\infty} \frac{n^{2\alpha_2-\alpha_1}}{n^{2\alpha_2} + b2^{2\alpha_2}\lambda_2^2\omega^\beta} \tag{31}$$

$$\frac{G'(\omega)}{\omega^2} = \frac{2^{\alpha_2}\lambda_2\eta_0}{\zeta(\alpha_1) - 1} \sum_{n=2}^{\infty} \frac{n^{\alpha_2-\alpha_1}}{n^{2\alpha_2} + b2^{2\alpha_2}\lambda_2^2\omega^\beta} \tag{32}$$

DETERMINATION OF THE MODEL PARAMETERS

The model parameters in the various constitutive equations can be determined by minimizing the total sum of squares of relative errors $\varepsilon_i = (y_i - f_i)/y_i$, i.e., in $\sum_{n=2}^{\infty} \varepsilon_i^2$ which y_i and f_i are the measured and calculated values of a property, i.e. non-Newtonian viscosity, η, dynamic viscosity, η', and storage modulus G' here. The summation includes the entire experimental data.

Table 1. Parameters of modified upper convected Maxwell model.

Fluid No.	1	2	3	4
η_0 (Nsm^{-2})	7.808	38.740	51.020	66.009
λ_0 (s)	11.857	34.15	42.42	34.24
a	2.676	7.217	6.640	7.715
b	0.341	0.351	0.383	0.342
c	7.182	15.879	22.601	25.858
d	0.385	0.347	0.323	0.335

The optimization toolbox of the computer software Matlab (version 5.1) for Windows is used for the minimization procedure.

Obtaining the model parameters as discussed above, other properties such as first normal stress coefficient, ψ_1, can be calculated. Hence, the results of the calculations can be compared with experimental values of ψ_1.

For modified Bogue-White model, a two-term series of eqn (20) and for modified Bird-Carreau model, five-term series of eqns (22 and 31) were used.

Model parameters are given in Tables 1–4.

EXPERIMENTAL

Experimental data were obtained on four solutions of

Table 2. Parameters of modified Oldroyd 4-constant model.

Fluid No.	1	2	3	4
η_0 (Nsm^{-2})	6.544	32.073	37.202	38.439
λ_{10} (s)	4.389	7.400	9.199	5.738
λ_{20} (s)	2.516	1.190	1.862	1.458
μ_0 (s)	14.404	36.856	6.208	8.310
c_1	0.105	0.072	0.029	0.042
c_2	0.425	0.501	0.555	0.539
c_3	1.150	1.354	0.537	0.637
c_4	0.365	0.223	0.316	0.286

Solutions of: (1) 0.6%, (2) 0.8%, (3) 1.0% and (4) 1.2% polyacrylamide (Separan AP30) in a 50/50 mixture by weight of water and glycerine.

Table 3. Parameters of modified Bogue-White model.

Fluid No.	1	2	3	4
G_1 (Nm^{-2})	58.760	56.014	57.498	57.251
G_2 (Nm^{-2})	1.569	1.857	1.856	1.760
λ_1 (s)	0.148	1.246	1.076	1.073
λ_2 (s)	0.120	1.184	3.242	1.105
α (s)	0.636	0.626	0.718	0.696
a	15.941	18.487	13.370	10.216

different concentrations as 0.6%, 0.8%, 1.0% and 1.2% polyacrylamide (Separan AP 30) in 50/50 mixtures by weight of glycerine and water designated here as fluids no. 1, 2, 3 and 4, respectively. The viscous properties were obtained using a rotational concentric cylinder viscometer, a Haake RV1, however, the geometry and construction of this instrument limit the shear rate range obtainable to approximately 10–1000 s^{-1} without the use of large gaps between the cylinders for which shear rate corrections would be necessary. The information not being available from measurements in the concentric cylinder viscometer is obtained using a cone-and-plate system on a Weissenberg Model R–18 Rheogoniometer. The opportunity was also taken to examine the elastic nature of these fluids by measuring the normal force on the lower platen. Furthermore, dynamic viscosities, η', and storage moduli, G', were measured through small-amplitude oscillatory shear experiments using the oscillatory mode of the

Table 4. Parameters of modified Bird-Carreau model.

Fluid No.	1	2	3	4
η_0 (Nsm^{-2})	7.809	37.840	51.020	66.009
λ_1 (s)	2.753	6.740	4.245	5.633
λ_2 (s)	12.211	143185	7.060	10.846
α_1	3.032	4.087	3.698	2.829
α_2	2.649	3.192	2.723	1.720
β	1.142	1.303	1.365	1.124
b	1.249	1.177	2.544	1.366

Solutions of: (1) 0.6%, (2) 0.8%, (3) 1.0% and (4) 1.2% polyacrylamide (Separan AP30) in a 50/50 mixture by weight of water and glycerine.

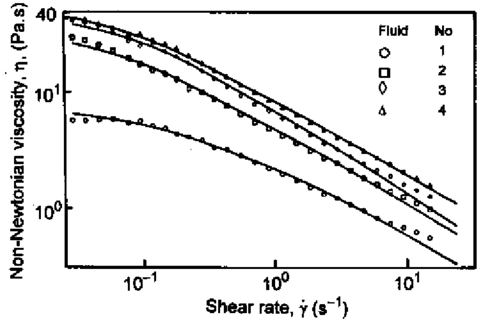

Figure 1. Evaluation of the modified convected Maxwell model with data.

Weissenberg rheogoniometer.

The results of the measurements are given graphically in Figures. 1, 2, 4–7.

RESULTS AND DISCUSSION

As discussed before, to evaluate the material parameters, non-Newtonian viscosity and dynamic viscosity data have been used. Data fitting ability of models, in this work, are evaluated by means of RMS Error defined as:

$$\text{RMS Error} = \left(\sum_{i=1}^{N} \varepsilon_i^2/N\right)^{1/2};\ \varepsilon_i = (y_i - f_i)/y_i \qquad (33)$$

in which y_i and f_i are the measured and calculated

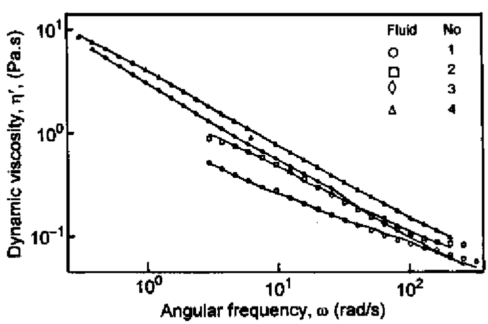

Figure 2. Evaluation of the modified convected Maxwell model with data.

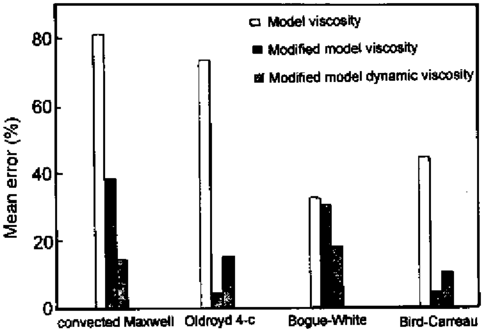

Figure 3. Evaluation of various rheological models with data.

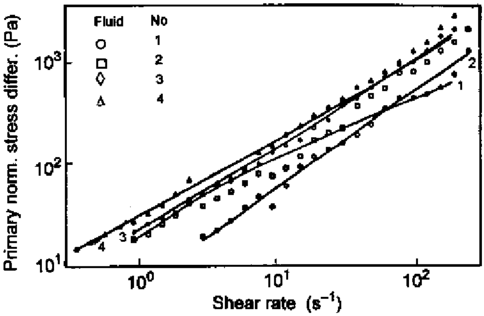

Figure 5. Comparison of the modified Oldroyd 4-constant model with data.

values of a property and ε_i is the local relative error. The summation includes the entire experimental data. For exemplification, two graphs are given, one for viscosity data and the other for dynamic viscosity data in Figures 1 and 2.

To compare the fitting ability more quantitatively, instead of giving similar graphs for all the models, only the averages of RMS Errors eqn (33) are given in Figure 3. This figure shows the mean error of three cases. First, the mean errors obtained by using the viscosity functions of models without any modifications; of course, for upper convected Maxwell model, the Spearot-Metzner modification [4] is used as the basic model. Second, the mean errors obtained by using the modifications of viscosity functions introduced in this work are given to show the improvements obtained by modified models. Third, the mean errors obtained by using the modified dynamic viscosity functions of this work are shown.

The study of Figure 3 leads to the fact that the Spearot-Metzner upper convected Maxwell model shows the most discrepancies while the Bogue-White model shows less error. However, after modification, the best result is that of modified Oldroyd 4-constant model and then modified Bird-Carreau model has a better fit to data. Modified upper convected Maxwell and Bogue-White models show similar results but that of modified Bogue-White is more satisfactory while no essential improvement has occurred through the modification because the only added parameter,

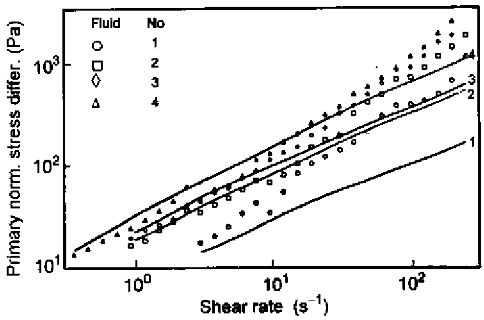

Figure 4. Comparison of the modified convected Maxwell model with data.

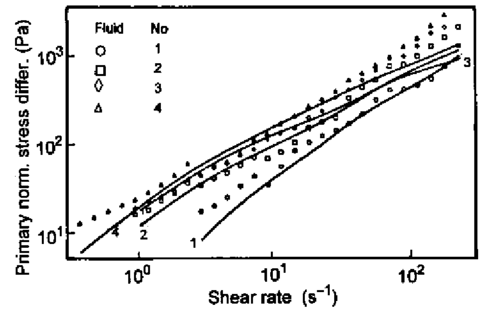

Figure 6. Comparison of the modified Bogue-White model with data.

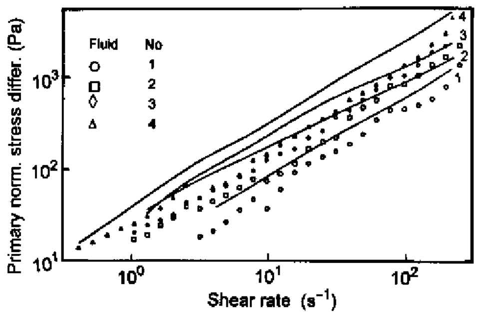

Figure 7. Comparison of the modified Bird-Carreau model with data.

α', seems to have little effect on the model performance. This figure also shows that the mean errors for dynamic viscosity of modified models are similar but that of modified Bird-Carreau is less than others.

To check the ability of the modified models in describing material functions other than those used in the process of determination of the model parameters, predicted first-normal-stress coefficients are compared with experimental data in Figures 4–7. It can be seen that the modified Oldroyd 4-c model fits best the data. This may justify its application in other kinds of flows such as free coating. Although the parameters of modified Bogue-White model are obtained from viscosity data alone, the model predictions yield rather good agreement with experimental data. This makes the modified model attractive. Poor agreement between predicted and experimental data is obtained for modified upper convected Maxwell and Bird-Carreau models, however, that of modified Bird-Carreau is more satisfactory.

CONCLUSION

For any constitutive equation, there exists a domain within which the model predictions are satisfactory. Application of the rheological model to a special flow field depends on how well the limits of the flow under consideration are embedded by the domain of the model validity. On the other hand, a complex flow field may be considered as constituted by simpler flows. For example, for the free coating process, the deformation is of two modes: one of the shear and the other of elongation. Thus, it is speculated that characterizing the fluids by means of those rheological models having the ability of predicting material functions related to different modes of deformation yields better results when dealing with the special flow field, e.g. coating. In the present study, it has been shown that the Oldroyd 4-constant model gives better results either in regenerating the non-Newtonian viscosity data by which the model parameters were determined or in prediction the first normal stress data. This may justify the application of these model parameters in other flow fields such as coating of viscoelastic fluids.

SYMBOLS

- d stretch tensor $d = \frac{1}{2}(\nabla v + (\nabla v)^{\dagger})$
- G' storage modulus
- G_i parameter of the Bogue-White model having dimension of stress, eqn (9)
- M memory function in integral-type models
- $\Re e$ real part of a complex number
- t, t' present and past times where $t' \leq t$
- ∇v velocity gradient tensor
- x_i, x_i' particle coordinates at times t and t′ respectively, $(t' < t)$

Greek Symbols

- $\gamma_{[0]ij}$ relative strain tensor, eqn (8)
- $\dot{\gamma}$ rate-of-strain tensor, eqn (2)
- $\dot{\gamma}$ shear rate, $\dot{\gamma} = |\partial v_1/\partial x_2|$
- δ_{ij} Kronecker delta
- ε phase shift between the oscillatory motion of cone and plate
- ε_j local relative error, $\varepsilon_i = (y_i - f_i)/y_i$
- $\zeta(\alpha)$ Riemann zeta function, $\sum_{k=2}^{\infty} k^{-\alpha}$
- η viscosity function
- η^* complex viscosity
- η' dynamic viscosity
- η_0 zero-shear-rate viscosity

θ_c gap angle between cone and plate
λ_j time constant of the models
μ_0 time constants in Oldroyd 4-constant model
ρ fluid density
τ stress tensor
ϕ_1, ϕ_2 angular amplitude of the plate and cone in a cone-and-plate instrument respectively
ψ_1 first normal stress difference
ω angular frequency of oscillatory shear flow
Π_d second invariant of the stretch, $\Pi_d = \frac{1}{2}(d:d)$

Subscript

(1) first upper convected time derivative, eqn (3)
1, 2, 3 direction of flow, direction of velocity gradient, and the neuter direction respectively

Superscript

° amplitude of a complex quantity
† transpose of a second order tensor

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