Korea-Australia Rheology Journal
Vol. 18, No. 1, March 2006 pp. 9-14

On the congruence of some network and pom-pom models

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(Received December 12, 2005)

Abstract

We show that some network and pom-pom constitutive models are essentially the same. Instead of the usual confrontation, we suggest that the two approaches can offer useful mutual support: vital information about network destruction rates found from detailed pom-pom calculations can be used to improve the network models, while deductions about network creation rates can pinpoint areas needing further attention in the tube modelling area. A new form of the PTT model, the PTT-X model, results in improved shear and elongational flow descriptions, plus an improved recoil behaviour. The remaining problems of strain-time separation, second normal stress difference description, and reduction of parameters are also discussed and some suggestions for progress are offered.

Keywords : constitutive equations, viscoelasticity, polyethylene, tube theories, networks, pom-pom

1. Introduction

Rheology has as its basic aim the object of being able to predict, from a given experimental data base, the results of other flows. In order to do so, it is often necessary to invent a mathematical description, or model, or constitutive equation, which will facilitate the computation of the flows of interest. The invention of the linear viscoelastic model of Boltzmann and the power-law and similar one-dimensional models, were followed after a long interval by the work of Weissenberg, which furthered the study of truly three-dimensional (as opposed to one-dimensional) rheological models. Reiner and Rivlin then both presented the first in a long line of fully three-dimensional nonlinear constitutive equations; the long list continues (Tanner and Walters, 1998).

The work of Lodge (1964) building on the Green-Tobolsky network theory assisted in focusing model builders' attention on the need to study material microstructure as well as continuum mechanics. This resulted in a number of new results for polymer flows based on network theory; the PTT model (Phan-Thien and Tanner, 1977) was one of the results. The coming of the ability to do extensive numerical computations was an essential ingredient in the success of the new models - they are simply too difficult to handle analytically in any but the simplest situations. More ideas from polymer physics were brought to rheology by the reptation concepts of de Gennes and Doi and Edwards, and these 'tube models' have now become a major preoccupation of polymer science. In the last twenty years one sees a host of improvements in the basic tube model, so that new rheological models continue to appear, based on this resource.

As is normal in rheology, a certain amount of friction between the proponents of the various schools has been evident (see Tanner and Walters (1998) for a discussion of the early continuum mechanics wars) and more recently one sees this in relation to the proponents of various microstructural theories. Here we seek to show, by contrast, a congruence between the viewpoints.

2. Reptative-based models

The initial Doi-Edwards models were quite simple, but in more recent developments much of this simplicity has been lost and some empiricism seems to have appeared. Several paths have been pursued, some leading to constitutive equations of exclusively integral form (Rubio and Wagner, 2000) and some to models expressible as either integral or differential models. We shall mainly consider the latter here; they are more popular in large computing applications.

It is not possible to survey the vast amount of work on the reptation concepts here: a recent article by Clemeur *et al.* (2003) can serve as a useful starting point for our work. In particular we shall focus on a 'pom-pom' model formulation. The "pom-pom" model molecule consists of a backbone to which a number (q) of arms are attached at the ends. The motion of the arms and backbones in "tubes" are then considered; clearly the arms suggest branched molecules. Verbeeten *et al.* (2001; 2002) developed these ideas

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further, producing an 'XPP' constitutive relation of the form, for a single mode, where σ is the total stress tensor (Tanner and Nasseri, 2003):

$$\sigma = -pI + 2\eta_s d + \tau, \tag{1}$$

Here p is the pressure, η_s is a 'solvent' viscosity, and I is the unit tensor. We have

$$\frac{\Delta \tau}{\Delta t} + \lambda^{-1}(\tau)\tau = 2G_o d, \tag{2}$$

where τ is the extra-stress tensor, and

$$\frac{\Delta \tau}{\Delta t} \equiv \frac{\partial \tau}{\partial t} + (v \cdot \nabla)\tau - \tau L^T - L\tau, \tag{3}$$

is the usual upper-convected time derivative; v is the velocity field, and L is the velocity gradient tensor ($L_{ij} = \partial v_i / \partial x_j$). G_o is a (constant) modulus and d is the rate of deformation tensor. The tensor λ^{-1} is here defined for the pom-pom model as (Verbeeten *et al.*, 2002)

$$\lambda^{-1} = \frac{1}{\lambda_b}\left[\frac{\alpha}{G_o}\tau + FI + G_o(F-1)\tau^{-1}\right] \tag{4}$$

Here α is a constant (Giesekus constant), λ_b is a relaxation time, and the function F, as deduced from the pom-pom model by Verbeeten *et al.* (2001), is

$$F(\tau) = 2r\exp(\nu(\Lambda - 1)) \cdot \left(1 - \frac{1}{\Lambda}\right) + \frac{1}{\Lambda^2}\left[1 - \alpha\frac{tr\,\tau^2}{3G_o^2}\right], \tag{5}$$

and

$$\Lambda = (1 + tr\,\tau/3G_o)^{1/2}; \quad r = \lambda_b/\lambda_s, \quad \nu = 2/q. \tag{6}$$

There are two relaxation times: λ_b is the usual relaxation time, λ_s is the relaxation time for stretch; in future we will drop the suffix b, so $\lambda_b \equiv \lambda$. As mentioned above, q is said to be indicative of the number of arms of the molecule. The Giesekus term is not part of the reptation idea (actually the original Giesekus theory was developed for dilute dumbbell solutions) and the coefficient α will be set equal to zero; it does little to the response except to produce a second normal stress difference (Tanner and Nasseri, 2003).

Considering Eqns (5) and (6) we see that each mode (each λ) contains four parameters (λ, G_o, ν, r) which is a considerable number, when one considers that around 10 relaxation modes may be needed for some applications.

3. General Network models

A simpler, less detailed view of polymer mechanics is found in network theory, which was begun by Green and Tobolsky and brought to maturity by Lodge (1964). A temporary, changing network is imagined and a balance between the creation and destruction of network links is set up. The result (Larson, 1988; Huilgol and Phan-Thien, 1997; Tanner, 2000) for the single-mode form is

$$\lambda\frac{\Delta S}{\Delta t} + HS = G_1 I, \tag{7}$$

where S is an extra stress tensor, H is a network destruction function, and G_1 is a network creation function; the (scalar) time constant is λ. While H and G_1 are assumed to be functions of the network link states, the usual closure, which will be assumed here, is that H and G_1 are functions of $tr\,S$. One can then rewrite (7) in the integral form (Huilgol and Phan-Thien, 1997)

$$S = \int_{-\infty}^{t} \frac{1}{\lambda} G_1(t')\exp\left(-\frac{1}{\lambda}\int_{t'}^{t} H(t'')dt''\right) C^{-1}(t')dt', \tag{8}$$

where C^{-1} is the strain tensor at t' relative to the present configuration (time t) (Tanner, 2000). If we now define $G_o = \eta_o/\lambda$ (constant), and let

$$S = (\eta_o/\lambda)I + \tau, \tag{9}$$

then substitution of (9) in (7) gives the result

$$\lambda\frac{\Delta \tau}{\Delta t} + H\tau + \left(\frac{\eta_o H}{\lambda} - G_1\right)I = 2\eta_o d, \tag{10}$$

where η_o is a constant viscosity. In (10) we now regard H and G_1 as functions of $tr\,\tau$, instead of $tr\,\mathbf{S}$.

If we compare Eqn (2) (with $\alpha = 0$) and Eqn (10), setting $H = F$, and $G_1 = G = \eta_o/\lambda$, we see that the pom-pom constitutive Eq. (2) is a special case of the general network constitutive equation; in this special case $G_1 = G_0 =$ constant.

If we set $G_1 = \eta_0 H/\lambda$ in (10) then we find the PTT family of models:

$$\lambda\frac{\Delta \tau}{\Delta t} + H\tau = 2\eta_o d. \tag{11}$$

These are also special cases of the general network theory.

The PTT models have traditionally used only two forms (Tanner, 2000):

(a) Linear form: $H = 1 + \varepsilon tr\,\tau/G_o$

(b) Exponential form (exp PTT): $H = \exp(\varepsilon tr\,\tau/G_o)$.

Here ε is a constant for each mode.

For polymer melts form (b) has been preferred (Larson, 1988) while the linear form has been used for solutions. No attempt to link the form of H to microstructural ideas was made in the early history of the PTT model. Given the connection shown above with the XPP model, we can now explore the use of the form (5) for H in the PTT model, thus making use of new microstructural ideas from the pom-pom modelling.

4. Asymptotic behaviour for single-mode models

As the trace of the stress increases, so does the tendency

for the network to disintegrate; hence the H function in (11) is expected to be an increasing function of $tr\,\boldsymbol{\tau}$. Two examples have been given above (linear PTT, expPTT), and the form (5) follows the pattern; the result (5) rises more steeply with $tr\,\tau$ than the linear form, and less steeply than the traditional exponential form, as $tr\,\tau$ becomes large.

Now consider a steady elongational flow, (along the x-direction). The direct stress τ_{xx} ($\equiv \tau_1$) becomes large as $\dot{\varepsilon}$ becomes large, and $\tau_{yy}=\tau_{zz}$ ($\equiv \tau_2$) is not large. Hence tr $\boldsymbol{\tau}\sim\tau_1$ and the equation for $\dot{\varepsilon}$ becomes, for large $\dot{\varepsilon}$, from (10)

$$-2\dot{\varepsilon}\lambda\tau_1+\tau_1 H+\frac{\eta_o H}{\lambda}-G_1=2\eta_o\dot{\varepsilon}. \tag{12}$$

Since τ_1 is large, and presuming G_1 is not larger than $H\eta_o/\lambda$, then the first two terms in (12) are dominant, and

$$H(\tau_1)=2\lambda\dot{\varepsilon}. \tag{13}$$

Thus, curiously, the network creation function G_1 does not enter into the asymptotic solution, and hence both the XPP and PTT models, setting $F=H$ in Eqns. (2) and (11), give the same asymptotic results. We shall call the PTT model with the Eqn. (5) kernel the PTT-X model. Tanner and Nasseri (2003) also show that the α or Giesekus term in (4) and (5) is unimportant in the elongational response of the XPP model.

For the case of simple shearing, $\boldsymbol{v}=\dot{\gamma}(y,\,0,\,0)$, a similar asymptotic analysis for large $\lambda\dot{\gamma}$ shows that $N_2=0$, $tr\,\boldsymbol{\tau}=\tau_1+2\tau_2$. One finds ($G$, H are functions of $tr\,\boldsymbol{\tau}$)

$$\tau_1\cong 2\lambda^2\dot{\gamma}^2 G_1/H^3. \tag{14}$$

$$\tau_{12}\cong\lambda\dot{\gamma}G_1/H^2. \tag{15}$$

Hence both the network creation and destruction functions contribute to the high shear-rate response. (Note the single-mode XPP model is statically unstable and shows a maximum in the $\tau_{12}-\dot{\gamma}$ curve; - this does not happen with the PTT models discussed here). Although the steady elongational result does not depend on G_1, it is found (Tanner *et al.*, 2005) that the recoil from elongation does depend on both H and G_1. We find that the recoil (Hencky) strain ε_r recovering from a steady elongational flow (strain rate $\dot{\varepsilon}$) which induces stresses τ_1, τ_2 along and across the flow respectively, is

$$\varepsilon_r=1/3\lambda n(\tau_1/\tau_2). \tag{16}$$

For a large strain rate $\dot{\varepsilon}$, we find, for the XPP and PTT-X models respectively:

$$\tau_1/\tau_2=3\lambda\dot{\varepsilon}\tau_1/G_o(XPP)\ \text{ and }\ \tau_1/\tau_2=3\tau_1/2G_o(PTT\text{-}X). \tag{17}$$

and there is a large difference between the recoil of the XPP and $PTT-X$ models (Table 1); the XPP model recoils much more.

Table 1. Here the recoil ε_r (Eqn. 16) is tabulated for $v=1$, $r=3$ for the two (single-mode) models, XPP and PTT-X; $\dot{\varepsilon}$ is the initially-applied elongation rate

$\lambda\dot{\varepsilon}$	ε_r	
	PTT-X	XPP
10	1.145	2.14
100	1.526	3.29
1000	1.789	3.55

5. Multiple relaxation times - experimental agreement

In order to compare the performance of models with experiments, it is usually necessary to use multiple relaxation times. Each mode i is assumed to have its own set of parameters (λ_i, η_i, ν_i, r_i) if we use the "destruction" form H of Eqn. (5), and the total stress $\boldsymbol{\sigma}$ will be given by

$$\boldsymbol{\sigma}=-p\boldsymbol{I}+2\eta_s\boldsymbol{d}+\sum_{i=1}^{N}\boldsymbol{\tau}_i, \tag{18}$$

where there are N modes. Each mode (i) will depend on $tr\,\boldsymbol{\tau}_i$. We will set $\eta_s=0$. Clearly the linear viscoelastic response can be adequately modelled if enough modes are used.

Verbeeten *et al.* (2002) have provided a set of data for a low-density polyethylene where four modes were assumed. Setting the Giesekus terms $\alpha_i=0$ for all modes, we can test the fit of the XPP and the PTT-X models. Both models use the same parameters (Table 2); only the "creation functions" are different. Although the parameters were presumably chosen for optimal fit by Verbeeten *et al.* (2002) it is obvious from Fig. 1 that the PTT-X model is a much better description in steady shear. For steady and transient elongation the models are nearly identical, as expected (Fig. 2).

Whilst the comparison between the PTT-X theory and the experiments is satisfactory in steady shearing and transient

Table 2. Linear and non-linear parameters used by Verbeeten *et al.* (2002) for fitting of the DSM Stamylan LD 2008 XC43 LPDE melt

Mode	Maxwell parameters		Pom-pom parameters	
i	g_i(Pa)	λ_i(s)	$q_i=2/\nu_i$	r_i
1	7.2006E+4	3.8946E-3	1	7.0
2	1.5770E+4	5.1399E-2	1	5.0
3	3.3340E+3	5.0349E-1	2	3.0
4	3.008E+2	4.5911	10	1.1

The parameters have been used for both the multi-mode XPP and PTT-XPP models, the α_i (Giesekus terms) are set equal to zero. Note $\eta_i=\lambda_i\,g_i$ for each mode; $r_i=\lambda_i/\lambda_{si}$.

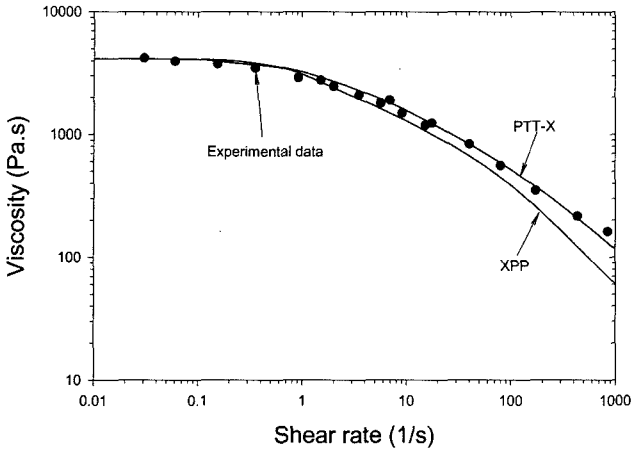

Fig. 1. Steady state shear viscosity, for multi-mode XPP (similar to the one obtained by Verbeeten *et al.* (2002) and multi-mode PTT-X model. Both models use the same parameters, shown in Table 2. No attempt has been made to further optimize the parameters for the PTT-X model, but results are very close to experimental values.

elongation of low-density polyethylene, it is not sufficient to rely on these tests only. The start-up of shear is also modelled quite well, and we turn to recoil as a more stringent test of the models.

Recoil can be tested against the famous LDPE experimental data of Meissner (1971). As one would expect from Table 1, the PTT-X results are much closer to experiment than the XPP results, and are fairly close to the Wagner 'irreversible' computations of recoil using an integral model (Tanner *et al.*, 2005) (Table 3).

In these computations nine relaxation modes were used; the parameters are given in Table 4. The parameters are those found in the literature and used by Tanner *et al.* (2005). Table 3 gives the recoil or recoverable strain ε_r for various conditions and models. In the tests, a uniform rate of elongation ($\dot{\varepsilon}$) was applied, then the specimen was cut and the recoil ε_r measured. The initial strain before cutting is $\dot{\varepsilon}t_s$, where t_s is the time of straining. In Table 3 $\dot{\varepsilon}t_s$ is always 4.0, and $\dot{\varepsilon}$ has the values 0.01, 0.1 and 1 s^{-1}.

The Wagner (1979) results are those of the 'irreversible' theory; clearly all three calculations show some excess recoil. Since ε_r is a Hencky strain, the excess stretch ratios recovered vary from 12% (Wagner) to 46% (XPP). Similar results are found for other initial strains (Tanner *et al.*, 2005); for a perfectly elastic recovery one gets, of course, $\varepsilon_r = \dot{\varepsilon}t_s$.

A further concern is the issue of strain-time separation. After the application of a sudden step shear strain, (magnitude γ_o, applied at $t=0$) one often observes a separation so that the shear stress τ obeys a rule

$$\tau = f(|\gamma_o|)G(t)\,. \tag{19}$$

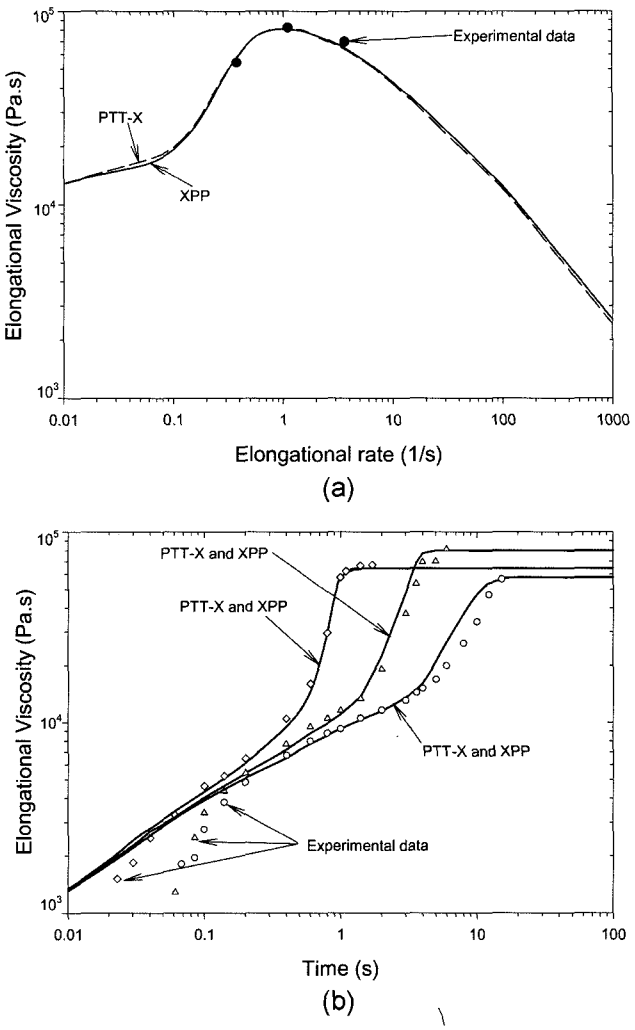

Fig. 2. Quasi-steady state (a) and transient uniaxial viscosity (b); showing a comparison between models and experimental data. The PTT-X and XPP models are used to describe the response of DSM Stamylan LD2008 XC403 low-density polyethylene (LDPE) at 170°C. Parameters used in the models shown in Table 2. Symbols show experimental data.

Table 3. Recoil ε_r for three models as a function of strain-rate $\dot{\varepsilon}$ for an initial strain $\dot{\varepsilon}t_s = 4.0$

Strain rate $\dot{\varepsilon}$	0.01 s^{-1}	0.1 s^{-1}	1 s^{-1}
Experimental ε_r	0.47	0.92	1.18
Wagner (1974)	0.46	0.97	1.29
PTT-X	0.50	1.09	1.38
XPP	0.50	1.15	1.56

where $G(t)$ is the linear relaxation function and $f(|\gamma_o|)$ is a nonlinear scaling factor. Rubio and Wagner (2000) have always insisted that this should be obeyed by models, and their integral models do this exactly. The general network

Table 4. Parameters used for recoil calculations of IUPAC A/ LDPE (Tanner *et al.*, 2005)

Mode no., i	Modulus, g_i (Pa)	λ_i (s)	q_i	r_i
1	1.520×10^{5}	1.0×10^{-3}	1.0	2.0
2	4.005×10^{4}	5.0×10^{-3}	1.0	2.0
3	3.326×10^{4}	2.8×10^{-2}	2.0	2.0
4	1.659×10^{4}	1.4×10^{-1}	2.0	2.5
5	8.690×10^{3}	7.0×10^{-1}	4.0	2.0
6	3.151×10^{3}	3.8×10^{0}	7.0	2.0
7	8.596×10^{2}	2.0×10^{1}	8.0	1.5
8	1.283×10^{2}	1.0×10^{2}	12.0	1.0
9	1.849×10^{0}	5.0×10^{2}	30.0	1.0

The $\nu_i=2/q_i$ See Eqn. (6). $r_i=\lambda_i/\lambda_{si}$.

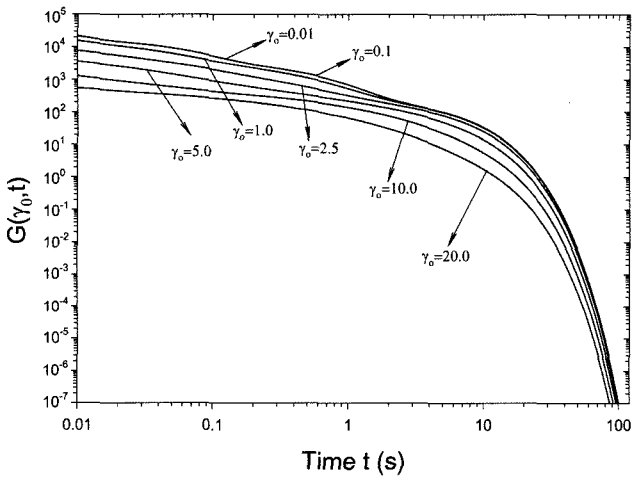

Fig. 3. Shear stress response of 4-mode LDPE model to step shear strains (γ_o) of various magnitudes. Data of Table 2.

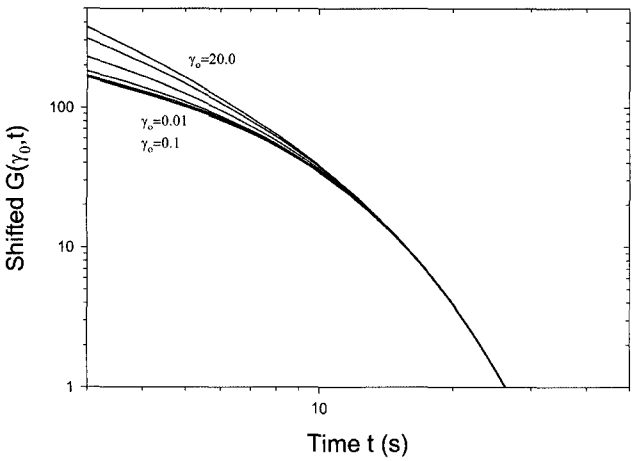

Fig. 4. Attempted superposition of data of Fig. 3 by vertical shifting. Strain-time superposition is not accurate for PTT-X model.

models do not obey this separation in principle. However, we can check the behaviour for any given material, and results were obtained for the LDPE described by the parameters given by Verbeeten *et al.* (2002) (Table 2) over a range of shear strain from $\gamma_o=0.01$ (linear) to 20. For short times (< 10 s) superposition fails, but a reasonable superposition is possible for $t>10$ s (Figs. 3 and 4).

The second normal stress difference has been introduced into the XPP model using a non-zero value of the Giesekus parameter (α in Eqn. 4). Clearly this can also be applied to the PTT-X model if required.

6. Reduction of parameter numbers

The large number of hard-to-find parameters in the models discussed is a drawback for practical use.

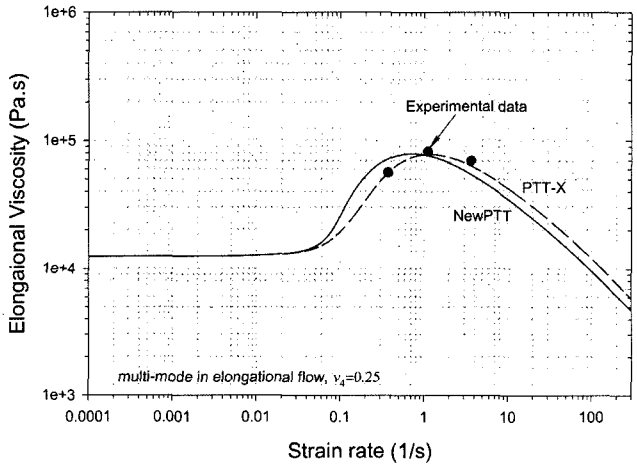

Fig. 5. Reduced parameters, setting $r=3\nu$ (labelled New PTT) for 4-mode LDPE of Table 2. The lack of fit to experimental data for steady elongation is shown; some shift in parameters would be needed to compensate for the change.

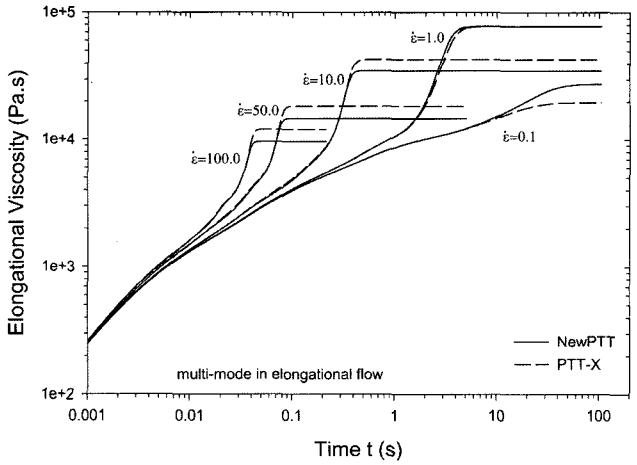

Fig. 6. Reduced parameter fit, as in Fig. 5, showing transient response inferior to PTT-X model.

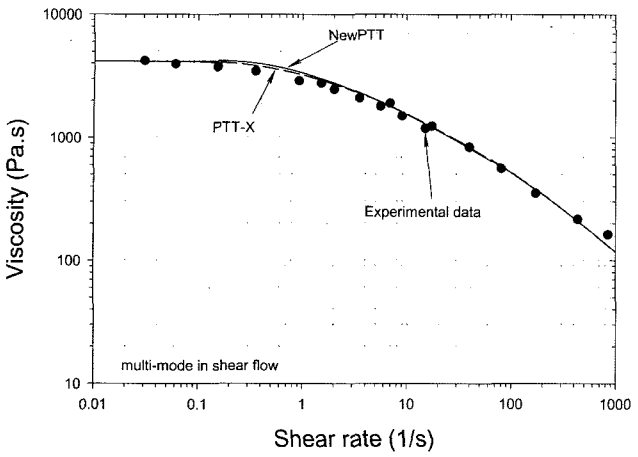

Fig. 7. Steady shear response for 4-mode LDPE. The reduced parameter New PTT model ($r=3\nu$) is completely adequate in shear.

In the PTT-X model parameters r and ν are needed for each mode. While there exist standard methods for finding the linear parameters λ and η, the task of fitting r and ν from scanty data is not easy. By studying the various XPP and other pom-pom proposals that have been fitted so far we can plot r against ν for the available data. A rough correlation is evident, and we shall set, for any mode, $r=3\nu$, with a consequent halving of parameters to be found (ν is from Table 2).

The results of this procedure are shown in Figs. 5 and 6. Some deterioration in the elongational response is noted and this would have to be compensated by shifting the ν-values. The steady shear result is unaffected (Fig. 7).

7. Conclusion

The procedure of adopting micromodel results into the network model shows how one can improve the PTT model response. Conversely, it appears that the rate of creation of load-bearing strands is insufficient in the XPP and related pom-pom models, and this point needs attention.

The need to explore more types of response has been addressed here by looking at recoil and network strain-time separation. Note that most general network models of the type of Eqn. (7), including the pom-pom family, cannot exhibit strain-time separation. The network models behave moderately well in these two flows, but the Wagner (1979) irreversible model actually does better in both of these cases. We shall need to explore this further.

Acknowledgements

This work was supported by the Polymer Cooperative Research Centre and the Australian Research Council. This support is gratefully acknowledged.

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