Simplification of Network Theory for Polymer Melts in Nonlinear Oscillatory Shear

Ranjit S. Jeyaseelan, A. Jeffrey Giacomin, and Jason G. Oakley
Rheology Research Lab., Mechanical Engineering Dept., Texas A&M University, College Station, TX 77843

Giacomin and Oakley (1991) have shown that an upper convected Maxwell model with a structure-dependent relaxation spectrum incorporating the three-parameter kinetic rate equation proposed by Mewis and Denn (1983) works remarkably well for a molten LDPE in large-amplitude oscillatory shear (LAOS). In a search for a simpler framework for interpreting LAOS based on network theory, four nonlinear, differential constitutive equations, each with less than three parameters, were evaluated. These models are compared with the Mewis-Denn model, and a two-parameter model has been found to work just as well for molten IUPAC LDPE X. The LAOS behavior of molten LLDPE is also adequately described by this model.

Introduction

Most polymer processing operations involve large, rapid deformations which cannot be modeled using the theory of linear viscoelasticity, which predicts a superimposable, linear dependence of the amplitude of the stress response on the amplitude of the imposed strain. Currently there is considerable interest in the prediction of the stress field in the nonlinear regime using linear models incorporating flow-field-dependent structure. In kinetic network theories, the flow field dependence is imparted through a hypothesis for the rate of destruction and reformation of entanglements in the material. These hypotheses are kinetic rate equations which can be solved to predict the flow-induced change in the structure of the material. The transient structure can be made to depend on the invariants of the rate of deformation tensor or the invariants of the extra stress tensor.

Since large deformation behavior of molten plastics is highly nonlinear, chemical engineers working on polymer processing problems employ nonlinear viscoelastic constitutive theories to model the flow. One of the most interesting tests of nonlinear behavior is large-amplitude oscillatory shear (LAOS). LAOS is an excellent flow to evaluate nonlinear constitutive equations for polymer melts, since the time scale of the experiment and the strain amplitude can be varied independently. Giacomin and Oakley (1992) recently showed that a three-parameter kinetic rate equation proposed by Mewis and Denn (1983) can accurately predict LAOS behavior of a low-density polyethylene (LDPE) melt. This is the only model ever to accurately predict LAOS behavior of a polymeric liquid. The principal objective of this article is to see if constitutive equations with less than three parameters can predict the response of molten LDPE in LAOS. We have undertaken this search to find the simplest framework for interpreting LAOS behavior of molten plastics.

Correspondence concerning this article should be addressed to A. J. Giacomin.

Structure-Dependent Viscoelasticity

When several Maxwell elements are used, the upper convected Maxwell model successfully predicts the linear viscoelasticity observed for polymer melts in mild deformations. The constitutive equation can be expressed as:

$$\tau = \sum_i \tau^i \tag{1}$$

$$\frac{\tau^i}{G_i} + \lambda_i \frac{\delta}{\delta t}\left[\frac{\tau^i}{G_i}\right] = 2\lambda_i D \tag{2}$$

where the upper convected derivative is:

$$\frac{\delta \tau^i}{\delta t} = \frac{d\tau^i}{dt} - \nabla v \cdot \tau^i - \tau^i \cdot \nabla v^T \tag{3}$$

This constitutive equation yields predictions identical to that of the Lodge rubber-like liquid model which does very poorly in predicting large-amplitude oscillatory shear behavior. Marrucci et al. (1973) were the first to introduce structure dependence into the Maxwell model by letting the relaxation times and moduli depend on a scalar structural parameter, x_i, in the following manner:

$$G_i = G_{0i} x_i \tag{4}$$

$$\lambda_i = \lambda_{0i} x_i^{1.4} \tag{5}$$

where λ_{0i} and G_{0i} are the relaxation time and modulus of the ith spectral element at equilibrium.

The kinetic rate equation arising from Marrucci's analysis of the entanglement kinetics results in the following one-parameter model (The Marucci model):

$$\frac{dx_i}{dt} = \frac{1-x_i}{\lambda_i} - \frac{a}{\lambda_i G_i}[-x_i \Pi(\tau^i)]^{1/2} \tag{6}$$

where the dimensionless nonlinear parameter a is obtained by fitting the model to steady shear viscosity data. The Marrucci model has no nonlinear transient parameter to fit transient nonlinear flow. Since the moduli are time-dependent, the upper convected derivative in the Maxwell model is evaluated as:

$$\frac{\delta}{\delta t}\left[\frac{\tau^i}{G_i}\right] = \frac{1}{G_i}\frac{d\tau^i}{dt} - \frac{1}{G_i^2}\frac{dG_i}{dt}\tau^i - \frac{1}{G_i}(\nabla v \cdot \tau^i + \tau^i \cdot \nabla v^T) \tag{7}$$

Since the advent of Marrucci's model, numerous other kinetic rate equations have been proposed. Acierno et al. (1976) (Acierno model), Mewis and De Cleyn (1982) (Mewis-De Cleyn model), and Mewis and Denn (1983) (Mewis-Denn model) have proposed kinetic rate expressions which include the trace of the extra stress tensor. Moldenaers and Mewis (1986) (Moldenaers model) used a kinetic rate expression which involves a combination of the trace of the extra stress tensor and the second invariant of the rate of deformation tensor to describe the behavior of low-density polyethylene in a tensile start-up experiment. Liu et al. (1984) (Liu model) proposed a kinetic rate expression involving strain rate dependence which can be generalized with the second invariant of the rate of deformation tensor.

Giacomin and Oakley (1992) evaluated the Acierno model, the Mewis-De Cleyn model, the Mewis-Denn model, and the Moldenaers model for IUPAC LDPE X at 150°C in large-amplitude oscillatory shear and have concluded that the Mewis-Denn model gives the best fit for the experimental data. This article will evaluate the Marrucci model, the Liu model, the Larson model (Larson, 1984), and the model proposed by Phan-Thien and Tanner (1977) (PTT model) in LAOS and compare these with the predictions of the Mewis-Denn model.

The kinetic rate equation for the Liu model can be expressed as:

$$\frac{dx_i}{dt} = k_1 \frac{1-x_i}{\lambda_i^m} - k_2 x_i[-\Pi(D)]^{m/2} \tag{8}$$

The parameters k_2 and m determine the extent to which the flow field affects the breakdown of the structure; larger values of k_2 and m indicate a greater dependence of the state of entanglement upon the imposed deformation. k_1 is the kinetic rate constant for thermal regeneration of entanglements, and k_2 is the kinetic rate constant for the destruction of entanglements. Typically, values of m are between 0.8 and 0.9. The magnitude of the parameter k_2 is approximately equal to the parameter a in the Marrucci model and is determined by fitting to steady shear viscosity data. For the IUPAC LDPE X, it has a value of about 0.4. The parameters k_1 and m are fitted to describe the observed large-amplitude oscillatory shear behavior. For the special case $m=1$, Eq. 8 reduces to the Simplified Liu model:

$$\frac{dx_i}{dt} = k_1 \frac{1-x_i}{\lambda_i} - k_2 x_i[-\Pi(D)]^{1/2} \tag{9}$$

The PTT model is qualitatively different from the other models in that it uses the Gordon-Scholwalter convected derivative. This derivative accounts for nonaffine deformation of the entanglement network relative to the deformation of the continuum. The Gordon-Schowalter derivative is:

$$\frac{\hat{\delta}\tau^i}{\hat{\delta}t} = \frac{d\tau^i}{dt} - \nabla v \cdot \tau^i - \tau^i \cdot \nabla v^T + \zeta(\tau^i \cdot D + D \cdot \tau^i) \tag{10}$$

where ζ measures how affine the network deformation is relative to the deformation of the continuum. This derivative produces the upper convected derivative for $\zeta = 0$. Tsang and Dealy (1981) have evaluated the PTT model with $\zeta \neq 0$ and $\epsilon = 0$ in large-amplitude oscillatory shear and concluded that while the model could accurately predict the maximum shear stress in a cycle, it failed to predict the shape of the stress response. In this article, the PTT model is evaluated with $\zeta = 0$ and $\epsilon \neq 0$.

The model is represented as follows:

$$\lambda_i \frac{\hat{\delta}\tau^i}{\hat{\delta}t} + Y[tr(\tau^i)]\tau^i = 2G_i\lambda_i D \tag{11}$$

where the following expression for Y is suggested:

$$Y[tr(\tau^i)] = 1 + \frac{\epsilon}{G_i} tr(\tau^i) \tag{12}$$

Another network theory that is qualitatively different from the structural network theories has been proposed by Larson (1984):

$$\frac{\delta\tau^i}{\delta t} + \frac{2\zeta'}{3G_{0i}} D:\tau^i\tau^i = \frac{-1}{\lambda_{0i}}(\tau^i - G_{0i}\delta) \tag{13}$$

The lefthand side of Eq. 13 represents a nonaffine convected derivative, which is employed to model partially extending network strand convection. The parameter ζ' is a measure of the extensibility of network strands and varies from 0 (affine limit, the upper convected derivative) to 1 (the nonaffine limit, which is an approximation to reptation theory).

Materials and Methods

The material IUPAC LDPE X is an international standard resin for nonlinear viscoelastic property measurements of mol-

Table 1. Discrete Relaxation Spectrum for LLDPE (Dow 2037) Calculated using the Method of Linear Regression with Regularization, from Orbey and Dealy (1991)

λ_i s	G_i Pa
0.00012	26,710.3
0.0012	230,607.7
0.012	111,501.4
0.12	12,132.1
1.2	807.2
12.0	27.8
120.0	0.54
1,200.0	0.034

ten plastics (Giacomin et al., 1989). This resin has the same properties as the previous standard, IUPAC LDPE A, which is no longer available (Meissner, 1972). An eight-component discrete relaxation spectrum for the IUPAC LDPE X at 150°C, proposed by Zülle et al. (1987), is used to describe the linear viscoelastic properties of this material. The LAOS data of Giacomin et al. (1989) for this material were generated using a sliding plate rheometer incorporating a shear stress transducer. The experiments were conducted at a frequency of 2π rad/s and strain amplitudes of 5 and 10, and the oscillations were continued until a standing stress wave was obtained. A discrete Fourier transform was used to obtain the higher harmonics, giving a precision of ± 5 Pa (Giacomin, 1987).

A commercial-grade molten LLDPE (Dowlex 2037) manufactured by Dow Chemical was experimentally evaluated in LAOS. The data were collected using a MTS Direct Shear Rheometer incorporating a shear stress transducer. The gap thickness of the sliding plate rheometer was 1.0 mm. The samples were compression-molded to 50 mm × 125 mm × 1.2 mm. Experiments were conducted at 190°C. An eight-component discrete relaxation spectrum at 190°C was calculated for this material using the technique suggested by Orbey and Dealy (1991), as shown in Table 1.

Analysis

The imposed shear strain in an oscillatory shear experiment is:

$$\gamma(t) = \gamma_0 \sin(\omega t) \tag{14}$$

and

$$\dot{\gamma}(t) = \gamma_0 \omega \cos(\omega t) \tag{15}$$

A linear shear stress response is sinusoidal:

$$\sigma(t) = \sigma_0 \sin(\omega t + \delta) \tag{16}$$

and a nonlinear response is given by a Fourier series:

$$\sigma(t) = \sum_{\substack{j=1\\ \text{odd}}}^{\infty} \sigma_j \sin(j\omega t + \delta_j) \tag{17}$$

In shear, Eqs. 2–5 become:

$$\sigma(t) = \sum_i \sigma^i \tag{18}$$

$$N(t) = \sum_i N^i \tag{19}$$

$$\frac{d\sigma^i}{dt} = \dot{\gamma} G_i - \frac{\sigma^i}{\lambda_i}\left(1 - \frac{\lambda_i}{x_i}\frac{dx_i}{dt}\right) \tag{20}$$

$$\frac{dN^i}{dt} = 2\dot{\gamma}\sigma^i - \frac{N^i}{\lambda_i}\left(1 - \frac{\lambda_i}{x_i}\frac{dx_i}{dt}\right) \tag{21}$$

where $N(t)$ is the first normal stress difference. Equations 20 and 21, coupled with the kinetic rate equation, are solved numerically using a fifth-order Runge Kutta method. The stress response of the PTT model is given by the following differential equations:

$$\frac{d\sigma^i}{dt} = \dot{\gamma} G_i - \frac{\sigma^i}{\lambda_i} \tag{22}$$

$$\frac{dN^i}{dt} = 2\dot{\gamma}\sigma^i - \frac{N^i}{\lambda_i} \tag{23}$$

with

$$G_i = G_{0i} \tag{24}$$

$$\lambda_i = \lambda_{0i}\left[1 + \frac{\epsilon}{G_i} tr(\tau^i)\right]^{-1} \tag{25}$$

The discrete Fourier transform of the shear stress response is used to make quantitative comparisons of the predictions. The deviation from an elliptical shape of the shear stress vs. shear rate loops indicates nonlinearity and is quantitatively analyzed in the frequency domain by comparing the amplitudes and the phase contents of the higher harmonics.

Figures 1 and 2 show the experimental shear stress response and the predictions of the Mewis-Denn model for the IUPAC LDPE X at a frequency of 2π rad/s in LAOS for strain amplitudes of 5 and 10, respectively. The integer C represents the cycles following commencement of flow, for which the data are presented. Figures 1 and 2 will be used as our benchmark for evaluation of the other models and represent the best predictions for LAOS behavior thus far.

Results

Figures 3 and 4 show the Marrucci model predictions for the shear stress response of IUPAC LDPE X at 150°C in LAOS. It can be seen that the model overpredicts the maximum shear stress by about 9 kPa for $\gamma_o = 5$ and 7 kPa for $\gamma_o = 10$. While the model does well in predicting the area of the loop for $\gamma_o = 5$, for $\gamma_o = 10$ it underpredicts the area of the loop and secondary loops appear. Tables 2 and 3 show that the model does not accurately predict the amplitudes of the higher harmonics. Table 2 shows that for $\gamma_o = 5$ the predicted phase contents for the 7th and the 9th harmonics are inaccurate. While the ambitious objective of modeling LAOS behavior

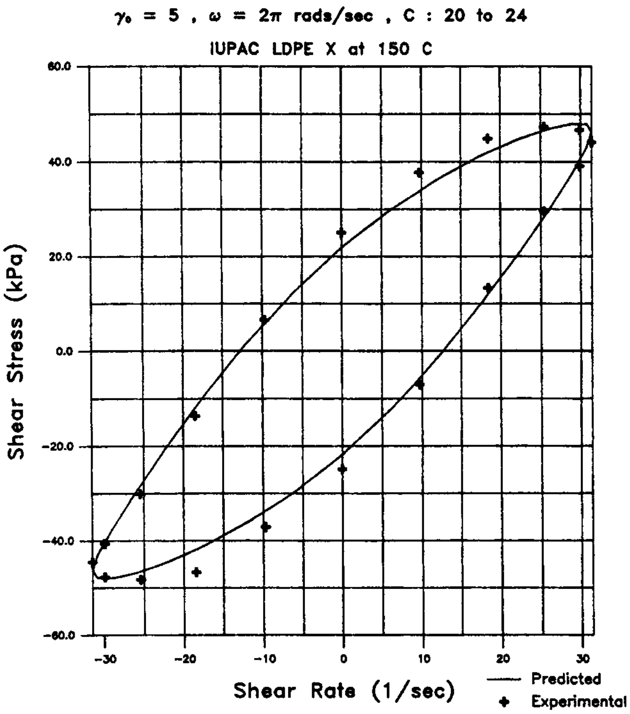

Figure 1. Mewis-Denn model prediction for the shear stress vs. shear rate loop with $\gamma_o = 5$, $\omega = 2\pi$ rad/s at 150°C for IUPAC LDPE X.

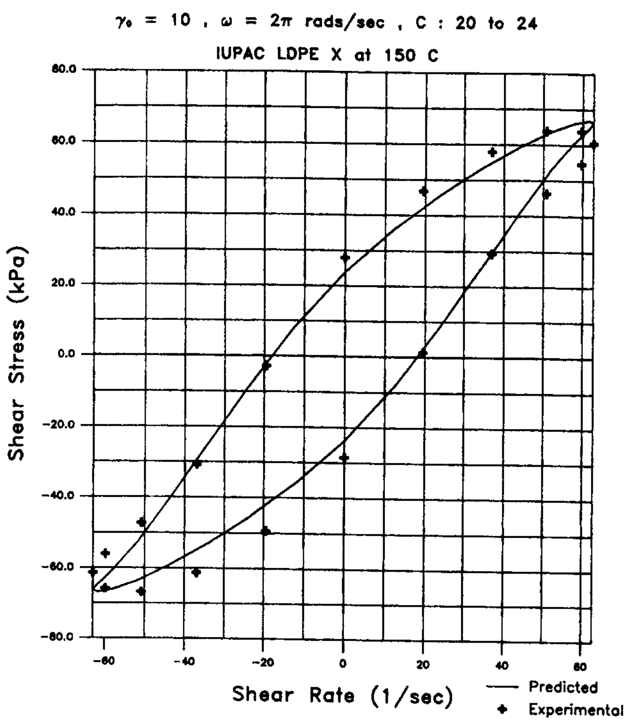

Figure 2. Mewis-Denn model prediction for the stress vs. shear rate loop with $\gamma_o = 10$, $\omega = 2\pi$ rad/s at 150°C for IUPAC LDPE X.

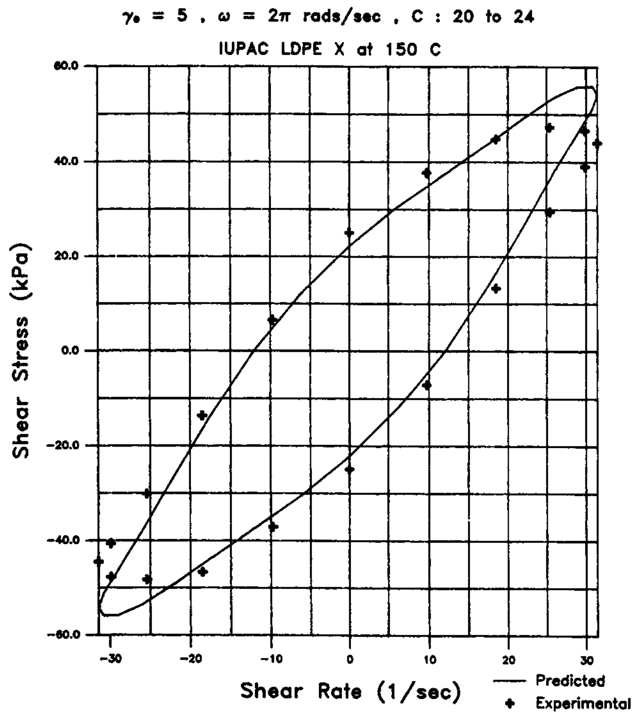

Figure 3. Marrucci model prediction for the shear stress vs. shear rate loop with $\gamma_o = 5$, $\omega = 2\pi$ rad/s at 150°C for IUPAC LDPE X.

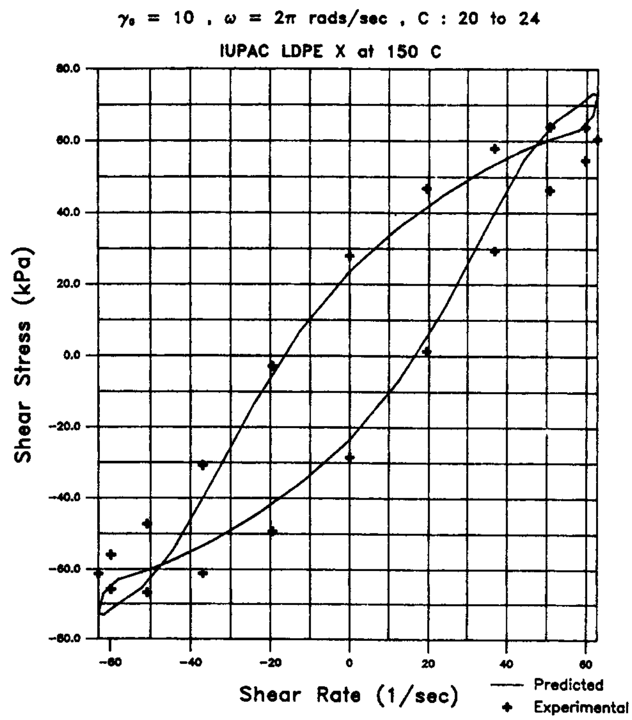

Figure 4. Marrucci model prediction for the shear stress vs. shear rate loop with $\gamma_o = 10$, $\omega = 2\pi$ rad/s at 150°C for IUPAC LDPE X.

Table 2. Model Predictions for Shear Stress Amplitudes (Pa) and Phase Angles (Rad) for IUPAC LDPE X at 150°C with $\gamma_o=5$ and $\omega=2\pi$ rad/s

Mat. Property	Data	Mewis-Denn $m=0.85$ $k_1=0.55$ $k_2=0.4$	PTT $\zeta=0$ $\epsilon=2.34$	Marrucci $a=0.4$	Liu $m=1.0$ $k_1=0.84$ $k_2=0.4$	Larson $\zeta'=0.4$
σ_1	51,401	50,143	67,545	57,527	52,050	59,971
σ_3	4,087	2,447	4,993	3,202	4,497	5,075
σ_5	549	121	932	1,109	1,077	661
σ_7	140	44	290	141	323	127
σ_9	257	17	136	13	118	33
δ_1	1.15	1.17	1.27	1.23	1.13	1.20
δ_3	3.63	3.05	3.31	2.77	3.34	2.82
δ_5	4.72	4.20	5.36	4.93	5.76	4.71
δ_7	1.83	3.36	1.35	5.22	2.17	0.57
δ_9	5.34	6.05	3.30	1.11	5.15	2.45

with a one-parameter model may result in computational ease, the results obtained here show that the Marrucci model is substantially inferior to the Mewis-Denn model which is our basis for evaluation.

The predictions of the PTT model, with $\zeta=0$, for the same conditions are shown in Figures 5 and 6. The value of $\epsilon=2.34$ used in this model was determined from fitting steady shear viscosity data for the IUPAC LDPE X at 150°C. Figures 5 and 6 show that the PTT model overpredicts the maximum shear stress by about 16 kPa for $\gamma_o=5$ and about 25 kPa for $\gamma_o=10$. Tables 2 and 3 show that the PTT model overpredicts most of the amplitudes of the shear stress response. Although the phase contents of the harmonics are predicted reasonably well, the serious overprediction of the amplitudes results in an inadequate prediction for the overall response.

Figures 7 and 8 compare the predictions of the Larson model for the same conditions. The model parameter, ζ', was 0.4. It is seen that the model does not predict the shape of the loop properly. The nonlinearity in the model seems to be qualitatively different from that of the data. Furthermore, at the higher strain amplitude secondary loops begin to appear.

Figures 9 and 10 compare the predictions of a simplified case of the Liu model with the experimental data. This special case corresponds to a scenario where the dependence of the entanglement loss rate on the flow field is strong ($m=1$). This reduces the number of parameters to two. The value of the parameter k_1 was determined to be 0.84. It is seen from Figures

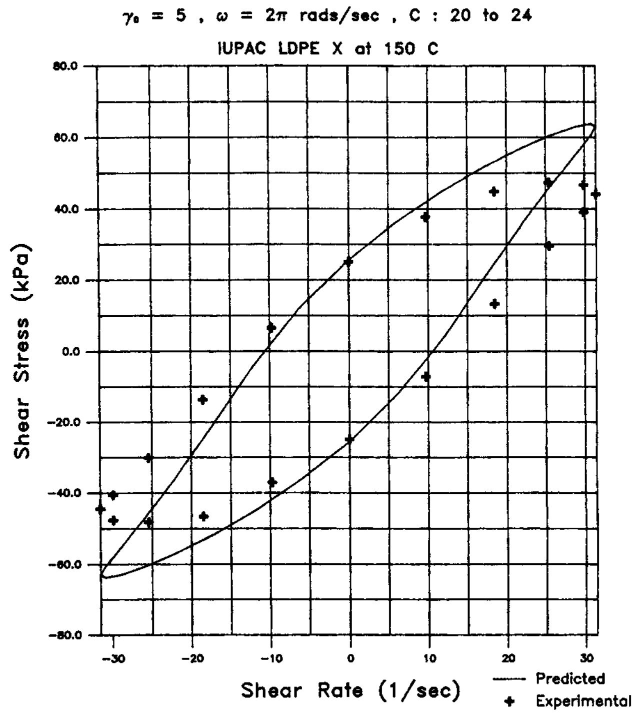

Figure 5. PTT model prediction for the shear stress vs. shear rate loop with $\gamma_o=5$, $\omega=2\pi$ rad/s at 150°C for IUPAC LDPE X.

Table 3. Model Predictions for Shear Stress Amplitudes (Pa) and Phase Angles (Rad) for IUPAC LDPE X at 150°C with $\gamma_o=10$ and $\omega=2\pi$ rad/s

Mat. Property	Data	Mewis-Denn $m=0.85$ $k_1=0.55$ $k_2=0.4$	PTT $\zeta=0$ $\epsilon=2.34$	Marrucci $a=0.4$	Liu $m=1.0$ $k_1=0.84$ $k_2=0.4$	Larson $\zeta'=0.4$
σ_1	70,315	71,375	97,686	75,513	76,234	78,158
σ_3	7,138	5,363	9,845	10,417	8,423	10,363
σ_5	1,658	922	2,465	1,244	2,531	2,799
σ_7	404	87	747	1,189	953	831
σ_9	78	79	305	656	392	261
δ_1	1.25	1.31	1.36	1.40	1.20	1.37
δ_3	4.09	3.48	3.72	3.39	3.57	3.50
δ_5	6.15	5.24	6.07	5.21	6.11	5.51
δ_7	3.00	4.39	2.15	1.60	2.50	1.28
δ_9	0.42	6.10	4.62	2.10	5.33	3.43

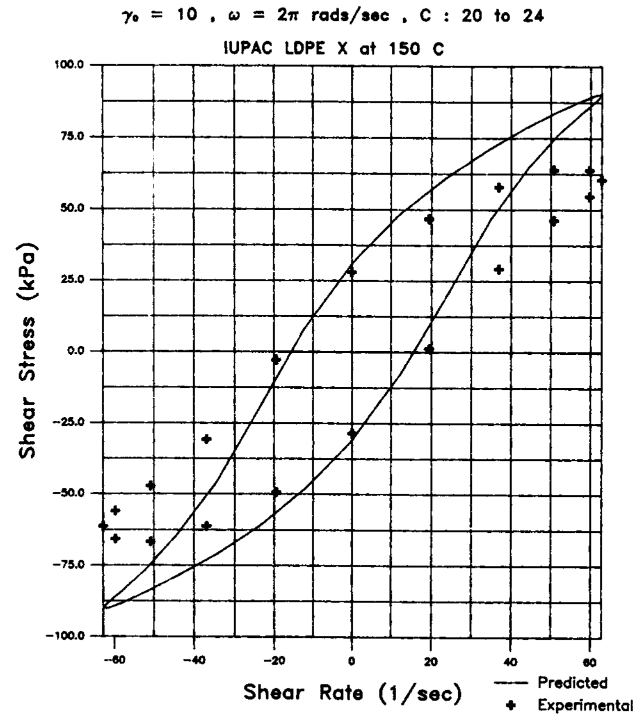

Figure 6. PTT model prediction for the shear stress vs. shear rate loop with $\gamma_o = 10$, $\omega = 2\pi$ rad/s at 150°C for IUPAC LDPE X.

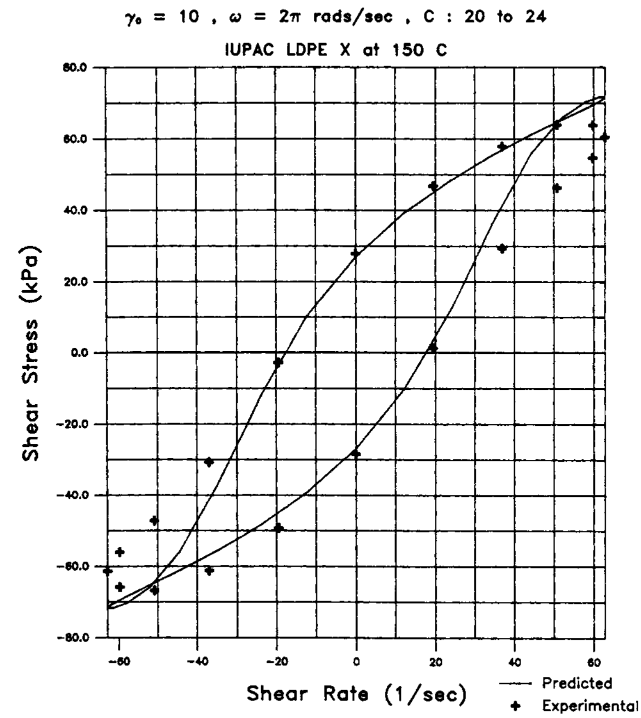

Figure 8. Larson model prediction for the shear stress vs. shear rate loop with $\gamma_o = 10$, $\omega = 2\pi$ rad/s at 150°C for IUPAC LDPE X.

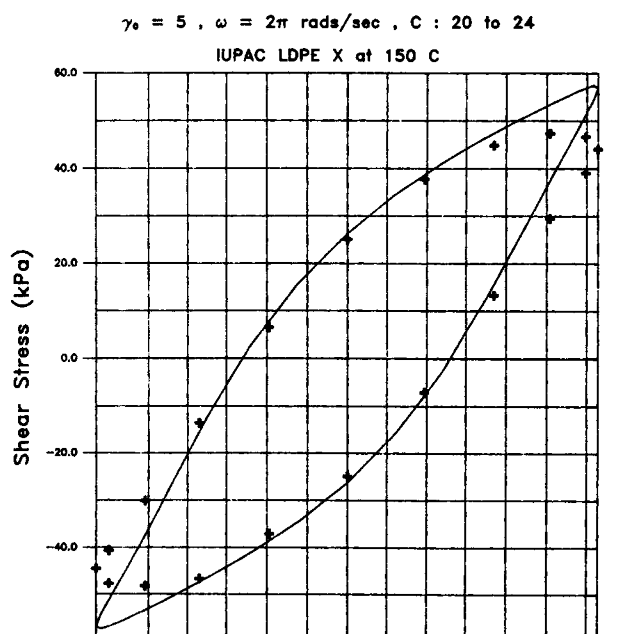

Figure 7. Larson model prediction for the shear stress vs. shear rate loop with $\gamma_o = 5$, $\omega = 2\pi$ rad/s at 150°C for IUPAC LDPE X.

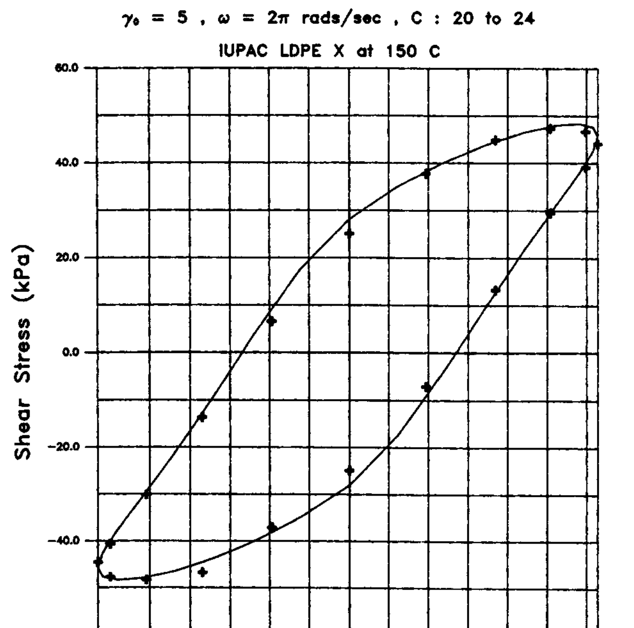

Figure 9. Simplified Liu model prediction for the shear stress vs. shear rate loop with $\gamma_o = 5$, $\omega = 2\pi$ rad/s at 150°C for IUPAC LDPE X.

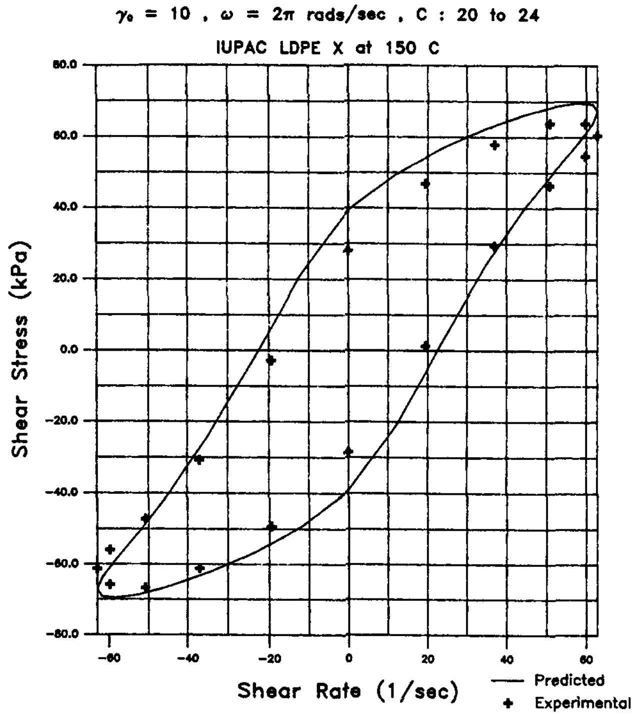

Figure 10. Simplified Liu model prediction for the shear stress vs. shear rate loop with $\gamma_o = 10$, $\omega = 2\pi$ rad/s at 150°C for IUPAC LDPE X.

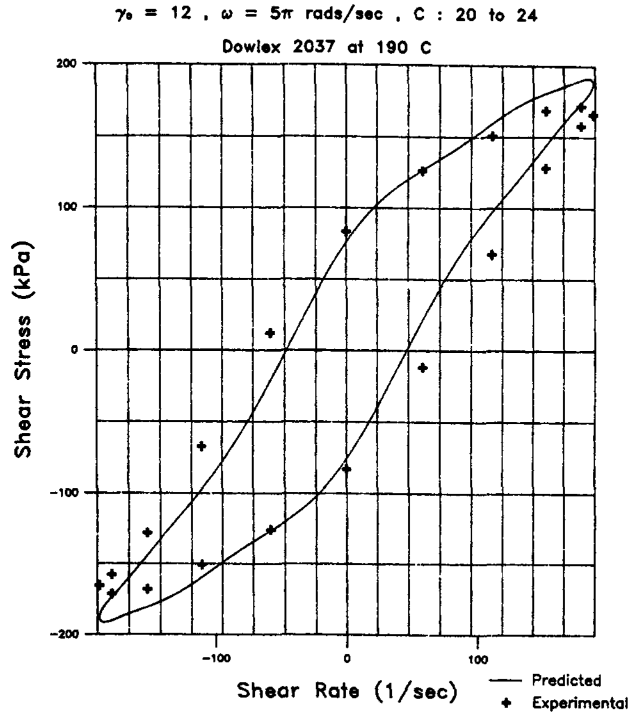

Figure 12. Simplified Liu model prediction for the shear stress vs. shear rate loop with $\gamma_o = 12$, $\omega = 5\pi$ rad/s at 190°C for LLDPE (Dowlex 2037)

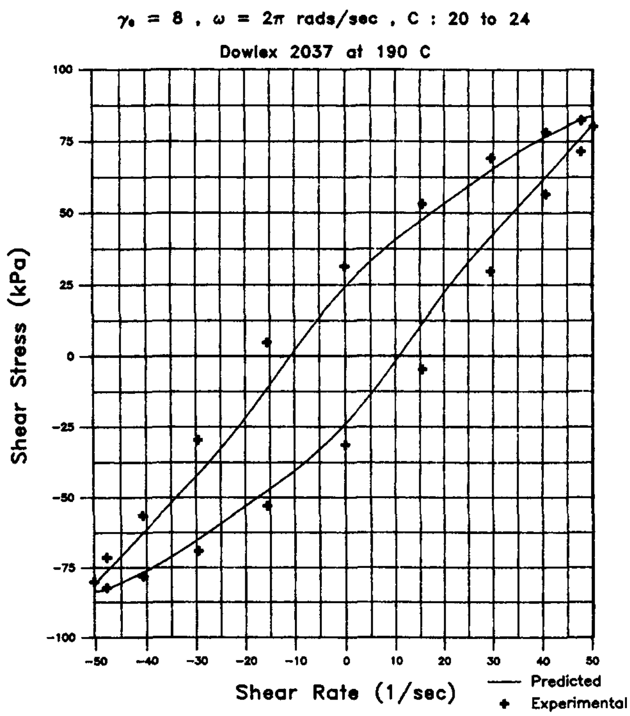

Figure 11. Simplified Liu model prediction for the shear stress vs. shear rate loop with $\gamma_o = 8$, $\omega = 2\pi$ rad/s at 190°C for LLDPE (Dowlex 2037).

9 and 10 that the predicted shear stress response agrees reasonably well with the experimental data on the basis of the area of the loop and the maximum value of the shear stress.

Tables 2 and 3 show that the model accurately predicts the amplitudes of the 1st and the 3rd harmonics. The minor inaccuracies in the prediction of the amplitudes of the other harmonics did not significantly influence the area or the shape of the loop. It is also seen that the phase angles of the harmonics predicted by this model agree with the experimental data.

Figure 11 compares the predictions of the Simplified Liu model for Dowlex 2037 with the experimentally generated LAOS data for $\gamma_o = 8$ and $\omega = 2\pi$ rad/s. The model parameters were $k_1 = 20.0$ and $k_2 = 5.0$. The model predicts the overall stress response reasonably well. Figure 12 makes the same comparison for $\gamma_o = 12$ and $\omega = 5\pi$ rad/s. The model is again able to describe the high level of nonlinearity adequately.

Figures 13 through 16 are predictions of the Simplified Liu model for the nonlinear dynamic rheological properties of IUPAC LDPE X at 150°C for a wide range of strain amplitudes and frequencies. Figure 13 is a three-dimensional plot of $G_d \equiv \sigma_1/\gamma_o$ as a function of strain amplitude and frequency (Hz). It is seen that for small γ_o, G_d is a stronger function of frequency than that of γ_o. Figure 14 is a plot of the stress amplitude of the 3rd harmonic, vs. frequency (Hz) and strain amplitude. The monotonic increase in σ_3 with increasing γ_o indicates that the model is able to properly describe the larger amount of nonlinearity observed for polymer melts at higher strain amplitudes. Figure 15 is a plot of the phase angle of the 1st harmonic and it is seen that at low strain amplitudes, δ_1 is a function of frequency, but not of strain amplitude, indicating a proper reduction to linear viscoelastic behavior. Figure 16

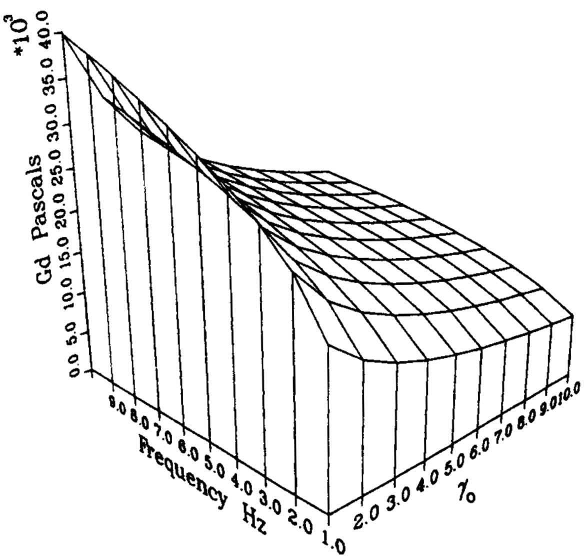

Figure 13. Simplified Liu model prediction for G_d at 150°C for IUPAC LDPE X.

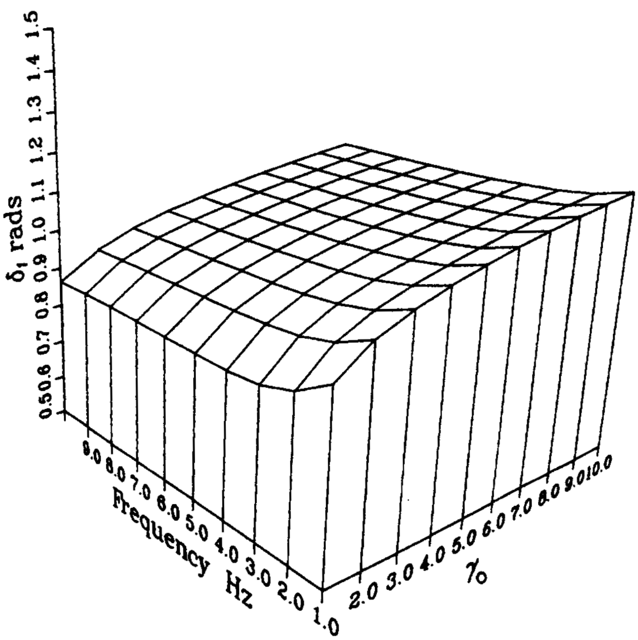

Figure 15. Simplified Liu model prediction for δ_1 at 150°C for IUPAC LDPE X.

shows the dependence of the phase angle of the 3rd harmonic as a function of frequency (Hz) and strain amplitude. In this range of strain amplitudes and frequencies, the model predicts that δ_3 is a very strong function of strain amplitude.

Conclusions

The new simplification of the Liu model ($m=1$) predicts LAOS behavior of IUPAC LDPE X at 150°C just like the Mewis-Denn model. Since the Simplified Liu model has only two parameters, it provides a simpler framework for interpreting LAOS. It would appear that LAOS behavior can be explained using only two kinetic rate constants: one for thermal regeneration and the other for shear-induced breakdown of structure. The Simplified Liu model is also able to adequately describe a molten LLDPE (Dowlex 2037) in LAOS.

Acknowledgment

The authors wish to acknowledge helpful communication with N. Phan-Thien and R. I. Tanner which contributed towards the evaluation of the PTT model undertaken in this work. We also acknowledge the financial support of the Advanced Research Program of the State of Texas. The support of the Academic Computing Services and the Supercomputer Center of Texas A&M University was invaluable.

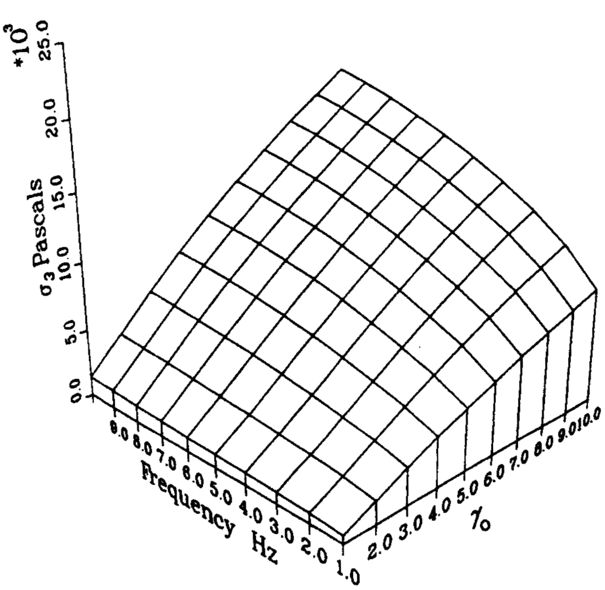

Figure 14. Simplified Liu model prediction for σ_3 at 150°C for IUPAC LDPE X.

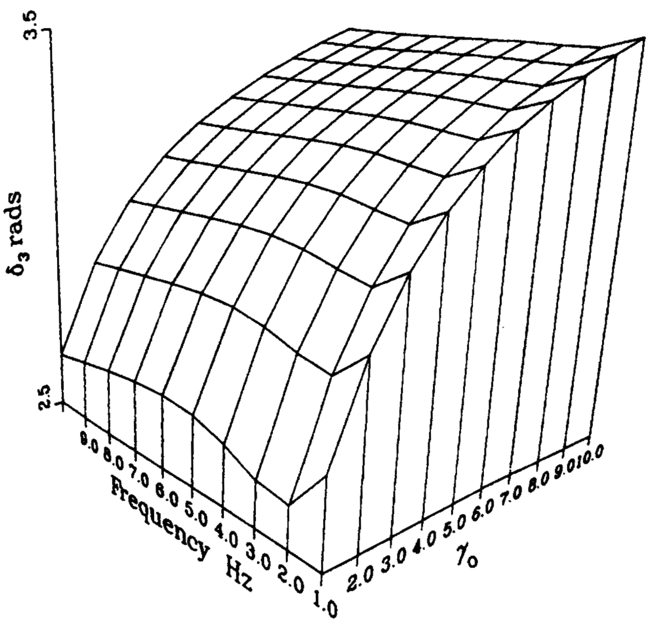

Figure 16. Simplified Liu model prediction for δ_3 at 150°C for IUPAC LDPE X.

Notation

a = Marrucci model parameter
D = rate of deformation tensor
G_i = structure dependent modulus of the ith Maxwell element
G_{0i} = equilibrium modulus of the ith Maxwell element
k_1 = Liu model parameter
k_2 = Liu model parameter
m = Liu model parameter
N^i = ith spectral element of the first normal stress difference
t = time
tr = trace of tensor
Y = PTT model parameter

Greek letters

γ = strain
γ_o = strain amplitude
$\dot{\gamma}$ = strain rate
δ = Kronecker delta
$\delta/\delta t$ = upper convected derivative
$\mathring{\delta}/\mathring{\delta} t$ = Gordon-Schowalter convected derivative
∇v = velocity gradient tensor
∇v^T = transpose of the velocity gradient tensor
ϵ = PTT model parameter
ζ = PTT model parameter
ζ' = Larson model parameter
λ_i = relaxation time of the ith Maxwell element
λ_{0i} = equilibrium relaxation time of the ith Maxwell element
Π = second invariant of a tensor
σ = shear stress
σ_{0j} = shear stress amplitude of the jth harmonic
σ^i = ith spectral element of the shear stress
τ = extra stress tensor
τ^i = ith spectral element of the extra stress tensor
ω = frequency

Literature Cited

Acierno, D., F. P. La Mantia, G. Marrucci, and G. Titomanlio, "A Non-linear Viscoelastic Model with Structure-Dependent Relaxation Times: I. Basic Formulation," *J. Non-Newt. Fluid Mech.*, **1**, 125 (1976).

Giacomin, A. J., and J. G. Oakley, "Upper Convected Maxwell Models for Molten Plastics in Large Amplitude Oscillatory Shear," *J. Rheol.*, **36**, 1529 (1992).

Giacomin, A. J., "A Sliding Plate Melt Rheometer Incorporating a Shear Stress Transducer," PhD Thesis, McGill Univ. (1987).

Giacomin, A. J., T. Samurkas, and J. M. Dealy, "A Novel Sliding Plate Rheometer for Molten Plastics," *J. Pol. Eng. Sc.*, **29**, 499 (1989).

Larson, R. G., "A Constitutive Equation for Polymer Melts Based on Partially Extending Strand Convection," *J. Rheol.*, **28**, 545 (1984).

Liu, T. Y., D. S. Soong, and M. C. Williams, "Transient and Steady Rheology of Polydisperse Entangled Melts: Predictions of a Kinetic Network Model and Data Comparisons," *J. Polym. Sci.*, **22**, 1561 (1984).

Marrucci, G., G. Titomanlio, and G. C. Sarti, "Testing of a Constitutive Equation for Entangled Networks by Elongational and Shear Data for Polymer Melts," *Rheol. Acta*, **12**, 269 (1973).

Meissner, J., "Modification of the Weissenberg Rheometer for Measurement of Transient Rheological Properties of Molten Polyethylene under Shear: Comparison with Tensile Data," *J. App. Polym. Sci.*, **16**, 2877 (1972).

Mewis, J., and G. De Cleyn, "Shear History Effects in the Spinning of Polymers," *AIChE J.*, **28**, 900 (1982).

Mewis, J., and M. M. Denn, "Constitutive Equations Based on the Transient Network Concept," *J. Non-Newt. Fluid Mech.*, **12**, 69 (1983).

Moldenaers, P., and J. Mewis, *Integration of Fundamental Polymer Science and Technology*, L. A. Kleintjens and P. J. Lemstra, eds., Elsevier Applied Science Publishers, London (1986).

Orbey, N., and J. M. Dealy, "Determination of the Relaxation Spectrum from Oscillatory Shear Data," *J. Rheol.*, **35**, 1035 (1991).

Tsang, W. K. W., and J. M. Dealy, "The Use of Large Transient Deformations to Evaluate Rheological Models for Molten Polymers," *J. Non-Newt. Fluid Mech.*, **9**, 203 (1981).

Zülle, B., J. J. Linster, J. Meissner, and H. P. Hürlimann, "Deformation Hardening and Thinning in Both Elongation and Shear of a Low Density Polyethylene Melt," *J. Rheol.*, **31**, 583 (1987).

Phan-Thien, N., and R. I. Tanner, "A New Constitutive Equation Derived From Network Theory," *J. Non-Newt. Fluid Mech.*, **2**, 353 (1977).

Manuscript received May 18, 1992, and revision received Oct. 14, 1992.