Predicting Nonlinear Viscosity and Elasticity from Zero-Shear Parameters in the Pao-Rouse Model*

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Synopsis

When the Rouse distribution of relaxation times is inserted into Pao's constitutive equation as expressed by Huseby and Blyler, a simple two-parameter model results. The parameters can be fitted using the limiting values of viscosity and modulus at low shear rates. The modulus in this case is defined as the ratio of shear stress during steady flow to the recovered shear during creep recovery with the stress removed. The mathematical model, is then used to predict the behavior at high shear rates where flow is pseudoplastic and elasticity is non-Hookean. A sample of polyisobutylene and several high molecular weight poly(dimethylsiloxanes) can be fitted reasonably well. Silicones of lower molecular weight (3.7 and 5.5×10^5) are not correlated successfully, perhaps because not all the "recoverable shear" stored during flow can actually be recovered experimentally. The Rouse distribution can be generalized for added flexibility.

INTRODUCTION

In 1957, Pao[1] introduced a constitutive equation which described the flow and deformation of pseudoplastic materials in terms of a distribution of relaxation times. Cox and Merz,[2] the next year, used the Pao model with a simple distribution to look at non-Newtonian flow of polymer melts. The distribution, introduced by Rouse[3] in 1953, characterizes the entire distribution by a single modulus and a maximum relaxation time. In theory, the number of elements used (each of which is related to the two parameters of modulus and maximum relaxation time) should be a function of molecular weight. The higher the molecular weight, the larger number of elements are used. Huseby and Blyler[4] have used the Pao equation to correlate and predict rheological properties of polymer melts. Since the equation is in a form which requires a distribution of relaxation times, it has been used to fit experimental data. The equation thus fitted has then been used to predict the behavior in another kind of experiment.

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For example, a distribution obtained from stress relaxation experiments can be used to predict non-Newtonian viscous flow.

It is the purpose of the present work to show that a much simpler modification can be used if the objective is to fit data with only a limited penetration into the non-Newtonian flow and non-Hookean elastic regions. The Rouse distribution has been used with the Pao equation before[2] in dealing with non-Newtonian flow. Since the Rouse distribution reduces the total number of parameters that can be fitted to two, it is obviously incapable of reproducing the many different shaped flow curves that even one polymer species may produce as a function of molecular weight distribution or branching.

PAO EQUATION

The general constitutive equation of Pao has been cast into the following forms by Huseby and Blyler[4] for laminar shearing flows involving shear stress τ_{12}, first normal stress difference $P_{11} - P_{22}$, and recoverable shear strain s as a function of shear rate $\dot\gamma$:

$$\tau_{12} = \eta(\dot\gamma)\dot\gamma \tag{1}$$

$$P_{11} - P_{22} = f(\dot\gamma)\dot\gamma^2 \tag{2}$$

$$\tau_{12} = G(\dot\gamma)s \tag{3}$$

$$\eta(\dot\gamma) = x[1 + (2\dot\gamma^2 y^2/x^2)] \tag{4}$$

$$f(\dot\gamma) = 2y[1 + (2\dot\gamma^2 y^2/x^2)] \tag{5}$$

$$G(\dot\gamma) = (x^2/2y)\,[1 + (2\dot\gamma^2 y^2/x^2)] \qquad s = 2\dot\gamma y/x \tag{6}$$

$$x = \sum_{p=1}^{N} (G_p\theta_p)/(1 + \theta_p{}^2\dot\gamma^2) \tag{7}$$

$$y = \sum_{p=1}^{N} (G_p\theta_p{}^2)/(1 + \theta_p{}^2\dot\gamma^2). \tag{8}$$

The set of quantities (G_p, θ_p) represents the distribution of relaxation times, and x and y are dummy parameters; G_p has the units of a shear modulus and θ_p, units of time. The parameter $\eta(\dot\gamma)$ is the ordinary viscosity which we expect to approach a constant value at low shear rates for most polymer melts and solutions; $G(\dot\gamma)$ is a shear modulus defined in terms of a recoverable shear strain s. It should be pointed out, since a *recovered* shear strain, γ_r, will be used later on, that the *recoverable* shear s is a measure of the energy actually stored in the fluid under steady flow conditions. Recovery can be, in itself, a dissipative process, so that it is conceivable that γ_r will be smaller than s. There is no reason to think that γ_r should ever exceed s.

ROUSE DISTRIBUTION

A simple mathematical model for $G_p(\theta_p)$ due to Rouse[3] has been used to approximate portions of stress relaxation behavior of real polymers. The model specifies

$$G_p = G_R \text{ (a constant)} \tag{9}$$

$$\theta_p = \theta_R/p^2 \qquad p = 1, 2, 3 \ldots \text{infinity} \tag{10}$$

where θ_R is the maximum observed relaxation time for a system. There are an infinite number of shorter relaxation times, each related to θ_R by eq. (10). Insertion of the Rouse distribution into eqs. (7) and (8) for x and y leads to

$$y = G_R\theta_R{}^2\sum_1^\infty 1/(p^4 + \theta_R{}^2\dot{\gamma}^2) \tag{11}$$

$$x = G_R\theta_R\sum_1^\infty p^2/(p^4 + \theta_R{}^2\dot{\gamma}^2). \tag{12}$$

The three observable phenomena, eq. (1) through (3), now are completely described in terms of only two parameters, G_R and θ_R.

One might question the applicability of the Rouse distribution where bulk polymer behavior is to be treated, since the model was originally derived for infinitely dilute polymer solutions. However, as Tobolsky[5] has pointed out, theoretical considerations allow the use of the model for undiluted amorphous polymers merely by using a different minimum relaxation time. Both Tobolsky and Cox and Merz[2] have used the Rouse distribution for undiluted systems with some success.

LOW-SHEAR BEHAVIOR

In order to test the usefulness of this relationship, we can examine first the behavior of viscosity and modulus at very low shear rates. As $\dot{\gamma}$ approaches zero, experience has shown that, for most polymer solutions and melts, $\eta(\dot{\gamma})$ approaches a steady value, $\eta(0)$, the "zero shear" or "lower Newtonian limiting" viscosity. Work by several groups[6,7] indicates a similar "zero shear" modulus for polymer melts, $G(0)$. Substituting eqs. (11) and (12) into eqs. (1), (3), (4), and (6), and letting $\dot{\gamma}$ approach zero, we have:

$$\eta(0) = G_R\theta_R\sum_1^\infty 1/p^2 \tag{13}$$

$$G(0) = [\eta(0)]^2 \Big/ \left(2G_R\theta_R{}^2 \sum_1^\infty 1/p^4\right) \tag{14}$$

$$\theta_R = 0.760\,\eta(0)/G(0) \tag{15}$$

$$G_R = 0.805G(0) \tag{16}$$

where $\Sigma 1/p^4 = 1.0823$ and $\Sigma 1/p^2 = 1.6449$, being pure numbers.[8] Thus, from two relatively accessible experimental numbers, $\eta(0)$ and $G(0)$, we should be able to project the behavior of $\eta(\dot\gamma)$, $G(\dot\gamma)$, and $f(\dot\gamma)$ into the non-linear regions as well as to predict the low-shear value of $f(\dot\gamma)$.

Now we can put the experimentally observable quantities stress τ_{12}, shear strain s, and rate of shear $\dot\gamma$ in dimensionless form:

$$s = 2\theta_R \sum_1^\infty \frac{1}{p^4 + \theta_R^2\dot\gamma^2} \Big/ \sum_1^\infty \frac{p^2}{p^4 + \theta_R^2\dot\gamma^2} \qquad (17)$$

$$\tau_{12}/G(0) = 0.805\,\theta_R\,(1 + s^2/2)\sum_1^\infty \frac{p^2}{p^4 + \theta_R^2\dot\gamma^2}. \qquad (18)$$
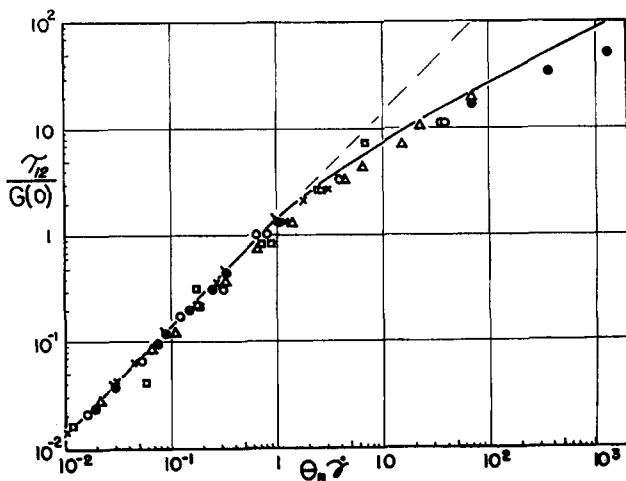

Fig. 2. Dimensionless plot of recovered shear strain γ_R vs. rate of shear for six polymers and for the Pao-Rouse model (continuous line). $\times$: Polyisobutylene; $\bullet$: Whole silicone; $\bigcirc$: Fraction F-1; $\triangle$: Fraction F-2; $\square$: Fraction F-3; $\blacklozenge$: Fraction F-4.

Fig. 1. Dimensionless flow curve, stress vs. rate of shear, for six polymers and for the Pao-Rouse model (continuous line). $\times$: Polyisobutylene; $\bullet$: Whole silicone; $\bigcirc$: Fraction F-1; $\triangle$: Fraction F-2; $\square$: Fraction F-3; $\blacklozenge$: Fraction F-4.
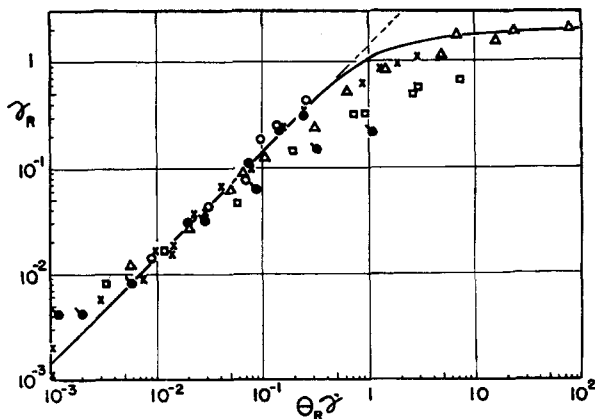
The right-hand sides of these equations are functions of θ_R only.   The behavior of s and $\tau_{12}/G(0)$ is shown as continuous lines in dimensionless plots (Fig. 1 and 2). $G(0)$ is used in place of G_R since it is directly observable and proportional to G_R, eq. (16).   The recoverable shear strain starts to deviate from linearity at about $\theta_R\dot{\gamma} = {}^1/_2$, whereas the viscosity does not decrease noticeably until $\theta_R\dot{\gamma} = 1$.   The strain rapidly approaches an asymptotic value of 2, while the reduced stress, $\tau_{12}/G(0)$, becomes approximately equal to $2.68 \ (\theta_R\dot{\gamma})^{0.5}$.   That is, for θ_R greater than 10, flow is representable by a "power law" with a slope of $^1/_2$.   This is a consequence of the behavior of the summation in eq. (18).   That summation can be approximated by an integration when $\theta_R\dot{\gamma}$ exceeds 10 to give

$$\sum_1^\infty \frac{p^2}{p^4 + \theta_R{}^2\dot{\gamma}^2} \cong \int_0^\infty \frac{p^2}{p^4 + \theta_R{}^2\dot{\gamma}^2} \, dp \ = \ \pi(8\theta_R\dot{\gamma})^{-0.5}. \tag{19}$$

CORRELATION OF EXPERIMENTAL DATA

Creep and recovered shear were reported on fractions of poly(dimethylsiloxanes) and a polyisobutylene in a previous paper.[7]   From the values of $\eta(0)$ and $G(0)$, we can calculate the parameter θ_R for each sample (Table I).   The plots on reduced coordinates are shown in Figures 1 and 2.   It

TABLE I
Rheological Parameters for Polymers Tested[a]

	$\eta(0)$, poise $\times 10^4$	G(0), dynes/ cm² $\times 10^{-4}$	θ_R, sec[b]
Polyisobutylene (Vistanex)	80	7.0	8.7
Whole polymer	25	1.2	16
Fraction F-1 ⎫	1600	0.8	1520
Fraction F-2 ⎪ silicones	87	1.9	35
Fraction F-3 ⎬	12.5	3.5	2.7
Fraction F-4 ⎭	3.1	6.6	0.36

[a] From Fruh and Rodriguez.[7]
[b] Equation (15).

is to be expected that the simple Pao-Rouse model, fitted without any reference to the nonlinear portion of the experimental data, can give only a qualitative prediction of the nonlinear behavior.   The recovered strains for the fractions F-3 and F-4 deviate markedly from the prediction at high rates of shear.   Perhaps in the case of these lower molecular weight polymers, the approximation that $\gamma_R = s$ becomes less valid, and dissipation of stored energy during recovery is appreciable.   The unequivocal Hookean behavior of higher molecular weight silicones and the polyisobutylene argues that dissipation either is a very small effect at lower shear stresses, or that it is a linear function of stress for high molecular weight and not linear for low molecular weights.   Since the correlation looks poorest for the low molecular weights, the possibility arises of using a
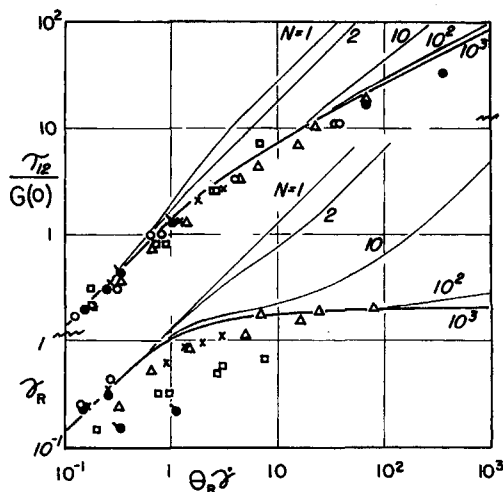
Fig. 3. Dimensionless stress and recovered strain vs. rate of shear for the Pao-Rouse model with a restricted number of elements. In these plots, 1000 elements give the same result as an infinite number. (Key to symbols same as in Figs. 1 and 2.)

finite number of elements rather than the infinite number used in the Rouse distribution in Figures 1 and 2.

Using only one element gives an anomalous increase in viscosity with rate of shear (Fig. 3). In the range of shear rates used here, there is no distinction visible between 1000 elements and an infinite numbe . By superimposing the flow data there seems to be no advantage in going to a finite number of elements.

Using a finite number of elements for the strain, the asymptotic value of shear strain at high rates of shear disappears (Fig. 3). As can be seen when the data are compared with the curves, the use of fewer elements predicts a change to higher recoverable shear strains which is in the opposite direction from the experimental results with lower molecular weights.

GENERALIZED DISTRIBUTIONS

In using an equation somewhat similar in form to the Pao equation, Bird and Carreau[9] have included as a variable the exponent on the parameter p of the Rouse distribution. The significance of n is that when n is less than 2, the elements of the distribution are closer together, and when n is greater than 2, the elements are further apart. Once again we might consider the spacing of the elements to be subject to variation with molecular weight. We are limited to exponents greater than 1 because, when the exponent becomes equal to or less than 1, the summations to infinity become infinite themselves. Now we replace eq. (10) by eq. (20):

$$\theta_p' = \theta_R'/(p)^n \qquad p = 1, 2, 3 \ldots \text{infinity} \qquad (20)$$

It is convenient to compare the results when $n = 1.25, 2$, and 4 on reduced coordinates such that s and $\tau_{12}/G(0)$ remain the same. The rest of the constants embodying the summations of reciprocal powers of p are lumped together in the coefficient C which multiplies the rate of shear.

The effect of changing the exponent is rather slight in the case of the flow curve (Fig. 4). When $n = 4$, there occurs the same increase in vis-
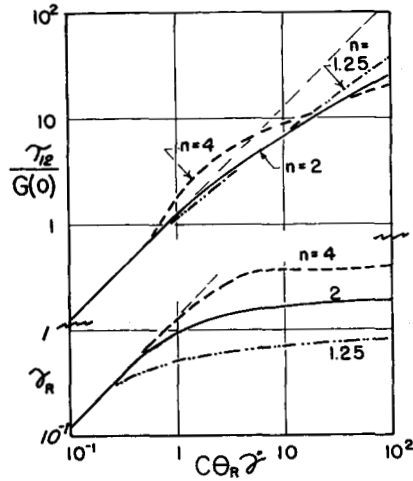

Fig. 4. Perturbing the Rouse distribution by increasing the exponent on the index for the relaxation time to 4 introduces distortions in stress and recovered strain plots. Decreasing the exponent to 1.25 makes the flow curve more Newtonian. Curves are shifted by the lumped constant C.
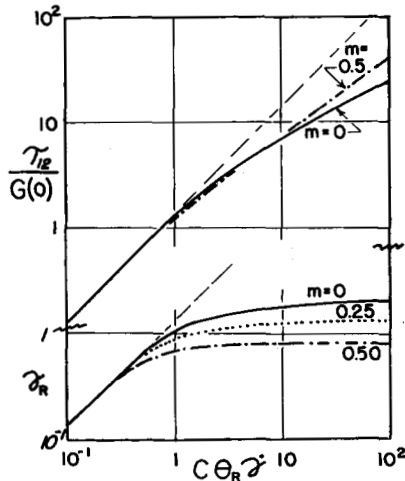

Fig. 5. Introducing a variable modulus term in the Rouse distribution makes the flow curve more Newtonian and decreases the asymptotic value of recovered shear strain at high rates of shear. Curves are shifted by the lumped constant C.

cosity with shear rate that was seen with one element. With the recoverable strain, the change in exponent gives a more well-ordered change in pattern. However, when $n = 4$, there is a predicted maximum in the strain. If we postulate that a lower molecular weight should have elements spaced further apart, that is, that n should be greater than 2, then the results are in the wrong direction since the lower molecular weights lie below the $n = 2$ line.

A second method of perturbing the Rouse model is to put in a variable modulus, so that eq. (9) is replaced by

$$G_p' = G_R'p^m \qquad p = 1, 2, 3 \ldots \text{infinity} \tag{21}$$

where G_R' is a constant as before. This corresponds to the physical situation when stress relaxation data are fitted by a series of Maxwell elements (Tobolsky's "procedure X").[10] It is usual to find that moduli of successive elements are greater as the relaxation times become shorter, realistic bonds are $0 < m < 1$. Negative values of m give a large increase in viscosity over the Newtonian value at the transition between Newtonian and power law behavior. When $m = 1$, the summations become infinite themselves. Exponents of $m = 0.25$ and $m = 0.50$ do indeed change the recoverable shear in a manner which might lead to a better fit (Fig. 5). However, the flow curve is changed in the direction of more Newtonian behavior, as was the case when $n = 1.25$ (Fig. 5). The conclusion is that simple modifications of the Rouse model do not improve it appreciably.

References

1. Y. H. Pao, *J. Appl. Phys.*, **28**, 591 (1957).

2. W. P. Cox and E. H. Merz, *Symposium on Plastics Testing and Standardization* ASTM Spec. Public. No. 247, 1958, p. 178.

3. P. E. Rouse, Jr., *J. Chem. Phys.*, **21**, 1272 (1953).

4. T. W. Huseby and L. L. Blyler, Jr., *Trans. Soc. Rheol.*, **11**, 77 (1967).

5. A. V. Tobolsky, *Properties and Structure of Polymers*, Wiley, New York, 1960, p. 169.

6. W. Philippoff, F. H. Gaskins, and J. G. Brodnyan, *J. Appl. Phys.*, **28**, 1118 (1957).

7. S. M. Fruh and F. Rodriguez, *ACS Polymer Preprints*, **9**, 1622 (1968).

8. M. Abramowitz and I. A. Stegun, Eds., *Handbook of Mathematical Functions*, Dover, New York, 1965, p. 811.

9. R. B. Bird and P. J. Carreau, *Chem. Eng. Sci.*, **23**, 427 (1968).

10. A. V. Tobolsky, *op. cit.*, pp. 188–194.