Non-Newtonian Flow and the Steady-State Shear Compliance

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Synopsis

A survey of viscoelastic data on amorphous polymer melts indicates that the steady-state shear compliance, J_e, of many systems can be approximated from a knowledge of their flow response. For systems with monomodel molecular weight distributions, the absolute value of the reduced complex viscosity, η^*/η_0, is found to equal 0.67 ± 0.03 at the frequency ω, where $\omega \eta_0 J_e = 1$. This result applies to a variety of polymer systems and to a wide range of molecular weights and distributions as long as the highest molecular weight dispersion of the distribution constitutes more than 20 weight per cent of the sample. This relationship determines J_e from non-Newtonian flow data and thus provides a consistent way to relate differently shaped reduced variable curves and to calculate compliances from characteristic times reported in the literature. The connection between some commonly used times and J_e is given. The method of calculating J_e is successfully applied to capillary measurements of melt viscosities and to characteristic times determined from steady-state shear measurements of concentrated polymer solutions.

INTRODUCTION

Different forms for characteristic times, τ, have been used to classify the non-Newtonian response of polymeric systems. In simple models, a time τ is defined as the ratio of the zero-shear viscosity to the elastic modulus, or equivalently the product of η_0 with the steady state shear compliance, J_e. The region of the onset of non-Newtonian flow is then characterized by a τ which is determined by the elastic properties of the system. More complex models involve multiple τ's which can be combined in prescribed ways to calculate the total compliance and viscosity. These measurable quantities, however, can only be used to determine an average characteristic time for non-Newtonian flow. When only a viscosity measurement is available, a τ is customarily determined by fitting data to standard viscosity–shear rate curves or by finding a form of reduced variables which produce one curve from all data.[1] Average times determined in this manner should depend on the elastic properties of the system. This study attempts to empirically relate measured elastic properties to the shape of the viscosity–shear rate curve. This correction

would provide a consistant method for describing non-Newtonian flow and would open data in the literature to the analysis of elastic properties.

In this study, the non-Newtonian response of several different types of polymer melts, with differing molecular weights and molecular weight distributions, is correlated with the measured steady-state shear compliance, J_e. This compliance is defined as the low frequency limit of the storage compliance, J'. The viscoelastic properties of these melts were measured at the General Electric Research and Development Center using a Weissenberg rheogoniometer equipped with a version of the Birnboim Ultra Low Frequency Phase Meter.[2] The result of this correlation is then tested with capillary flow measurements of the melt viscosities of narrow distribution polystyrenes and with the reported characteristic times of concentrated solutions of linear polystyrenes and branched poly(vinyl acetates).

ANALYSIS

Two of us[3] have formerly reported the approximately equal compliances for high molecular weight commercial polydimethylsiloxanes with similar molecular weight distributions. It was noted that the reduced viscosity, the first normal stress difference, and the shear storage modulus of these samples could be superimposed if the time scale for each sample was multiplied by the zero shear viscosity η_0. The equal compliances of these samples makes this data reduction equivalent to using an average characteristic time, $\eta_0 J_e$, as the reduced variable.

Dynamic data for seven polystyrene samples with weight-average to number-average ratios from 1.06 to 2.6 were compared as a function of $\omega \eta_0 J_e$, where ω is the frequency of the dynamic measurement. It was noted that the absolute value of the reduced complex viscosity, η^*/η_0, of each sample is generally 0.67 at $\omega \eta_0 J_e = 1$. This agreement is apparently independent of the differences in the shapes of the viscosity curves. The value of 0.67 for the reduced viscosity corresponds to the point where the Bueche[4] theoretical curve crosses the Bueche-Harding[1] standard curve (Fig. 1 of Bueche and Harding[1]). Table I gives typical data on these

TABLE I
Characterization Parameters and Reduced Complex Viscosity
at $\omega \eta_0 J_e = 1$ of Polystyrene Samples

Polystyrene sample	$M_w \times 10^{-3}$	M_w/M_n	η^*/η_0 at $\omega \eta_0 J_e = 1$
Pressure Chemical	411	1.06	0.68
Pressure Chemical	97.2	1.06	0.67
160 Blend[10]	98	1.3	0.68
411 Blend[10]	98	1.7	0.67
NBS 706	257.8	2.1	0.66
T-666	230	2.2	0.66
QX4451	190	2.6	0.67

samples.   Figure 1 gives a comparison of η^*/η_0 for two samples with approximately the same M_w but with different molecular weight distributions. The reduced complex viscosities of a series of narrow distribution polystyrenes with molecular weights from 4,800 to 411,000 and a tetra-branched
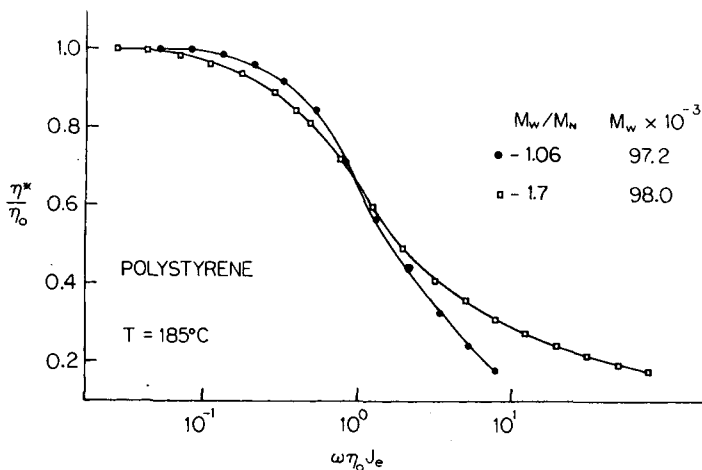
Fig. 1. Reduced complex viscosity of two polystyrene samples with different molecular weight distributions as a function of $\omega\eta_0 J_e$.
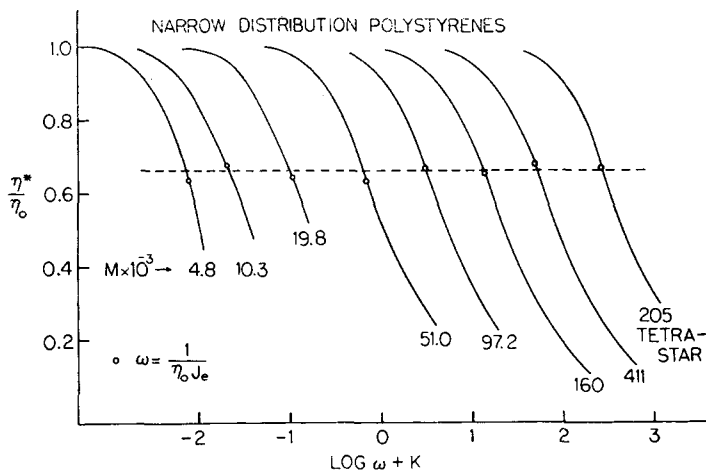
Fig. 2. Reduced viscosity curves of narrow distribution polystyrene samples, showing the point at which $\omega\eta_0 J_e = 1$. K is an arbitrary constant.   Dashed line corresponds to $\eta^*/\eta_0 = 0.67$.

star polystyrene with $M_w = 205,000$ are shown in Figure 2, where the time scales have been arbitrarily shifted for display purposes.   The dot marks the point at which $\omega\eta_0 J_e = 1$, and the dashed line corresponds to $\eta^*/\eta_0 = 0.67$.
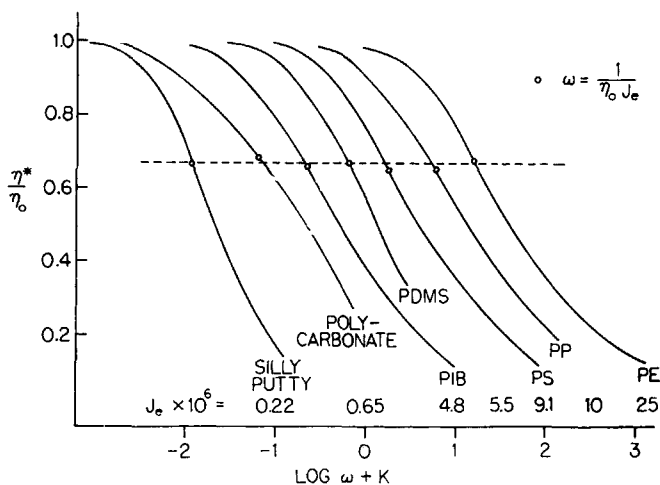
Fig. 3. Reduced viscosity curves of several polymer systems, showing the point (O) at which $\omega\eta_0 J_e = 1$. From left to right: commercial samples of Silly Putty, polycarbonate, polyisobutylene, polydimethylsiloxane, polystyrene, polypropylene, and high density polyethylene. Dashed line corresponds to $\eta^*/\eta_0 = 0.67$.

This same relationship is found for a variety of commercial melts as is shown in Figure 3. These are samples of high density polyethylene, polydimethylsiloxane, polyisobutylene, polycarbonate, and Silly Putty, with compliances from 2.5×10^{-5} to 2.2×10^{-7} cm²/dyne. The compliances used to calculate the value of $\omega\eta_0 J_e = 1$ are defined to within $\pm 15\%$. On the curves presented this corresponds to $\eta^*/\eta_0 = 0.67 \pm 0.03$. For most of the samples, $\eta^*(\omega)$ coincides with the apparent steady shear viscosity $\eta_a(\dot\gamma)$, until the onset of steady-state flow instabilities. In cone
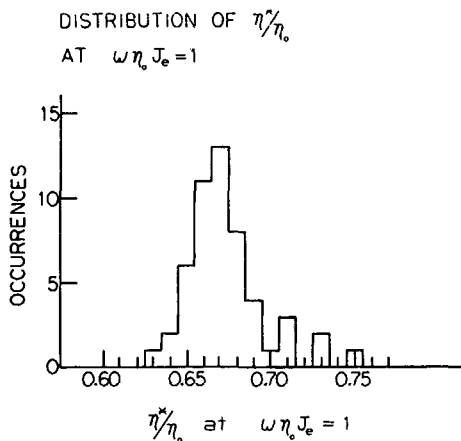

Fig. 4. Distribution of η^*/η_0 at $\omega\eta_0 J_e = 1$ for 52 experiments on 32 different commercial polymer melts.

and plate measurements, this instability appears as a break in the free surface of the sample which creates an abnormally low apparent viscosity because of the reduced size of the sample.

Many other experimenters[5-9] have reported the equivalent of $\eta_a(\dot{\gamma})$ and $\eta^*(\omega)$. This observation was used to verify and in some cases determine η_0 from $\eta^*(\omega)$. Figure 4 presents the distribution of the values of the reduced viscosity at $\omega\eta_0 J_e = 1$ for 52 experiments on 32 different polymer melts. The average reduced viscosity is 0.67. The standard
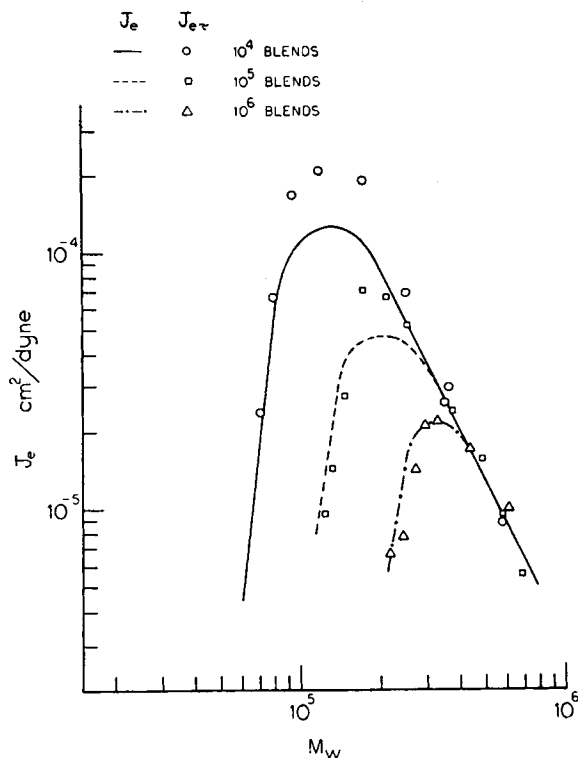

Fig. 5. Calculated compliances (points) of binary blends of high molecular weight polydimethylsiloxanes as a function of their weight-average molecular weight. Lines represent the measured values.[12]

deviation of these measurements is 0.023, in agreement with the uncertainties expected from the experimental determination of J_e.

Measurements on the samples used in this study gave well-defined values of the zero shear viscosity. This necessarily excluded samples with molecular weight distribution containing a broad, high molecular weight tail because η_0 could not be determined. This class of materials would test the extent of the applicability of the correlation, since the high molecular weight components are the first to contribute to non-Newtonian flow and have the greatest effect on J_e. The difficulty in measuring η_0

can be circumvented using blends of well-defined samples to simulate the extreme effect of different molecular weight distributions.

The correlation between non-Newtonian flow and J_e was tested in this manner with the binary blends of high molecular weight polydimethyl-siloxanes which were previously used to study the molecular weight distribution dependence of J_e.[10] The non-Newtonian behavior of the blends was used to calculate a compliance J_{er} defined as $(\omega\eta_0)^{-1}$, where ω is the frequency at which $\eta^*/\eta_0 = 0.67$. These results are compared in Figure 5 with the measured compliances, which are shown as solid lines. The apparent agreement of J_{er} with J_e is deceptive. When samples contain small amounts of high molecular weight material, the calculated compliance J_{er} is less than J_e. This difference is not apparent in Figure 5 because of the high dependence of J_e on M_w in this region. The sign of this deviation reverses near the maximum in the compliance (see Fig. 5), where the calculated compliance is greater than J_e. Importantly, beyond the maximum, where the high molecular weight components comprise more than 20 weight per cent of the system, J_{er} is found to be within 15% of J_c. These results imply that the correlation is not applicable to solutions of polymers with concentrations less than 20%. The correlation may also not apply to samples with molecular weight distributions containing a small amount of very high molecular weight polymer.

Alternatively, the correlation appears to apply to systems in which the compliance is primarily controlled by the high molecular weight components (i.e., in Fig. 5, M_w above the maximum in J_e). Experimentally this included all melts which had measurable zero shear viscosities, with the exception of the extreme binary blends. It is concluded that the compliance of a polymer melt can be calculated from the measured non-Newtonian response, provided the high molecular weight components of the system comprise more than 20 weight per cent of the sample.

APPLICATIONS

Calculation of J_e from Reported Characteristic Times

The connection between J_e and the non-Newtonian response provides a consistent method for relating the characteristic times of different viscosity–shear curves. The point at which the reduced viscosity becomes 0.67 is some fraction ζ of the particular time τ such that

$$\eta_0 J_{er} = \zeta\tau. \tag{1}$$

Values of ζ for commonly used τ's are given in Table II. Calculations of compliances from these τ's require that the original data fit the master curve at the point where the reduced viscosity equals 0.67. Note that ζ_{Bueche} is not twice ζ_{Rouse}, as would be expected from the explicit forms of the characteristic times. This reflects the differences in the shapes of the Bueche[4] and Rouse[11] theoretical curves. Direct calculations from the

TABLE II
The Relationship Between Characteristic Times and J_e

Master curve of:	Characteristic time τ	$\zeta \equiv \dfrac{\eta_0 J_e}{\tau}$
Rouse[11]	τ_R	0.69
Bueche[4]	τ_B	1.44
Bueche and Harding[1]	τ_{BH}	1.44
Graessley[13]	$\tau_{z=\infty}$	0.54
	$\tau_{z=10}$	0.64
	$\tau_{z=0}$	1.85

Rouse theory yield $\zeta_{Rouse} = 0.658$. This corresponds to a reduced viscosity of 0.65, within the standard deviation of the observed result.

The correspondence of $\eta^*(\omega)$ with $\eta_a(\dot{\gamma})$ permits compliances to be calculated from characteristic times for steady flow reported in the literature. Graessley, Hazleton, and Lindeman[12] find that concentrated solutions of narrow distribution polystyrenes obey the following equation:

$$\tau_R/\tau_0 = \frac{(1 + \beta cM)}{A} \tag{2}$$

where $\tau_R = \dfrac{6}{\pi^2} \dfrac{\eta_0 M}{cRT}$ is the Rouse relaxation time, and τ_0 is the characteristic time of the system found by fitting the experimental $\eta_a(\dot{\gamma})$ data to Graessley's[13] theoretical master curve. The experimental constants A and β were determined by a least-squares fit of the data. These results can be used to test the correlation since the concentration of the polystyrene component comprises no less than 20% of the sample. Equation (3) is the compliance calculated from eqs. (1) and (2):

$$J_{er} = \frac{6\zeta MA}{\pi^2 cRT (1 + \beta cM)}. \tag{3}$$

Graessley and Segal[14] find $A = 2.0$ and $\beta = 0.962 \times 10^{-5}$ by fitting data to a master curve, which assumes that the polystyrene samples can be represented by a Schultz-Zimm distribution with $M_w/M_n = 1.09$. For this curve ζ is 0.64. The compliances of bulk polymers ($c = 1$) predicted with these constants are represented by the solid line in Figure 6 and are in good agreement with the measured melt compliance of the Pressure Chemical polystyrene samples determined previously by us.[15,16] The brackets on the data give the range of several measurements. The point represents the best value of these measurements. The dashed portion of the curve is the extrapolation of eq. (3) outside the experimental region of eq. (2). The measured compliances in this low molecular weight region[16] are in approximate agreement with the predictions of the Rouse theory.[11] The difference between the dashed line and the data results from $A = 2.0$, which keeps eq. (2) from reducing to Rouse-type behavior for $\beta cM \ll 1$.
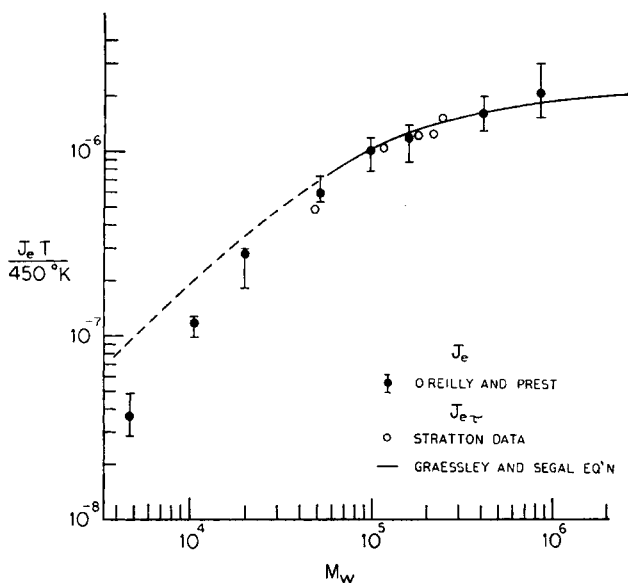
Fig. 6. Measured[16,17] and calculated compliances of narrow distribution polystyrene Solid points represent the most probable value of J_e. The brackets on these points span the range of results of several experimental measurements. J_e. (●) O'Reilly and Prest.[3] J_{er}. (○) data of Stratton[19]; (——) Graessley and Segal equation.[14]

This reflects the different types of polymeric behavior at high and low molecular weights.

The compliance of each solution can be estimated from the reported characteristic time,[14]

$$\tau_N \equiv \frac{15\eta_0 M_w{}^2}{2\pi^2 M_z M_{z+1}} \lim_{\dot{\gamma} \to 0} \frac{P_{11} - P_{22}}{\dot{\gamma}^2 \eta^2}, \qquad (4)$$

which is based on measurements of $P_{11} - P_{22}$, the first normal stress difference. This can be written in terms of a compliance where

$$J_{eN} \equiv \lim_{\dot{\gamma} \to 0} \frac{P_{11} - P_{22}}{2\dot{\gamma}^2 \eta^2}. \qquad (5)$$

The theory of second-order viscoelastic fluids[17] implies that the steady-state shear compliance, J_e, equals the compliance defined from normal stress measurements, J_{eN}. Graessley and Segal[14] find that eq. (2) represents the concentration–molecular weight dependence of τ_N when τ_N is used in place of τ_0. A least-squares fit of τ_R/τ_N data gives $A = 2.2$ and $\beta = 1.92 \times 10^{-5}$. These coefficients are not as well defined as those found for τ_R/τ_0 because the τ_N data are scattered at high values of cM. The compliance estimated from these constants, J_{eN}, has a different functional form than J_{er} since the coefficient β is twice that found from the τ_R/τ_0

measurements. At the lowest experimental point ($cM = 7.2 \times 10^4$), J_{eN} is 1% greater than J_{er}. At the highest experimental point ($cM = 3.05 \times 10^5$), J_{eN} is 18% less than J_{er} and is distinctly less than the measured melt compliances. Values of τ_R/τ_N calculated from the measured melt compliance for $M = 4.11 \times 10^5$ and $M = 8.60 \times 10^5$ fall below the given least-squares line. These values are in approximate agreement with the concentration–molecular weight dependence of the τ_R/τ_0 data (i.e., $\beta \approx 1 \times 10^{-5}$). This is what would have been found for the τ_R/τ_N data if the three lowest concentrations of the $M = 8.60 \times 10^5$ polymer solutions are ignored. These solutions also appear to have unusual values of the reduced viscosity at $\dot{\gamma}\eta_0 J_{eN} = 1$, as is discussed below. Without these three points, the steady-state shear compliance and the characteristic time of non-Newtonian flow have the same concentration–molecular weight dependence.

The Estimated Reduced Viscosity at $\dot{\gamma}\eta_0 J_{eN} = 1$

The reduced viscosity at $\dot{\gamma}\eta_0 J_e = 1$ of each of the concentrated solutions can be estimated from the master viscosity–shear rate curve using J_{eN} in eq. (4). The narrow distribution samples, without the three solutions in question, gives $\eta/\eta_0 = 0.66 \pm 0.043$. Including these samples (whose average reduced viscosity is 0.55) lowers the average η/η_0 to 0.63 and increases the standard deviation by 50%, to 0.065. Similar τ_0 and τ_N data are available for concentrated solutions of samples with broad molecular weight distributions. The average reduced viscosity of four polystyrene experiments[14] is 0.66 ± 0.054. For 16 branched poly(vinyl acetate) systems,[18] $\eta/\eta_0 = 0.64 \pm 0.056$. This average includes three samples with exceptionally low reduced viscosities (0.54, 0.54, and 0.56). Without these samples, $\eta/\eta_0 = 0.66 \pm 0.035$.

These estimates of η/η_0 and J_{er} assume that the viscosity–shear rate data fit the master curve at $\dot{\gamma}\eta_0 J_{eN} = 1$ and that the limiting low shear value of J_{eN} is obtained. If this last requirement is not fulfilled, the calculated reduced viscosity will be too low. This may account for the few estimates of η/η_0 that are exceptionally low. The sensitivity of J_{er} to the type of data fit can be demonstrated by assuming that the Pressure Chemical polystyrene samples are monodisperse. The characteristic times τ_0, obtained by fitting the data to the differently shaped monodispersed master curve,[13] are described by eq. (2) with $A = 3.57$ and $\beta = 1.33 \times 10^{-5}$.[12] This change increases J_{er} by 27% at $cM = 10^5$ and by 14% at $cM = 10^6$.

The average reduced viscosity obtained from melt data (0.67 ± 0.023) is above the averages estimated from concentrated solution measurements but within the standard deviation of these measurements. Considering the magnitude of the standard deviation and the assumptions involved in the estimates of η/η_0, no distinctions can be made between the solution and melt results.

Calculation of J_e from Capillary Measurements

Capillary measurements of the apparent viscosity have been found to agree with $\eta^*(\omega)$[8,9] for several polymer systems. For these cases the flow curves should define the compliance of the melt. Stratton's[19] flow data for the Dow series of narrow distribution polystyrenes were used to test the applicability of the J_{er} calculation for capillary measurements. These results, shown as the open points in Figure 6, agree well with the measured compliances of the Pressure Chemical melts and those calculated from Segal and Graessley's characteristic times.

It is concluded that the correlation between the steady-state shear compliance and non-Newtonian flow, found for dynamic measurements of polymer melts, applies to apparent viscosity measurements of polymer melts and concentrated solutions.

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