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# Relation between viscoelasticity and shear-thinning behaviour in liquids

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With 10 figures and 1 table

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## 1. Introduction

For shear-thinning fluids with no yield stress three main regions are commonly identifiable in the flow curve:

(i) an initial Newtonian region at low rates of shear, with viscosity $\eta_0$,
(ii) an intermediate shear-thinning region where the shear stress $\sigma$ at shear rate $\dot{\gamma}$ is given approximately by a power law relation, $\sigma = K\dot{\gamma}^n$,
(iii) a second Newtonian region with a limiting viscosity $\eta_\infty$ at high rates of shear.

Shear-thinning is usually attributed to structural breakdown in the fluid, but analogy with the dynamic viscous response to oscillatory shear suggests a close association with viscoelasticity. This is the subject of the present investigation.

A good representation of the complete flow curve is given by the equation

$$\eta = \eta_\infty + (\eta_0 - \eta_\infty)/[1 + (\lambda\dot{\gamma})^m]. \qquad [1]$$

This equation was originally derived (1) from a consideration of particle interactions in a disperse system but it has also found wide application to polymer melts and solutions (2, 3).

At intermediate rates of shear ($\eta_0 \gg \eta \gg \eta_\infty$) eq. [1] gives an approximation to power law behaviour with $m = 1 - n$, i.e. in this region $d \log \eta/d \log \dot{\gamma} = -m$.

Previous work (3) has shown that the exponent $m$ is related to polydispersity, with an upper limit of unity for a monodisperse system. In the case of bulk linear polymers it has been related to molecular weight distribution through the empirical equation

$$m = (\bar{M}_W/\bar{M}_N)^{-1/5}. \qquad [2]$$

With increasing polydispersity there is a decrease in the value of $m$ and hence in the gradient, $d \log \eta/d \log \dot{\gamma}$, in the shear thinning region, i.e. a broadening of the flow curve in the sense that shear-thinning extends over a wider range of shear rates.

The present work is primarily concerned with the significance of the parameter $\lambda$. Clearly this has the dimensions of time, with $\eta = (\eta_0 + \eta_\infty)/2$ when $\lambda\dot{\gamma} = 1$, i.e. at a shear rate $\lambda^{-1}$. If the fluid is regarded as a viscoelastic system it should be possible to identify $\lambda$ with a relaxation time defined by a ratio $\eta/G$ of viscous and elastic constants. In general $\eta$ and $G$ will both show shear dependence but one may postulate that at sufficiently low rates of shear there will be both a Newtonian viscosity $\eta_0$ and a Hookean shear modulus $G_0$ with

$$\lambda = \eta_0/G_0. \qquad [3]$$

Eqs. [1] and [3] provide a possible basis for deriving relaxation times and elastic shear moduli from viscosity/shear data. This paper examines the validity of this approach.

## 2. Experimental procedure

In outline the procedure was to evaluate $\lambda$ from shear-thinning data and to compare values of $\lambda$ with relaxation times obtained from normal-stress measurement and from stress relaxation. The measurements were carried out using a model R.16 Weissenberg Rheogoniometer (ex Sangamo Weston Controls Limited) at 25 °C.

### 2.1. Evaluation of $\lambda$

$\lambda$ was evaluated by graphical means from viscosity/shear data using eq. [1].

At low rates of shear ($\eta \gg \eta_\infty$), eq. [1] implies a linear relation (1) between $1/\eta$ and $\dot{\gamma}^m$, with an intercept $1/\eta_0$, and gradient $\alpha/\eta_0$, where $\alpha = \lambda^m$.

Figure 1 shows data for an aluminium laurate solution plotted in this way, with $m = 1$.

Knowing the value of $\lambda$ the corresponding elastic shear modulus can be expressed by $\eta_0/\lambda$.

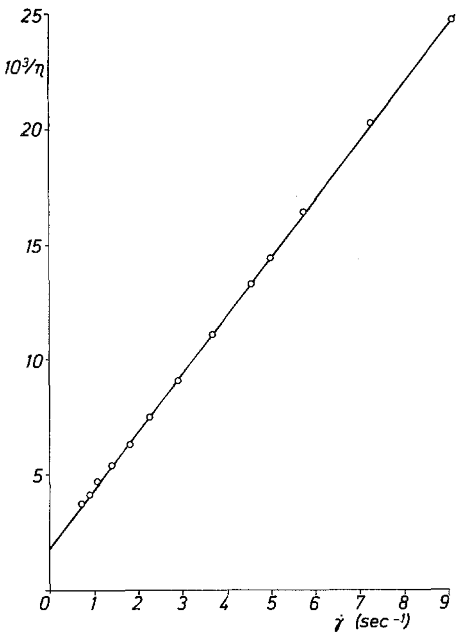


Fig. 1. Graphical evaluation of $\eta_0$ and $\lambda$. 6% solution of aluminium laurate in decalin

## 2.2. Normal stress measurement

From measurements of shear stress $\sigma$ and first normal-stress difference $N_1$, Weissenberg's relations (4) were used to derive a recoverable elastic shear strain $\gamma_w$, an associated elastic shear modulus $G_w$ and relaxation time $\lambda_w$ given by

$$\gamma_w = N_1/\sigma\,, \qquad [4]$$

$$G_w = \sigma/\gamma_w = \sigma^2/N_1\,, \qquad [5]$$

and

$$\lambda_w = \eta_0/(G_w)_0\,, \qquad [6]$$

$(G_w)_0$ representing the Hookean value at zero shear rate.

## 2.3. Stress relaxation measurements

With the Rheogoniometer coupled to a UV recorder, a steady shear rate was applied and the equilibrium shear stress $\sigma_0$ recorded. The electromagnetic brake was then applied and the relaxation recorded. Consistent with the behaviour of a simple Maxwell fluid, relaxation was approximately exponential and the Maxwell relaxation time $\lambda_M$ was taken as the time for the stress to fall to $\sigma_0/e$. The corresponding elastic shear modulus $G_M = \eta_0/\lambda_M$.

## 3. Comparison of results

### 3.1. Hookean behaviour

Hookean behaviour was observed in aqueous solutions of ammonium polymethacrylate. In figure 2 data for a 15% solution gives a linear plot of recoverable strain, expressed as $N_1/\sigma$, against shear stress $\sigma$. $G_w$ is obtained from the slope and $\lambda_w = \eta_0/G_w$.

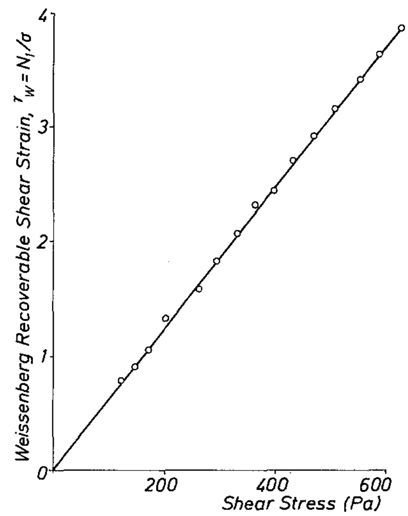


Fig. 2. Hooke's law in shear. 15% aqueous solution of ammonium polymethacrylate

In Figure 3 values of $\lambda_w$ derived in this way for five different solutions of ammonium polymethacrylate are compared with the corresponding values of $\lambda$ from viscosity/shear data. Good correlation is shown, with $\lambda$ corresponding to $\lambda_w/3$.

Table 1 lists the values of $\lambda_w$, $\lambda$, and $\lambda_M$ obtained by the three different methods. $\lambda$ shows good agreement with the Maxwell relaxation time $\lambda_M$ and it appears that

$$\lambda = \lambda_M = \lambda_w/3 \qquad [7]$$

or

$$G_M = 3\,G_w\,. \qquad [8]$$

This implies a recoverable elastic shear strain $\gamma_e$ given by

$$\gamma_e = N_1/3\sigma, \qquad [9]$$

i.e. one third the Weissenberg value, and an elastic shear modulus given by

$$G = 3\sigma^2/N_1. \qquad [10]$$

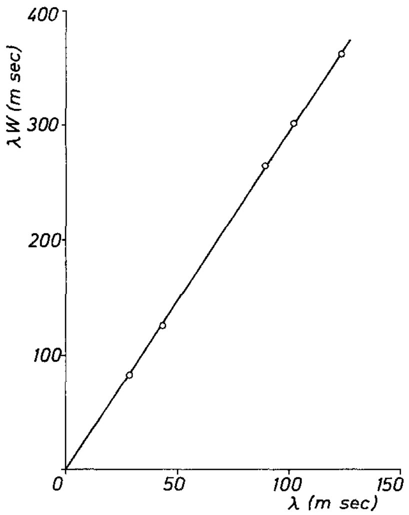


Fig. 3. Correlation of relaxation times. $\lambda_w$ from normal-stress data, $\lambda$ from viscosity data

Table 1. Comparison of relaxation times by different methods. Values in msec at 25 °C for five solutions of ammonium polymethacrylate

| Normal stress value $\lambda_w$ | Shear-thinning value $\lambda$ | Stress relaxation value $\lambda_M$ |
|---|---|---|
| 82 | 28.4 | 30 |
| 126 | 43.8 | 42 |
| 264 | 89 | 90 |
| 302 | 102 | 105 |
| 362 | 123 | 130 |

### 3.2. *Non-Hookean behaviour*

Figures 4 and 5 show two examples of non-linear stress-strain behaviour.

Here the shear strain has been expressed as $N_1/3\sigma$ in accordance with eq. [9]. The dotted lines through the origin correspond to the values of $G_0$ evaluated from viscosity/shear data using eqs. [1] and [3]. In each case the line appears tangential to the curve, indicating that $G_0$ has been correctly evaluated.

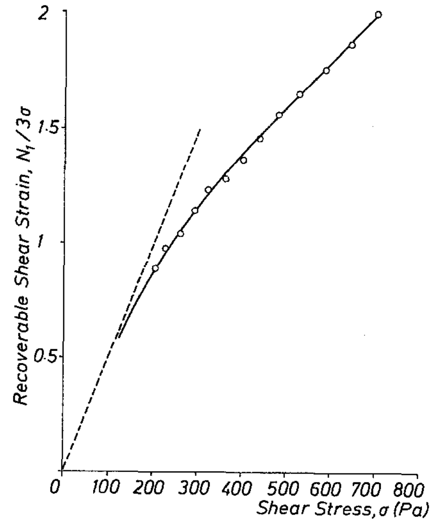


Fig. 4. Non-Hookean behaviour. Aqueous polyacrylamide solution

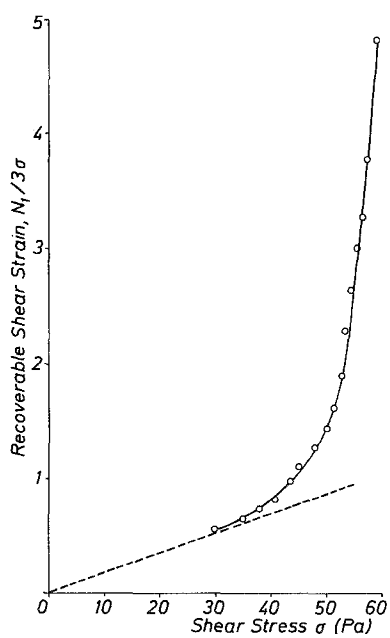


Fig. 5. Non-Hookean behaviour. 5% aluminium laurate/decalin

## 4. Measurement of recoverable shear strain

The present work provides indirect evidence that in the solutions examined the recoverable elastic shear strain can be expressed by $N_1/3\sigma$. In view of this unexpected result it was decided to undertake direct measurements of recoverable strain using a Deer Rheometer. This instrument was not available at the commencement of the investigation.

The Deer Rheometer is a rotational instrument with the essential feature that shear stress can be applied or removed virtually instantaneously by means of an electromagnetic field and the instrument response recorded in terms of either angular displacement or angular velocity.

Low inertia cone and plate geometry was used and the sample subjected to a period of steady shear flow at a selected shear stress, recording the angular displacement on a chart-drive pen recorder. At a convenient time the stress was removed and the recoverable strain derived from the angular recoil of the cone. A typical recorder trace is reproduced in figure 6.

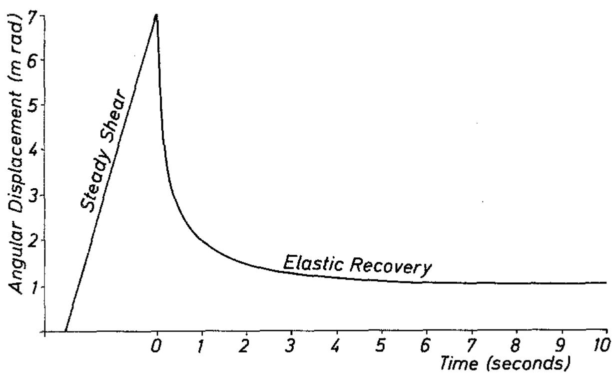


Fig. 6. Recovery curve for 6% aluminium laurate solution. Deer Rheometer. 50 mm, 1° cone. $\sigma = 71.2$ Pa

In figure 7 values of $\gamma_e$ derived in this way for a 4% solution of aluminium laurate in decalin show good agreement with $N_1/3\sigma$ from normal measurement on the Rheogoniometer.

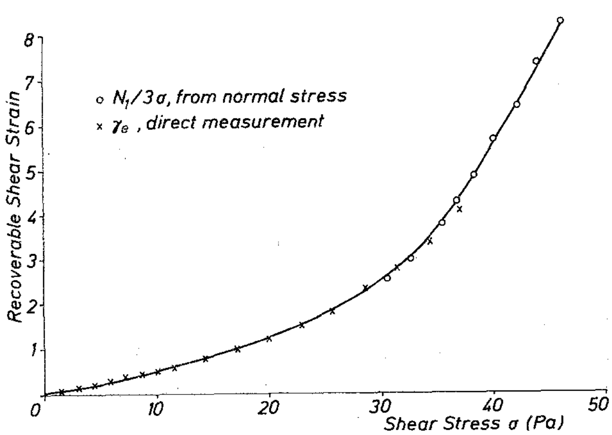


Fig. 7. Comparison of $N_1/3\sigma$ with direct measurement of $\gamma_e$. 4% aluminium laurate/decalin

In figure 8 direct measurement of $\gamma_e$ for a 6% aluminium laurate solution shows initial Hookean behaviour with a shear modulus of 400 Pa. Shear thinning data, shown in figure 1, gives $\eta_0 = 513$ Pa s, $\lambda = 1.29$ s and $G_0 = \eta_0/\lambda = 397$ Pa.

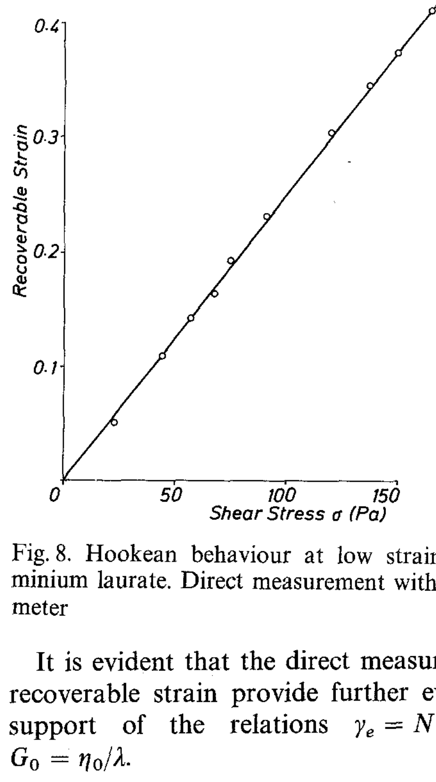


Fig. 8. Hookean behaviour at low strains. 6% aluminium laurate. Direct measurement with Deer rheometer

It is evident that the direct measurements of recoverable strain provide further evidence in support of the relations $\gamma_e = N_1/3\sigma$ and $G_0 = \eta_0/\lambda$.

## 5. Application to polymer melts

The present measurements have been confined to solutions of aluminium laurate in decalin and aqueous polymer solutions. The treatment may be extended to a polymer melt by reference to data published by *Han* (5) for a low density polyethylene melt at 200 °C.

It is convenient to introduce the normal-stress coefficient $\Psi = N_1/\dot{\gamma}^2$ and to write $\Psi_0 = \lim_{\dot{\gamma}\to 0} \Psi$ then

$$\Psi_0 = \lim_{\dot{\gamma}\to 0}\left(\frac{N_1}{\sigma^2}\cdot\frac{\sigma^2}{\dot{\gamma}^2}\right) = 3\eta_0^2/G_0,$$

$$\text{i.e.}\quad \Psi_0 = 3\eta_0\lambda. \qquad [11]$$

The shear dependence of $\Psi$ is basically similar to that of $\eta$, and by analogy with eq. [1] *Ueda* and *Kataoka* (6) have proposed the equation

$$\Psi = \Psi_\infty + (\Psi_0 - \Psi_\infty)/(1 + \beta\dot{\gamma}^{m'}) \qquad [12]$$

with

$$m' = 2m. \qquad [13]$$

For the LDPE melt $\bar{M}_W/\bar{M}_N = 20$ and eqs. [2] and [13] give $m = 0.55$, $m' = 1.1$. Using these values, figures 9 and 10 show plots of the viscosity and normal-stress data in accordance with eqs. [1] and [12]. From the viscosity data we obtain $\eta_0 = 14300$ Pa s and $\lambda = 3.68$ s, while eq. [11] gives $\Psi_0 = 3\eta_0\lambda = 158 \cdot 10^3$ Pa s$^2$. The normal stress plot (fig. 10) gives $\Psi_0 = 154 \cdot 10^3$ Pa s$^2$.

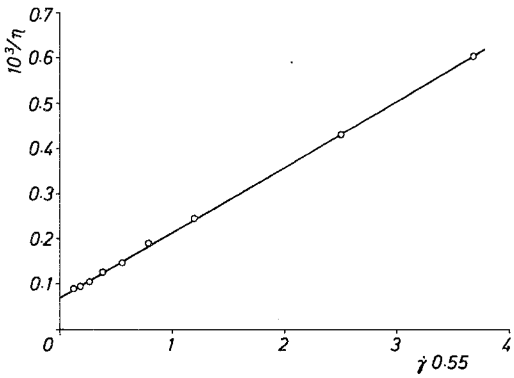


Fig. 9. Graphical evaluation of $\eta_0$ and $\lambda$. LDPE melt (5) at 200 °C

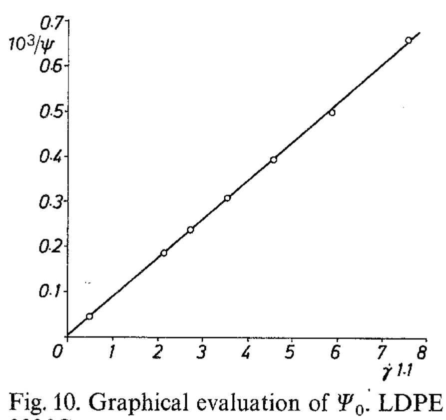


Fig. 10. Graphical evaluation of $\Psi_0$. LDPE melt (5) at 200 °C

## 6. Conclusions

A simple relationship has been established between the shear-thinning behaviour of a liquid and its viscoelastic properties, enabling relaxation times and elastic shear moduli to be predicted from viscosity/shear data. Predicted values show good agreement with stress relaxation measurement and with direct measurement of recoverable shear strain. There is also good agreement with normal-stress data provided the recoverable elastic shear strain is expressed by $N_1/3\sigma$.

Weissenberg's relation $\gamma_e = N_1/\sigma$ for recoverable shear strain has been the subject of some controversy. *Lodge* (7) suggests that *Weissenberg's* theory probably relates to free recovery and is not applicable to any situation where lateral movement is constrained by instrumental factors, as in a rotational viscometer. For his theoretical rubberlike liquid Lodge shows that the ultimate constrained recoverable shear strain is $N_1/2\sigma$, i.e. half the *Weissenberg* value. Although the two theories differ by a factor of 2 both find experimental support in the literature. As the present work gives an experimental result $N_1/3\sigma$ further evidence appears necessary.

It has been shown that relaxation times and elastic moduli can be evaluated graphically from viscosity/shear data using eq. [1]. However, when shear-thinning is marked ($\eta_0 \gg \eta_\infty$) an alternative and simpler procedure is possible. All that is required is a knowledge of $\eta_0$ and the shear rate $\dot{\gamma}_{1/2}$ at which $\eta = \eta_0/2$. From eq. [1] we note that when $\lambda\dot{\gamma} = 1$,

$$\eta = (\eta_0 + \eta_\infty)/2 \cong \eta_0/2 .$$

Hence

$$\lambda = 1/\dot{\gamma}_{1/2}$$

and

$$G_0 = \eta_0 \dot{\gamma}_{1/2} . \quad [14]$$

Thus applying the relation $G_0 = 3\sigma^2/N_1$ to the normal-stress data shown in figure 2 gives $\eta_0 = 483$ Pa. Viscosity data give $\eta_0 = 48.8$ Pa s and $\dot{\gamma}_{1/2} = 10.2\,\text{s}^{-1}$, giving $G_0 = \eta_0\dot{\gamma}_{1/2} = 498$ Pa.

A very simple relation between viscoelasticity and shear thinning is thus established. The controlling parameter is the relaxation time $\lambda$ and it can be postulated that significant shear-thinning will be experienced by any fluid when the applied shear rate approaches the reciprocal of its relaxation time. Thus water has a very low viscosity and high elastic modulus giving a relaxation time of the order $10^{-14}$ seconds. For all practical purposes it behaves as a Newtonian fluid but shear-thinning would be expected at shear rates in the region of $10^{14}\,\text{sec}^{-1}$.

*Summary*

The shear-thinning behaviour of a liquid is represented in terms of a relaxation time $\lambda$, defined by the ratio $\eta_0/G_0$ of initial viscous and elastic constants. The relationship provides a very simple basis for the evaluation of $\lambda$ and $G_0$ from viscosity/shear data.

Results are compared with relaxation times and moduli from primary normal-stress measurement, from stress relaxation and from direct measurement of recoverable shear strain. Good agreement is found but there is experimental evidence the recoverable shear strain $\gamma_e$ is related to normal stress $N_1$ and shear stress $\sigma$ by $\gamma_e = N_1/3\sigma$, which does not agree with the theoretical prediction of either *Weissenberg* or *Lodge*.

*Zusammenfassung*

Das Scherentzähungsverhalten einer Flüssigkeit wird mittels einer Relaxationszeit $\lambda$ beschrieben, die durch das Verhältnis der Anfangswerte von Viskosität und Elastizitätsmodul $\eta_0/G_0$ definiert ist. Diese Beziehung eröffnet eine einfache Methode zur Bestimmung von $\lambda$ und $G_0$ aus Scherviskositätsmessungen. Die damit erhaltenen Ergebnisse werden mit Relaxationszeiten und Moduln verglichen, die durch Messung der ersten Normalspannungsdifferenz, der Spannungsrelaxation und der Scherdehnungsrückstellung (recoverable shear strain) gewonnen worden sind. Es wird eine gute Übereinstimmung gefunden, zugleich aber wird der experimentelle Nachweis geführt, daß die Scherdehnungsrückstellung $\gamma_e$ mit der ersten Normalspannungsdifferenz $N_1$ und der Schubspannung $\sigma$ durch die Beziehung $\gamma_e = N_1/3\sigma$ verknüpft ist, was sowohl zu der theoretischen Voraussage von *Weissenberg* als auch zu derjenigen von *Lodge* im Widerspruch steht.

*References*

1) *Cross, M. M.*, J. Colloid Sci. **20**, 417 (1965).

2) *Cross, M. M.*, European Polymer J. **2**, 299 (1966).

3) *Cross, M. M.*, J. Appl. Polymer Sci. **13**, 765 (1969).

4) *Weissenberg, K.*, The Testing of Materials by Means of the Rheogoniometer, Sangamo Weston Controls Limited.

5) *Han, C. D.*, Rheology in Polymer Processing, Academic Press (New York 1976).

6) *Ueda, S., T. Kataoka*, J. Polymer Sci. (Polymer Physics Edition) **11**, 1975 (1973).

7) *Lodge, A. S.*, Elastic Liquids, Academic Press (London 1964).

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