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Equations for the interpretation of normal stress differences in polymer solutions and melts

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With 4 tables

Polymer solutions and melts are known to exhibit two types of anomalies, viz. viscous (resulting in shear dependent viscosity under steady flow conditions) and elastic (manifesting in normal stresses under steady flow conditions). An industrial rheologist is faced with the pressing problem of describing such experimentally observed viscous and elastic anomalies in mathematical terms of general utility or specifying in turn explicit constitutive equations with a small number of constants so as to be able to correlate the phenomena satisfactorily. Once such equations are found one hopes to apply these equations directly to the problem of interest. If the problems under consideration are too complicated then one may be able to at least suggest relevant dimensionless groups based on these equations.

Although most processing equipment does not operate in viscometric flow, the simplicity of the flow field makes viscometric flow a logical starting point for any characterisation. It has been shown (1) that three material functions, namely a shear stress function and two independent normal stress combinations, are required to completely specify the rheological properties of a viscoelastic material in viscometric flows. For a simple shear flow described by the velocity field $v_1 = v_1(x_2)$ the three material functions are determined as

$$S_{12} \quad = \tau(\dot{\gamma}) \tag{1}$$

$$S_{11}-S_{22} = F_1(\dot{\gamma}) \tag{2}$$

$$S_{22}-S_{33} = F_2(\dot{\gamma}) \tag{3}$$

where $\tau(\dot{\gamma})$ is the shear stress function and $F_1(\dot{\gamma})$ and $F_2(\dot{\gamma})$ are primary and secondary normal stress difference functions, respectively. The three material functions τ, F_1 and F_2 are related

to the viscosity (η) and the normal stress coefficients, F, by

$$\tau \quad = \dot{\gamma}\eta(\dot{\gamma}) \tag{4}$$

$$F_1 = \dot{\gamma}^2\sigma_1(\dot{\gamma}) \tag{5}$$

$$F_2 = \dot{\gamma}^2\sigma_2(\dot{\gamma}). \tag{6}$$

The theories which have been proposed on the basis of molecular considerations are able to interpret both the shear dependent viscosity (2, 3, 4) as well as the presence of normal stresses (3, 4). The description is, however, successful only partially in that the functional dependence of these material functions on the rate of shear is far from satisfactorily described, particularly in the range shear rates of practical interest.

In the frame work of non-linear continuum mechanics, several constitutive equations have been proposed which depict the flow behaviour of liquids. A useful summary of these equations is made by *Bogue* and *Doughty* (5). The minimum desirable properties of any of these constitutive equations are as follows (5): 1. They should be coordinate invariant. 2. They should be capable of predicting shear dependent viscosities and normal stresses in steady shear. 3. They should be able to reconcile with the dynamic experiments of linear viscoelasticity. 4. They should express the stress relaxation phenomena. 5. They should be explicit with definite constants to be fitted to experimental data.

To satisfy all these imposed restrictions is a formidable task for any constitutive equation. As a net result of this the constitutive equations somewhat manage to describe all the relevant phenomena qualitatively but do only a mediocre job when dealing with one of the phenomena in an exact quantitative manner. Thus, for instance, the prediction of the viscosity function $\eta(\dot{\gamma})$

made by *Oldroyd*-3 constant model (6) or a *Coleman-Noll* third order fluid (7) is found to be completely unsatisfactory except for correlating either dilute solution data or data obtained at very small rates of deformation. It is of course possible to increase the complexity of the model (e.g. using *Oldroyd*-8 constant model or using a higher order approximation for a *Coleman-Noll* fluid), but the undetermined constants involved in the function $\tau(\dot{\gamma})$ also increase considerably and the equations become devoid of any practical utility.

The attempts to circumvent these difficulties in the case of viscosity function are well known. Two or more parameter Generalised *Newtonian* Fluid models (GNF models) have been used for a number of years (8). These empirical or semi-empirical models prescribe arbitrarily a functional form for the viscosity function as either $\eta(II_D)$ or $\eta(\dot{\gamma})$. These equations have found enormous use in correlating rheological data as well as in treating engineering flow situations.

This is, however, not the case with the two other material functions related to the normal stress differences. It is well recognised that the second order approximation predicting a linear dependence between F_1 and $\dot{\gamma}^2$ is far from satisfied in practical situations. It is also agreed that F_1 and F_2 are functions of the second invariant of the rate of deformation tensor, i.e. $F(II_D)$ or in simple shear flow, $F(\dot{\gamma})$. However, the exact functional forms of $F(\dot{\gamma})$ have not been well established so far. Suitable empirical models devised to describe these functions are likely to have a considerable importance for a rheologist as well as an engineer. Some of the areas of their utility have been discussed later.

In view of this, in this work we have examined the possibility of devising suitable empirical models capable of interpreting normal stress differences in liquids. Some data from this laboratory and extensive data from the literature have been examined to find out the best models which describe these functional relationships. Based on this study recommendations are made which will help in selecting suitable empirical models for the correlation of normal stress data.

Selection of empirical models

The selection of the empirical models to be tested was based on three primary considerations:

1.

The chosen model should correlate the normal stress data for sufficient number of liquids in a large range of shear rates.

2.

The model should have minimum number of unknown parameters.

3.

The mathematical expression should be simple so that it can be handled easily in engineering applications.

We have sought functional forms for both the primary normal stress difference function, $F_1(\dot{\gamma})$ as well as the secondary normal stress difference function, $F_2(\dot{\gamma})$. There is some dispute in the literature about the magnitude of $F_2(\dot{\gamma})$ in comparison to $F_1(\dot{\gamma})$ as well as about the sign of $F_2(\dot{\gamma})$ [see ref. (21)]. However, it has been generally agreed that both F_1 and F_2 are directly proportional to each other. In view of this both the functions are expected to have the same functional forms. Further in the ensuing discussion we have used F to signify either F_1 or F_2.

The first functional forms chosen were analogous formally to the GNF models used for describing the functional dependence of $\tau(\dot{\gamma})$. The models resembling a power-law model, *Ellis* model, *Sisko* model and a *Prandtl-Eyring* model respectively, were given by

$$F = K(\dot{\gamma})^n \qquad [7]$$

$$\dot{\gamma} = AF^\alpha + BF \qquad [8]$$

$$F = A_1 \dot{\gamma}^{\alpha_1} + B_1 \dot{\gamma} \qquad [9]$$

$$F = A_2 \sinh^{-1}(\dot{\gamma}/B_2). \qquad [10]$$

An examination of eqs. [7]–[10] indicates that these equations, although possibly useful in correlating the normal stress data, do not bring out the even character of the normal stress difference functions. Further, all of them are bound to fail in the lower region of shear rates where the theoretical considerations predict that F varies directly as $\dot{\gamma}^2$, whereas eqs. [7] to [10] predict that F varies directly as $\dot{\gamma}$.

In view of this we thought of examining another set of models which could overcome these difficulties. A simple superposition of the behaviour in the limit of lower shear rate range

$(F \propto \dot{\gamma}^2)$ and a power-law dependence in the higher shear rate range $(F \propto \dot{\gamma}^n)$ gives on rearrangement,

$$\frac{1}{F/\dot{\gamma}^2} = 1/G(1 + (F/F_0)^{Q-1}). \qquad [11]$$

This is an analog of the *Ellis* model for the viscosity function. It is seen that the value of G is the zero shear normal stress coefficient. The constant Q in the equation gives an indication of the non-linearity of the normal stress difference-shear rate curve as compared to a second order fluid. The term G/F_0 describes the scale by which different normal stress difference-shear rate curves will be shifted for different materials.

Evidently several other superpositions could be attempted to fit the $F - \dot{\gamma}$ data. Some of them are listed below,

$$F/\dot{\gamma}^2 = G[1 - (\dot{\gamma}/\gamma_0)^{n-1}] \qquad [12]$$

$$F/\dot{\gamma}^2 = G\left(\frac{\sinh^{-1}\beta\gamma}{\beta\gamma}\right)^Z. \qquad [13]$$

Similar significance could be attached to the parameters involved in the above equations as well. Some constitutive equations [e.g. *Oldroyd* 5 or 8 constant models (9), *Pao* model (10)] predict the presence of a lower limiting value of normal stress coefficient as well as an upper limiting value in the region of very high shear rates. This behaviour is analogous to the presence of a lower limiting viscosity (η_0) and an upper limiting viscosity (η_∞) in the case of the viscosity function, $\eta(\dot{\gamma})$. Empirical models to take into account this type of behaviour could also be devised on similar lines, e.g. eqs. [14] and [15] below

$$\frac{F/\dot{\gamma}^2 - H}{G - H} = \frac{\sinh^{-1}\beta\dot{\gamma}}{\beta\dot{\gamma}} \qquad [14]$$

$$\frac{F/\dot{\gamma}^2 - H}{G - H} = \frac{1}{1 + m_1\dot{\gamma}^{m_2}}. \qquad [15]$$

where G and H are the values of the lower and upper limiting values of the normal stress coefficient, respectively.

The suitability of the above models to correlate the data was examined by using several data points obtained in this work as well as from the literature. It was thought desirable to choose data on rather a wide variety of liquids obtained in a rather large range of shear rates. The data obtained in this laboratory have been collected on a *Weissenberg* rheogoniometer (Model R-18).

The list of the liquids used, the range of shear rates, the range of normal stress differences and the relevant source of data have been listed in table 1. It is seen that an impressive range of all the above variables was covered.

Two procedures were used for examining the suitability of various equations. The first procedure involved the use of a least square procedure. The equations were first suitably linearised. This required an accurate differentiation of the data. This was done graphically. The linearised equations were fitted by the least square technique on an ICL-KDF 9 digital computer.

Another procedure involving an optimisation technique was also used. For this minimisation procedure a programme XPOWMIN available at the University of Salford computing library was used. The details of the programme could be found in ref. (17).

Results and discussion

Considering the vast extent of the data which were analysed it is not possible to list the parameters of each model. The suitability of different models in describing the data is best examined by reporting the percentage absolute deviations in the case of each model tested. The average percentage deviation corresponds to the mean of all the individual percentage deviations obtained while testing a given empirical model. The minimum and the maximum percentage deviations have also been listed for the sake of comparison. In the first class of models (eqs. [7], [8], [9] and [10]) all the models were tested. Eqs. [14] and [15] could not be tested for the data analysed in this work, because no suitable set of data were reported in the literature which showed the variation of F as required by eqs. [14] and [15]. Among the second class of models eq. [11] was found to be a representative superposition and has been most extensively tested in the case of all the solutions used. Some typical values of the parameters in the case of some of the solutions used are listed in table 2.

An examination of table 3 indicates that eq. [11] is found to be far more satisfactory in comparison to eqs. [7], [8], [9] and [10]. The power law form of eq. [7] appears to be the next best form. However, it should be emphasized that this equation best describes the data in rather a narrow range of shear rates and never more than for about decades of shear rates. Models presented by eqs. [7], [8], [9] and [10] fail particularly

Table 1. Normal stress data analysed in this work

No.	Solutions or melts	Concentration (wt.-%)	Approximate shear rate range, sec^{-1}	Technique	Source of data
1	Polyacrylamide (ET-597)	0.01–0.05	$10^4 - 5 \times 10^6$	jet thrust	11
2	Polyhall (295)	0.01–0.05	0.1 – 500	cone and plate	12
3	Polyethylene oxide (WSR-301)	0.01–0.05	$10^4 - 5 \times 10^6$	jet thrust	11
4	Polyethylene oxide (WSR-301)	1–2	$2 \times 10^2 - 10^6$	cone and plate	13
5	Polyethylene oxide (WSR-205)	2–5.63	$1 - 5 \times 10^3$	cone and plate	13
6	Polyethylene oxide (WSR-301)	0.7–1.1	$10 - 10^3$	axial annular flow, cone and plate	14
7	Polyacrylamide (Separan AP-30)	0.0025–0.5	$0.5–10^3$	cone and plate	15
8	Polyacrylamide (Separan AP-30)	0.5–2	$1 - 10^3$	cone and plate	16, 17
9	Polyacrylamide (Separan MGL)	0.05–1.19	$1 - 10^3$	cone and plate	15
10	Hydroxy-ethyl cellulose	0.5–0.9	$10 - 10^3$	cone and plate	13
11	Hydroxy-ethyl cellulose	0.9	$2 \times 10^2 - 10^3$	separated cone and plate	18
12	Carboxy methyl cellulose (P-75-XH)	0.4–0.5	$10 - 10^3$	axial annular flow, cone and plate	14
13	Carboxy methyl cellulose (P-75-XH) (med)	1.1–1.5	$10 - 10^3$	axial annular flow, cone and plate	14
14	Carboxy methyl cellulose (P-75-XH) (low)	2.6	$10 - 10^3$	axial annular flow, cone and plate	14
15	Carboxy methyl cellulose (P-75-XH) (Hercules, High)	1–3	$5 - 10^3$	parallel plate	19
16	Jaguar (A-20-D)	0.3–0.6	$10 - 10^3$	axial annular flow, cone and plate	14
17	Natrosol (250-H)	0.5–0.9	$10 - 10^3$	axial annular flow, cone and plate	14
18	Polyisobutylene in decalin	5	$4 - 5 \times 10^2$	cone and plate, parallel plate	20
19	Polyisobutylene in decalin	6.5–10.5	0.4 – 100	cone and plate, parallel plate	21
20	Polyisobutylene in decalin	0.25–9	$10^{-1} - 500$	cone and plate parallel plate	22
21	Polyisobutylene in cetane	3.9–8.54	$1 - 5 \times 10^2$	cone and plate, parallel plate	23
22	Polystyrene in toluene	5–35	$1 - 10^2$	parallel plate	24
23	Polystyrene in decalin	12–31	$8 - 10^2$	parallel plate	19
24	Polystyrene in dioctylphthalate	0.8–2	$10 - 10^2$	parallel plate	25
25	Polystyrene in chlorinated diphenyl	0.3–2	$1 - 10^2$	parallel plate	26
26	Polystyrene in Aroclor (1232)	2–5	$1 - 10^2$	separated cone and plate	18
27	Silicone oil (MS 200–60000 cs)	–	$1 - 10^2$	cone and plate	27
28	Molten polyethylene	–	$10^{-1} - 10$	parallel plate	28
29	Molten polyethylene	–	$10^{-1} - 30$	parallel plate	29

Table 2. Some typical values of the parameters of the empirical model based on eq. [11]

Solution or melt	Concentration (wt.-%)	G (gm/cm)	F_0 (dyne/cm^2)	Q	Source
Polyhall (295)	0.01	3.93	0.0047	1.258	12
Polyhall (295)	0.025	24.87	0.758	3.268	12
Polyhall (295)	0.05	165.36	0.765	3.227	12
Polyacrylamide (Separan-AP-30)	0.5	70	50.5	3.31	16, 17
Polyacrylamide (Separan-AP-30)	1	200	41.5	2.933	16, 17
Polyacrylamide (Separan-AP-30)	1.5	445	230	3.165	16, 17
Polyacrylamide (Separan-AP-30)	2	1000	216	3	16, 17
Polyethylene melt (PE I)	–	1.37×10^5	3.91×10^4	3.90	28
Polyethylene melt (PE II)	–	1.1×10^6	1.31×10^5	1.66	28

Table 3. Suitability of different empirical models for the correlation of normal stress functions

Empirical model	The mean deviation (%)	The maximum deviation (%)	The minimum deviation (%)
Eq. [7]	11.02	45.88	0.24
Eq. [8]	12.89	37.40	2.076
Eq. [9]	18.93	72.59	1.43
Eq. [10]	36.61	89.54	8.60
Eq. [11]	2.14	7.40	0.16

in the region of low shear rates. The model given by eq. [11], however, was able to correlate the data in about three to four decades of shear rates and could hence be recommended as a satisfactory equation for the correlation of normal stress difference-shear rate data.

An attempt towards molecular interpretation of the parameters

It should be emphasized that the above mentioned models are simply *empirical* functions designed to describe experimentally observed normal stress differences under steady state conditions in simple flow systems. The parameters appearing in these models may not be directly related to the structure or concentration of the fluid by means of the molecular theory. However, an attempt has been made to analyse the empirical functions derived in terms of the molecular theories.

Most of the analyses agree (9) that the fluid relaxation time λ_f is related to the zero shear primary normal stress coefficient by an equation of the type

$$\lambda_f = \frac{(F_1/\gamma^2)_{\gamma \to 0}}{\eta_0} \qquad [16]$$

where η_0 is the zero shear viscosity.

For the case of the model proposed in eq. [11], $(F_1/\gamma^2)_{\gamma \to 0} = G$. Hence the fluid relaxation time would be given by

$$\lambda_f = \frac{G}{\eta_0}. \qquad [17]$$

Based on the molecular considerations, the molecular relaxation time λ_m has been obtained by several workers, e.g. *Bueche* (2), *Rouse* (30), *Zimm* (31) etc. A comparison of the molecular relaxation time λ_m obtained on the basis of molec-

ular theories and the fluid relaxation time λ_f obtained on the basis of rheogoniometric measurements may reveal some relevant information. The molecular relaxation time, λ_m obtained from the *Bueche* theory (2) is given by

$$\lambda_m = \frac{12\eta_0 M}{\pi^2 c R T}. \qquad [18]$$

For an estimation of the value of λ_f and λ_m we require accurate values of the zero shear viscosity, η_0 the weight average molecular weight, M, etc. Many of the systems examined in this work were not completely characterised so as to yield all the necessary information. Only those data in table 1 could be used for comparison where such information was available. The value of η_0, however, was not directly available since the shear stress-shear rate data were usually reported in the proper non-*Newton*ian regime. The value of η_0 was hence estimated by making use of the extrapolation principles developed by *Subbaraman* et al. (32) and *Mashelkar* et al. (7) for non-viscometric translational and rotational flows. The viscometric data were plotted as logarithm of apparent viscosity versus the shear stress. The plots were found to be linear. The value of η_0 was obtained by reading the value of η when the shear stress was extrapolated to zero.

Table 4 lists the values of G, η_0, λ_f and λ_m estimated by using the above procedures. Generally the values of λ_f and λ_m are found to agree reasonably well, particularly for dilute solutions in high viscosity solvents. It must be emphasized that none of the materials tested in this work had well established molecular weight distribution and some of the discrepancy observed may be really due to the rather wide molecular weight distribution in some of the systems.

The success observed above prompted us to correlate the normal stress data for different systems by using dimensionless plots of reduced normal stress difference (normal stress coefficient divided by the zero shear normal stress coefficient) against the reduced shear rate $\dot{\gamma}\lambda$. This attempt, however, was not very successful and hence has not been dealt with any further.

In conclusion, the empirical models tested in this work may be of significance in a number of situations. For instance, they may be used to correlate the experimental data on normal stresses over a rather wide range of shear rates. The mathematical forms of these models are far simpler as compared to the other equations based

Table 4. Comparison of the fluid relaxation time ($\lambda_f = G/\eta_0$) with the molecular relaxation time obtained from *Bueche* theory (λ_m)

No.	Solution or melt	Molecular weight	Concentration (wt.-%)	G (gm/cm)	η_0 poise	Fluid relaxation time $\lambda_f = G/\eta_0$	Molecular relaxation time λ_m	Source
1	Polystyrene in chlorinated diphenyl	1.2×10^6	0.3	0.6091	5.9	0.1032	0.1153	26
2	,,	1.2×10^6	0.5	0.7454	9.4	0.0956	0.1006	26
3	,,	1.2×10^6	1	2.5521	19.5	0.1308	0.1131	26
4	,,	5×10^6	0.5	2.0239	8.99	0.2251	0.44	26
5	,,	0.66×10^6	0.5	0.1296	8	0.0162	0.0517	26
6	,,	0.54×10^6	2	1.8769	43.5	0.0431	0.055	26
7	,,	0.27×10^6	2	0.4925	29.5	0.0166	0.0158	26
8	,,	0.239×10^5	2	0.0304	17.5	0.0017	0.0102	26
9	Polystyrene in dioctyl phthalate	0.66×10^6	2	0.0253	3.78	0.0066	0.0062	25
10	,,	1.2×10^6	2	0.1031	4.75	0.0217	0.0142	25
11	,,	5×10^6	0.8	0.0248	2.07	0.0118	0.0646	25
12	,,	5×10^6	1	0.07869	2.55	0.0308	0.0635	25
13	,,	5×10^6	1.5	0.4695	5.08	0.0924	0.083	25
14	,,	5×10^6	2	1.6893	10	0.1689	0.1224	25
15	Polystyrene in toluene	1.82×10^6	12.5	568	400	1.4	0.29	24
16	Polyisobutylene in cetane	1.2×10^6	3.9	0.1885	4.79	0.039	0.0072	23
17	,,		5.39	2.0846	18.5	0.1126	0.0201	23
18	,,		6.86	9.8141	60.2	0.1630	0.0515	23
19	Polyethylene melt	0.79×10^6	–	1.36×10^5	7.5×10^4	1.822	0.2059	28
20	Polyethylene melt	1.31×10^6	–	1.09×10^6	4.2×10^5	2.61	2.26	28

on the formal constitutive equations [e.g. *Spriggs* four constant model (33)]. The latter are too complex to have any practical utility and the former may find preference in these instances. If the flow behaviour of the liquids being processed is characterised by these models, then they may also be helpful in formulating relevant dimensionless groups. This will help in the proper correlation of the transport processes involving viscoelastic liquids. *Kelkar* et al. (27) have recently used the empirical model (eq. [11]) for correlating their primary normal stress data and have made use of the resulting dimensionless groups for correlating the dynamics of the agitation of viscoelastic liquids. It is conceivable that such a utility may be found in many other engineering situations as well. Lastly, some of the techniques of normal stress measurements [e.g. measurement of radial pressure drop in axial annular flow (14)] require that a model be fitted for $F(\dot{\gamma})$ curve. The parameters of the model could be obtained by curvefitting the model to the data. The form of such models could be judiciously selected based on the results of this work.

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