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ANALYSIS OF FLOW DATA ON MOLTEN POLYMERS

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Abstract—On the basic assumption that viscosity is a continuous function of shear rate it is deduced that any non-Newtonian fluid should conform to a flow equation of the form

$$\eta = \eta_\infty + \left(\frac{\eta_0 - \eta_\infty}{1+\alpha D^n}\right)$$

where η is the viscosity at shear rate D, η_0 and η_∞ are limiting values at respectively zero and infinite rate of shear, and α is a constant.

With a value of $\frac{2}{3}$ for the index n the equation is applied successfully to published data on both polystyrene and polyethylene melts.

An analysis by Bingham[1] in which the non-Newtonian flow of polymer melts is attributed solely to elasticity is shown to be inadequate.

INTRODUCTION

It has recently been shown that a wide range of pseudoplastic systems conform to a flow equation of the form

$$\eta = \eta_\infty + \left(\frac{\eta_0 - \eta_\infty}{1+\alpha D^{2/3}}\right) \tag{1}$$

where η is the viscosity at shear rate D, η_0 and η_∞ are limiting values at respectively zero and infinite rate of shear, and α is a constant.[2]

The equation was originally introduced for disperse systems and was derived on the assumption that pseudoplastic flow results from structural changes involving interconnected particles. In practice it has been found equally valid for polymer solutions in both aqueous and non-aqueous media. Since basically similar pseudoplastic flow curves are also encountered with bulk polymers or melts it is natural to enquire whether the same basic mechanism is operative, i.e. whether pseudoplastic flow results from the progressive breakdown of structure within the melt, and whether the same form of equation is applicable. This is the subject of the present investigation. It is based on capillary rheometer data drawn from the literature.

THEORETICAL

For disperse systems Eqn. 1 has been derived on the assumption that particles link together in the form of random chains and that non-Newtonian flow can be attributed to the effect of shear rate on mean chain length. It is evident that such a model of connected particles is inapplicable to a polymer solution or melt. Here any structural changes probably involve chain entanglements. It is widely recognized that for any polymer there is a critical molecular weight (M_c) above which chain entanglement becomes significant, and in this region there is a discontinuity in the viscosity–molecular weight relationship of the polymer.(3) Porter and Johnson(4) have also observed that for a series of polyethylenes the onset of non-Newtonian flow occurs abruptly above a critical molecular weight corresponding approximately to M_c. Similarly Bagley and West(5) have independently observed that for poly(dimethyl siloxanes) non-Newtonian flow occurs only for molecular weights greater than M_c.

For a molten polymer it would therefore seem appropriate to adapt the treatment given in the earlier paper to a model involving chain entanglements, on the assumption that shearing action reduces the number of entanglements in unit volume and hence the viscosity. A polymer solution might be treated in a similar manner. However, any physical model will have limited application and a more general consideration of non-Newtonian flow appears desirable.

One basic assumption is required. It is assumed that the viscosity of the system varies continuously with shear rate, with limiting values η_0 and η_∞ at respectively zero and infinite rate of shear.

At any finite rate of shear η must assume some value which lies between η_0 and η_∞. Accordingly, it can be expressed by a relation

$$\eta = \eta_\infty + \frac{(\eta_0 - \eta_\infty)}{x}$$

where x assumes a value between unity (when $\eta = \eta_0$) and infinity (when $\eta = \eta_\infty$).

Clearly x must must be some function of the shear rate (D) and must equal unity when $D = 0$ and infinity when $D = \infty$. It must accordingly assume the form $x = 1 + \alpha_1 D^{n_1} + \alpha_2 D^{n_2} + \cdots$.

Such a power series gives complete generality but is also implies that for a given value of x, and hence of η, D may assume more than one value, i.e. the expression has multiple roots. If, on the contrary, we assume a unique relationship between η and D, x must reduce to the form $x = 1 + \alpha D^n$ and hence

$$\eta = \eta_\infty + \left(\frac{\eta_0 - \eta_\infty}{1 + \alpha D^n}\right) \tag{2}$$

The generality of the treatment indicates that Eqn. 2 should be valid for any non-Newtonian fluid, including dilatant as well as pseudoplastic systems.

With $n = \frac{2}{3}$ it is identical to Eqn. 1. The significance of n has previously been discussed,(2) and the argument advanced that n may assume any fractional value p/q where p is even and q odd. This argument is based on the consideration that the value of η should be independent of the direction of applied shear, and hence of the sign of D. $n = \frac{2}{3}$ represents the simplest case of a non-zero fractional value. It may be noted from Eqn. 1 that the quantity αD^n is dimensionless. Hence $\alpha^{-1/n}$ has the dimensions of rate of shear and substituting $D = \alpha^{-1/n}$ we note that η assumes the value $(\eta_0 + \eta_\infty)/2$. The quantity $\alpha^{-1/n}$ thus represents a characteristic shear rate at which the viscosity is the mean of its two limiting values, η_0 and η_∞.

ANALYSIS OF DATA

Molten polystyrene

Pezzin(4) has published capillary rheometer data at 232°, covering a very wide range in both shear rate and viscosity, on polystyrene of molecular weight 174,000. The Rabinowitsch correction(7) for the true shear rate at the capillary wall has been incorporated in the data selected for analysis.

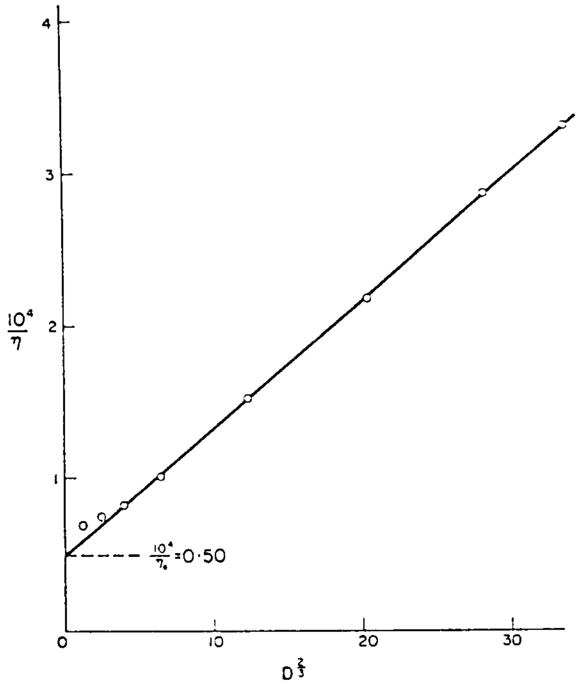

FIG. 1. Evaluation of η_0 for molten polystyrene.

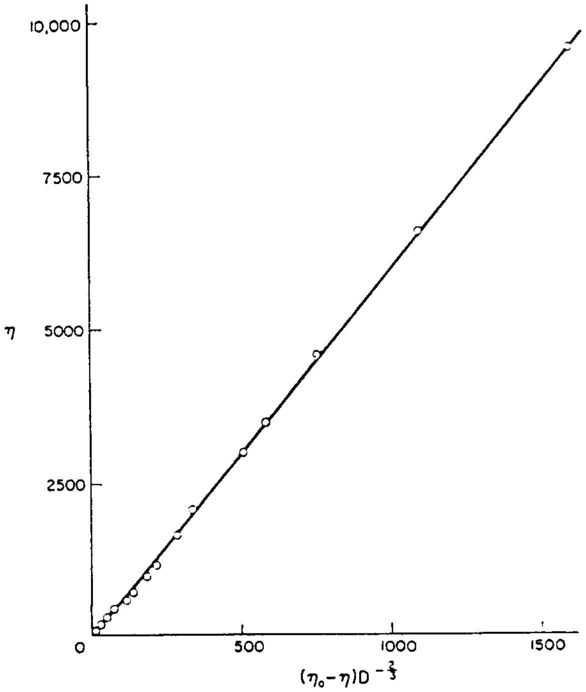

FIG. 2. Data for molten polystyrene plotted in accordance with Eqn. 1.

If Eqn. 1 is applicable there should be an approximately linear relationship between $1/\eta$ and $D^{2/3}$ at low rates of shear.$^{(2)}$ This is shown in Fig. 1, where the intercept is $1/\eta_0$. Having established the value of η_0 the applicability of Eqn. 1 is further tested by a graph of η against the quantity $(\eta_0 - \eta)D^{-2/3}$ (Fig. 2). This should be linear over the whole range of measurements. Here the intercept gives η_∞ (in this case virtually zero) whilst the slope is $1/\alpha$.

TABLE 1. MEASURED AND CALCULATED VISCOSITIES FOR MOLTEN POLYSTYRENE

Shear rate D (sec^{-1})	$D^{2/3}$	η (poises)	$\dfrac{2{\cdot}0 \times 10^4}{(1+0{\cdot}167\, D^{2/3})}$
1·5	1·31	14,300	16,400
3·76	2·42	13,200	14,200
7·83	3·95	12,000	12,000
16·6	6·50	9580	9580
43·1	12·3	6570	6530
91·8	20·4	4580	4540
150·3	28·3	3490	3490
195·5	33·6	3000	3020
398	54·1	2080	1990
509	63·7	1660	1720
816	87·4	1320	1280
1070	104·6	1000	1080
1655	140	735	819
2140	166	580	598
4140	258	452	453
8270	409	301	288
16,550	650	192	183
41,400	1197	105	99·3
82,700	1900	66·7	62·7
165,500	3014	40	39·7

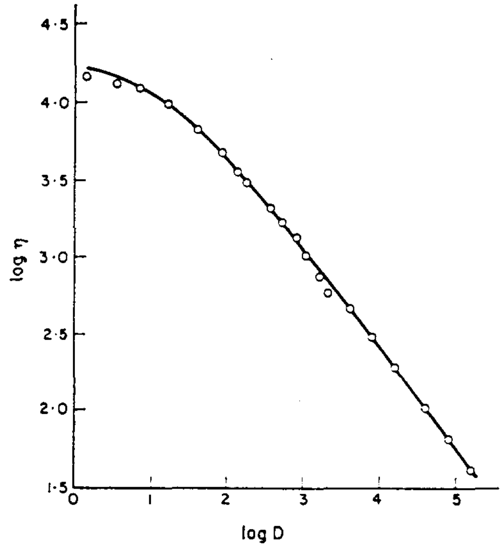

FIG. 3. Viscosity of polystyrene: ○ data from Pezzin$^{(3)}$; — theoretical curve (Eqn. 1).

In Table 1 viscosities computed from Eqn. 1 are compared with the measured values. The results are also displayed graphically in Fig. 3, where the experimental points are shown in relation to the theoretical curve, using logarithmic scales. It will be noted that on a logarithmic plot approximate linearity is achieved only at relatively high rates of shear, indicating the limitations of the widely used "power-law" relationship.

Molten polyethylene

Capillary rheometer data on two samples of polyethylene at 190° have been given by Bagley.(8) Polyethylene B is a high density linear polymer whereas Polyethylene C is low density and branched. Again the selected data incorporates the Rabinowitsch correction. For both polymers extrudate distortion was observed above a certain critical shear stress but for Polyethylene B the published data does not extend beyond this point.

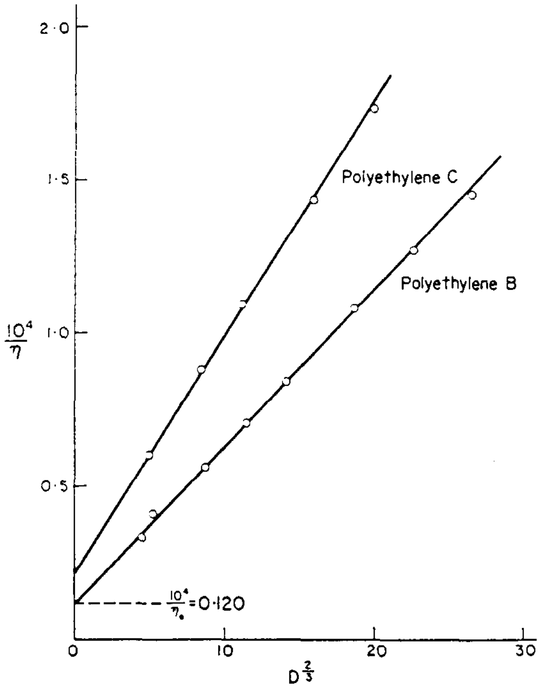

FIG. 4. Evaluation of η_0 for polyethylene.

Using the data at lower shear rates Fig. 4 is a graph of $1/\eta$ against $D^{2/3}$ for the two polymers. For Polyethylene B the intercept $(1/\eta_0)$ establishes the value of η_0 as $8{\cdot}33 \times 10^4$ poises. Using this value η is plotted against $(\eta_0-\eta)D^{-2/3}$ in Fig. 5. From the intercept and slope it is deduced that $\eta_\infty = 100$ poises and $\alpha = 0{\cdot}425$. For Polyethylene C the value of η_0 derived from Fig. 4 is $4{\cdot}55 \times 10^4$ poises and the graph of η against $(\eta_0-\eta)D^{-2/3}$ is shown in Fig. 6. Here the onset of turbulent flow is clearly indicated by the break at point A. The linear region to the right of A represents stable flow at lower rates of shear, and ignoring the anomalous behaviour at higher shear rates, values of $\eta_\infty = 400$ poises and $\alpha = 0{\cdot}370$ are derived.

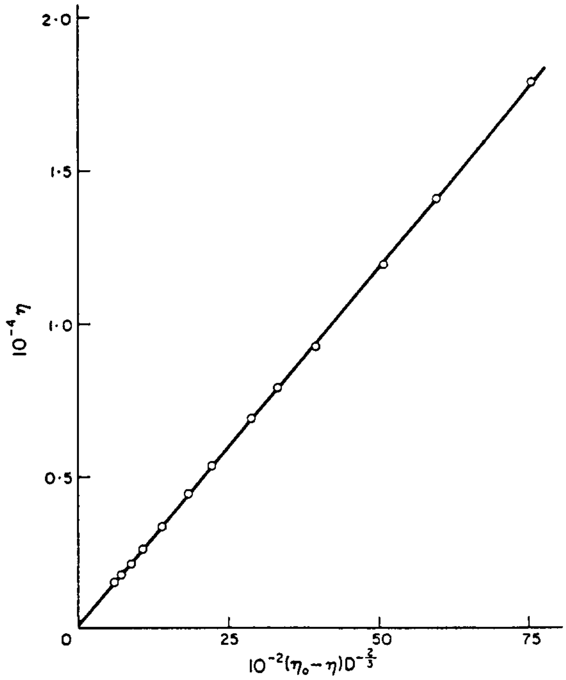

FIG. 5. Data for polyethylene B plotted in accordance with Eqn. 1.

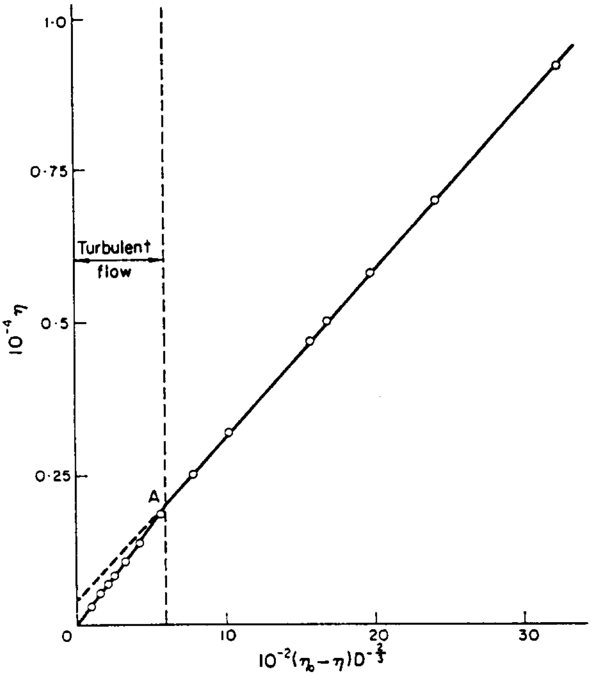

FIG. 6. Data for Polyethylene C plotted in accordance with Eqn. 1.

Conformity to Eqn. 1 is shown by the linearity of the plots in Figs. 5 and 6, and it is concluded that in the region of stable flow this equation is applicable to both polyethylene and polystyrene melts.

DISCUSSION

Equation 1 has been found applicable to a wide range of disperse systems, to polymer solutions and to bulk polymers or melts. This strongly suggests that in each case a similar mechanism is operative, i.e. whether one considers a molten polymer or a limestone suspension the basic cause of non-Newtonian flow is a shear-induced reorganisation of physical structure.

On the other hand Bagley's data on polyethylene has recently been examined by Bingham$^{(1)}$ with a very different conclusion, namely that non-Newtonian behaviour is a direct consequence of melt elasticity and that no structural changes are involved.

Bingham argues that if τ_c is the shear stress at the capillary wall this will be augmented by an elastic "pull" $\tau_c S_R$ where S_R is the recoverable elastic strain. His expression for the total force T acting in steady flow is

$$T = \tau_c(1+S_R)\left(1+\frac{S_R^2}{4}\right)^{1/2} \tag{3}$$

and it is contended that the ratio T/D represents the "true viscosity" and is a constant. In support of this Bingham shows that whereas graphs of τ_c against D show marked curvature those of T against D are approximately linear. However, in the case of Polyethylene C this linearity appears rather questionable and it is of interest to take the analysis a stage further.

If G is the elastic shear modulus $S_R = (\tau_c/G)$ and hence from Eqn. 3

$$T = \tau_c\left(1+\frac{\tau_c}{G}\right)\left(1+\frac{\tau_c^2}{4G^2}\right)^{1/2} \tag{4}$$

The "true" viscosity T/D should be identical with η_0 and if $(\tau_c/D) = \eta$ we have

$$\eta = \frac{\eta_0}{\left(1+\frac{\tau_c}{G}\right)\left(1+\frac{\tau_c^2}{4G^2}\right)^{1/2}} \tag{5}$$

The observed viscosity (η) is thus expressed as a function of the shear stress (τ_c) by means of an equation which involves only two constants, η_0 and G.

For Polyethylene B, Bingham gives a value of $5{\cdot}48 \times 10^4$ poises for η_0, while Bagley's value for G is $3{\cdot}6 \times 10^5$ dyne cm^{-2}. It is of interest to compute viscosity values from Eqn. 5 using these figures. Table 2 shows viscosities calculated on this basis, together with the measured values and those calculated from Eqn. 1.

Using Bingham's value of $2{\cdot}38 \times 10^5$ poises for η_0 and Bagley's value of $8{\cdot}6 \times 10^4$ dyne cm^{-2} for G, a similar computation for Polyethylene C is shown in Table 3.

Tables 2 and 3 show that Bingham's treatment is inadequate, particularly at lower rates of shear. However, it is interesting to consider the behaviour at higher shear rates. Effectively Bingham's equation is

$$\frac{\eta_0}{\eta} = (1+S_R)\left(1+\frac{S_R^2}{4}\right)$$

TABLE 2. MEASURED AND CALCULATED VISCOSITIES FOR POLYETHYLENE B

Shear rate D (sec^{-1})	Viscosity (poises) × 10^{-4}		
		Calculated	
	Measured	Eqn. 1*	Eqn. 5
9·52	3·01	2·87	2·82
12·3	2·44	2·55	2·62
25·6	1·79	1·78	2·02
39·3	1·41	1·42	1·71
52·8	1·19	1·20	1·49
81·6	0·922	0·935	1·23
108	0·790	0·793	1·05
137	0·688	0·687	0·917
207	0·536	0·533	0·728
280	0·444	0·443	0·614
432	0·339	0·339	0·475
662	0·260	0·260	0·366
888	0·215	0·217	0·307
1180	0·179	0·181	0·259
1520	0·159	0·156	0·227

* $\eta = 100+\dfrac{8{\cdot}32\times 10^4}{1+0{\cdot}425\,D^{2/3}}$

TABLE 3. MEASURED AND CALCULATED VISCOSITIES FOR POLYETHYLENE C

Shear rate D (sec^{-1})	Viscosity (poises) × 10^{-4}		
		Calculated	
	Measured	Eqn. 1*	Eqn. 5
11·0	1·68	1·63	5·13
24·4	1·14	1·135	2·98
37·5	0·915	0·915	2·14
64·0	0·695	0·692	1·39
90·3	0·577	0·576	1·17
117·5	0·498	0·498	0·868
132·5	0·466	0·464	0·787
265·0	0·319	0·317	0·440
400·5	0·250	0·254	0·320

* $\eta = 400+\dfrac{4{\cdot}51\times 10^4}{1+0{\cdot}370\,D^{2/3}}$

At high rates of shear, if $S_R \gg 1$

$$\frac{\eta_0}{\eta} = \frac{S_R{}^2}{2} = \frac{\tau^2}{2G^2} = \frac{\eta^2 D^2}{2G^2}$$

or

$$\frac{1}{\eta^3} = \frac{D^2}{2\eta_0 G^2}$$

Hence $$\frac{1}{\eta} = \text{constant} \times D^{2/3}$$

At high rates of shear Bingham's equation thus leads to a linear relationship between the fluidity and $D^{2/3}$. Equation 1 gives a similar relationship at *low* rates of shear.

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Résumé—Suivant l'assomption de base que la viscosité est une fonction continue du nombre proportionnel de cisaillement, il est déduit qu'un fluide non-Newtonien devrait se conformer à l'équation de la formule

$$\eta = \eta_\infty + \left(\frac{\eta_0 - \eta_\infty}{1+\alpha D^n}\right)$$

où est la viscosité au taux de cisaillement D, η_0 et η_∞ sont les valeurs limitantes aux valeurs respectives de taux de cisaillement de zéro et infini et × est constant.

Avec une valeur de $\frac{2}{3}$ pour l'index n l'équation est effectuée avec succès dans des données publiées de coulées de polystyrène et de polyéthylène. Une analyse par Bingham⁽¹⁾ dans laquelle le courant non-Newtonien de coulée de polymères est attribué uniquement à l'élasticité est prouvé inadéquat.

Sommario—Assumendo che la viscosità è una funzione continua della resistenza, si deduce che qualsiasi fludio che non segua la legge di Newton dovrebbe conformare alla equazione di flusso della forma seguente:

$$\eta = \eta_\infty + \left(\frac{\eta_0 - \eta_\infty}{1+\alpha D^n}\right)$$

dove η è la viscosità con resistenza di valore D, e η_0 e η_∞ sono i valori del limite rispettivamente a zero ed infinito della quantità di resistenza, e α è una costante.

Con un valore di $\frac{2}{3}$ per l'indice n l'equazione è applicata con successo a dati pubblicati sia su colate di polisterina e polietilene.

Un'analisi del Bingham⁽¹⁾ in cui il flusso non-Newtoniano di colate polimere è attribuito alla elasticità soltanto, ha dimostrato di essere inadeguata.

Zusammenfassung—Unter der Annahme, daß die Viskosität eine stetige Funktion der Schergeschwindigkeit ist, wird abgeleitet, daß alle Flüssigkeiten von nicht Newtonschen Verhalten einer Gleichung der Form

$$\eta = \eta_\infty + \left(\frac{\eta_0 - \eta_\infty}{1+\alpha D^n}\right)$$

gehorchen sollten. Hierin ist η die Viskosität bei der Schergeschwindigkeit D, η_0 und η_∞ sind die Grenzwerte bei den Schergeschwindigkeiten null und unendlich und α ist eine Konstante.

Mit einem Wert von $\frac{2}{3}$ für die Potenz n ist diese Gleichung erfolgreich auf veröffentlichte Daten von Polystyrol und Polyäthylenschmelzen angewendet worden.

Es wird gezeigt, daß eine Betrachtungsweise von Bingham,⁽¹⁾ bei der das nicht Newtonsche Fließen auf Elastizität zurückgeführt wird, unzureichend ist.