On the Characterization of Non-Newtonian Flow

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Introduction

The determination of molecular weights and molecular weight distributions involves long and tedious procedures.   Indirect measurements, such as of the intrinsic viscosity of polymer solutions and the zero shear viscosity of polymer melts, yield only half of the information sought.   It is the purpose of this paper to present a new equation describing the non-Newtonian flow of high polymer melts   This equation, together with some recently published developments, has been used to determine parameters related to molecular weight and molecular weight distribution of polyethylene and several other polymers.

Mathematical Relationships

The dependence of the zero shear viscosity η_0 on the weight average molecular weight $\overline{M_w}$ has been widely confirmed[1] and is given by

$$\eta_0 = K\overline{M_w}^{3.4} \tag{1}$$

It has been proposed recently that for broad molecular weight distributions η_0 depends on $\overline{M_z}$, the z-average molecular weight.[2]

The drop in the apparent viscosity η as a function of the shear rate $\dot{\gamma}$ has been theoretically treated by various authors.[3-5]   The results can be generally expressed as

$$\eta/\eta_0 = f(\dot{\gamma}\tau) \tag{2}$$

where τ, the characteristic relaxation time, is given by

$$\tau = K'\overline{M_r}\eta_0 \tag{3}$$

The molecular weight $\overline{M_r}$, which depends on the number of molecules per unit volume, should be proportional to the viscosity-average molecular weight.   However, the derived functionalities of eq. (2) do not agree with experimental data.   Bueche has used an experimentally derived relation

$$\eta_0/\eta = 1 + 0.60(\dot{\gamma}\tau)^{1/4} \tag{4}$$

to characterize the non-Newtonian flow of concentrated solutions of polystyrene,[6] polymethyl methacrylate,[6] and rubber.[7]   He reports $\overline{M_r}$ to be proportional to $\overline{M_v}$, and to be dependent on branching and molecular weight

distribution. An independent observation[8] is that, at the same η_0, the more pronounced the non-Newtonian flow the broader the distribution.

It appears, then, that the non-Newtonian flow of linear polymers can be characterized by the parameters η_0 and τ. As a side benefit, the ratio $\overline{M}_r/\overline{M}_w$ might correspond to a dispersity factor:

$$K''\overline{M}_r/\overline{M}_w = \tau/\eta_0^{1.294} \tag{5}$$

Experimental

The non-Newtonian flow of polyethylenes has been studied by means of a gas-operated extrusion rheometer.[9] The die characteristics are as follows:

Diameter = 0.043 in.
Length = 0.835 in.
Entrance angle = 80°

Stabilized polymer in pellet form was employed and the shear stress–shear rate values were determined from one loading. Fifteen samples characterized by their number-average and weight-average molecular weights were obtained from Phillips Petroleum Company.

Each determination covered approximately three decades of shear rate. The data were not corrected for end effects[9] nor for the fact that the shear rate at the wall is non-Newtonian.[10]

The curve-fitting method was analogous to the one outlined by Bueche and Harding[6] and Spencer.[11]

Results

Polyisobutylene

Leaderman et al.[12] have characterized the non-Newtonian flow of a series of polyethylene fractions and blends by the Ferry relation[13]

$$\eta_0/\eta = 1 + S/Gi \tag{6}$$

and the molecular weight distribution by the ratio $\overline{M}_z \, \overline{M}_{z+1}/\overline{M}_w$. The parameter S is the shear stress. On assuming that the "internal rigidity modulus" Gi is proportional to η_0/τ, eq. (5) becomes

$$k\overline{M}_r/\overline{M}_w = 1/(Gi\eta_0^{0.294}) \tag{5a}$$

The expression at the right of eq. (5a) has been plotted against $\overline{M}_z \, \overline{M}_{z+1}/$ $\overline{M}_w$ in Figure 1. The relationship between the two sets of parameters is apparent. The rheological distribution factor shows promise.

Polystyrene

A series of polystyrenes have been characterized[14] by a variation of eq. (6) and by the ratio $\overline{M}_w/\overline{M}_n$.[14] Making the same assumptions as in the previous case we have, in Figure 2, appreciable scatter in the data. This
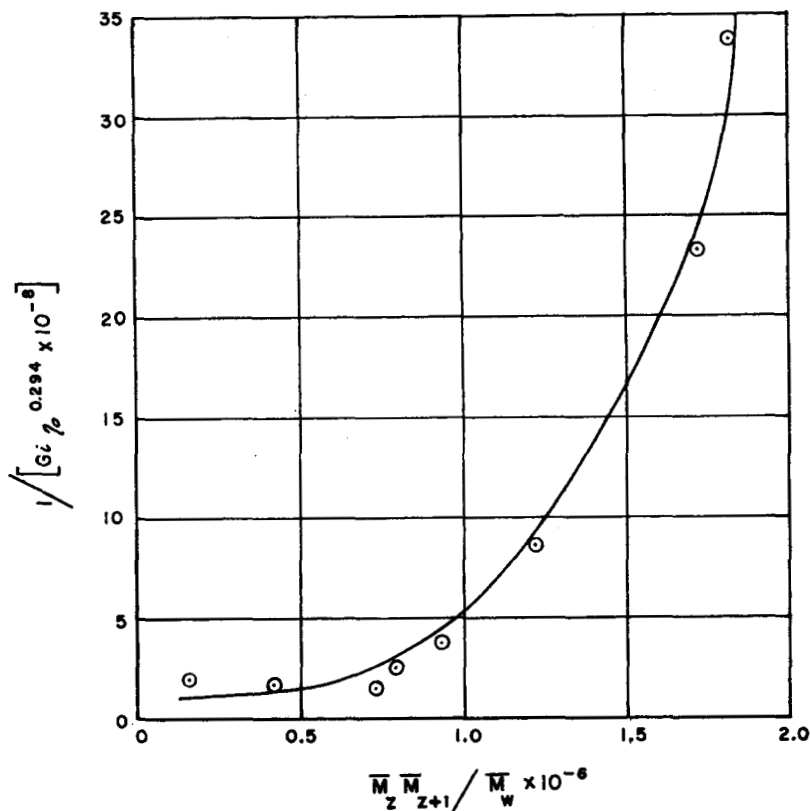
Fig. 1. Relationship between the rheological distribution factor and high moments of the molecular weight distribution curve: polyisobutylene.

leads us to believe that eq. (5) expresses higher moments of the molecular weight distribution than $\overline{M}_w/\overline{M}_n$.

Polyethylene

We have obtained η_0 and τ for a series of polyethylenes characterized as to $\overline{M}_w/\overline{M}_n$. The empirical flow equation employed will be discussed below. The data in Figure 3 are scattered, as in the preceding case. The same tentative explanation applies.

Non-Newtonian Flow Equation

Equation (4) was found unsatisfactory in describing the non-Newtonian flow of polyethylene melts. Other relationships in the literature[15] were found limited in scope. It was observed that the apparent viscosity of polyethylene was non-Newtonian over a large range of shear rates and that at high shear rates it approached a limiting slope. The former behavior
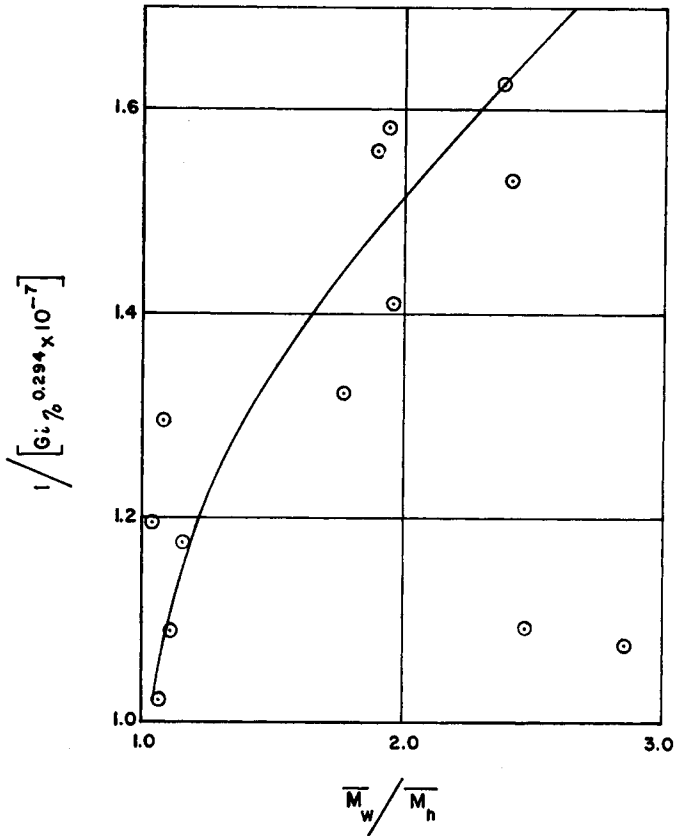
Fig. 2. Relationship between the rheological distribution factor and $\bar{M}_w/\bar{M}_n$: polystyrene.

can be duplicated empirically through an equation of flow with a variable exponent. Expressed logarithmically:

$$\ln \eta/\eta_0 = (\eta/\eta_0 - a) \ln [1 + (\dot{\gamma}\tau)^b] \tag{7}$$

The above equation fulfills the latter observation; i.e., at high shear rates:

$$\eta/\eta_0 = (\dot{\gamma}\tau)^{-ab} \tag{8}$$

At low shear rates eq. (7) simplifies to

$$\eta_0/\eta \cong 1 + a(\dot{\gamma}\tau)^b \tag{9}$$

which is of the same form as that employed by Bueche.

When $\dot{\gamma}'\tau$ equals 1:

$$a = \eta/\eta_0 - \ln \eta/\eta_0 \tag{10}$$

Since $\eta/\eta_0 \leq 1$, a must be positive and equal to or greater than 1. At a given value of η/η_0 other than 1:
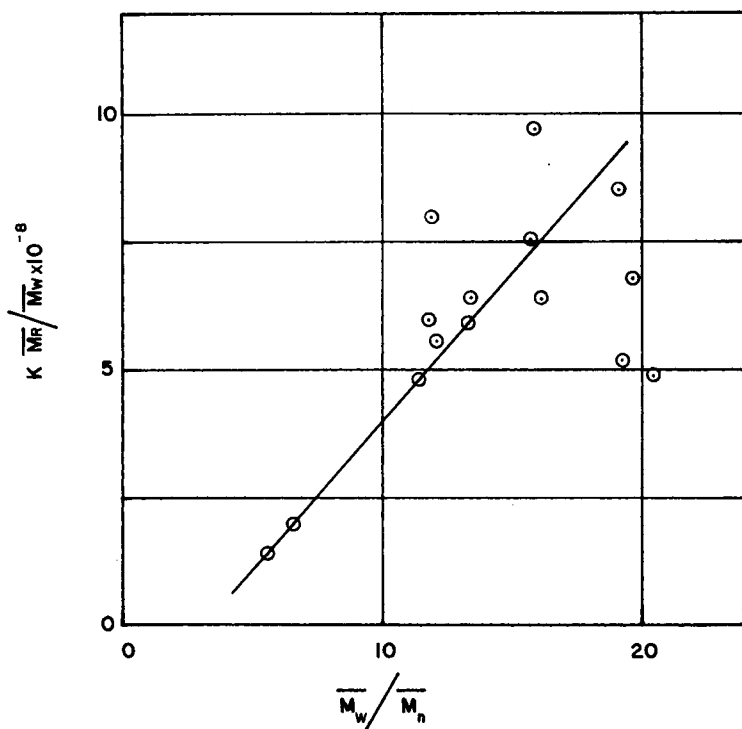
$$K(a) = (\dot{\gamma}\tau)^b \tag{11}$$

Fig. 3. Relationship between the rheological distribution factor and $\bar{M}_w/\bar{M}_n$: polyethylene.

where the values of $K(a)$ depend inversely on a.   From Eq. (8) and experimental observation of the viscosity as a function of shear rate, b is positive.   Thus, the larger the value of a the more pronounced is the non-Newtonian flow, while with a constant, b reflects a lateral shift.   These deductions are illustrated in Figures 4 and 5.

   The values of a and b have been tentatively determined for a series of polymers by curve-fitting experimental data to families of curves representing eq. (7).   Only the first of these has been extensively studied.   The latter two polymers are taken from literature data.[16,17]

Polymer	a	b	ab
Polyethylene	2	1/3	2/3
Polypropylene	2	1/3	2/3
Polyvinylbutyral	3	1/3	1
Polystyrene	2	1/2	1

   Data on low and high density polyethylenes of low and high molecular weights have been curve-fitted to eq. (7).   Some data taken from Philippoff[16] on low density polyethylene are shown in Figure 6.   Our own ex-
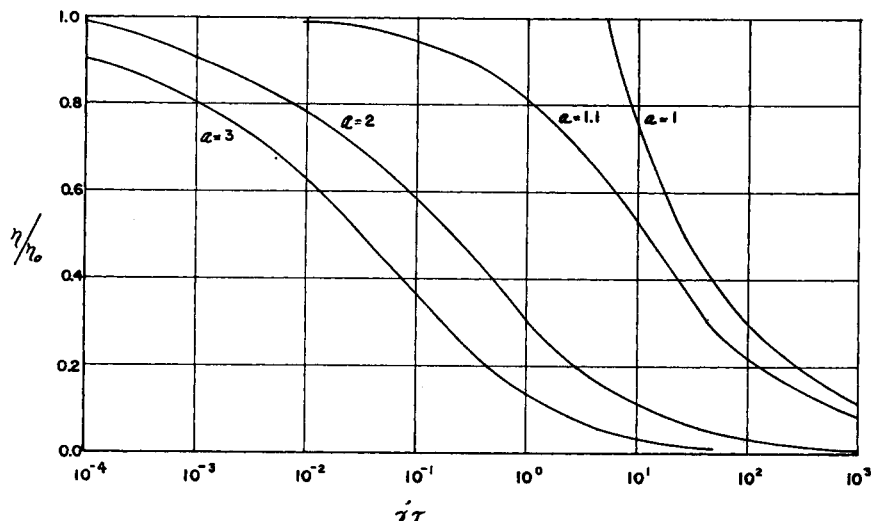
Fig. 4. Flow curves for different values of a at constant b ($= {}^1/_3$); eq. (7).
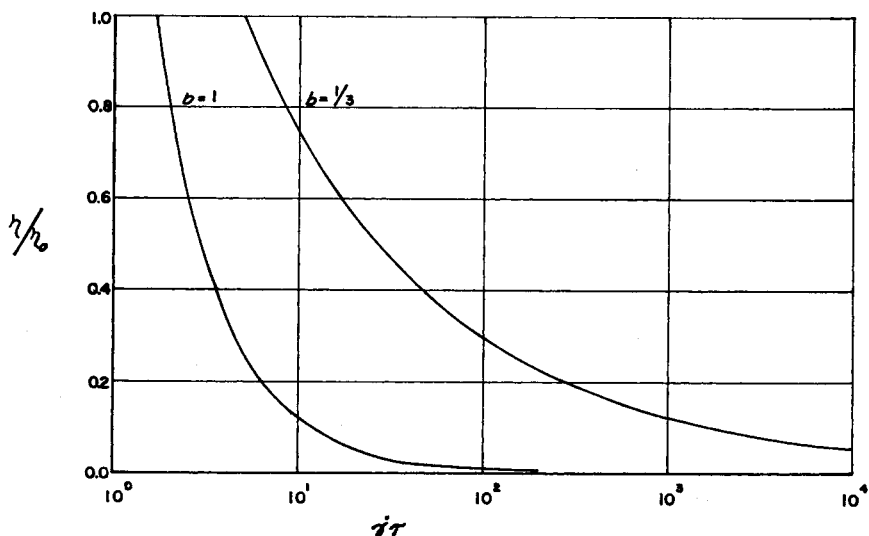

Fig. 5. Flow curves for different values of b at constant a ($= 1$); eq. (7).

periments on high density polyethylene, Figure 7, covered only three and one-half decades of shear rates. In the curve-fitting process, the apparent viscosity at high shear rates is often off the curve. In a study now in progress, this has been traced to rough extrudates and onset of melt fracture.[18] The direction and magnitude of deviation has been found to depend on die geometry, η_0, and τ. At low shear rates, the experimental apparent viscosity still being determined from one loading was usually high and could be traced to slight crosslinking and to errors in determining
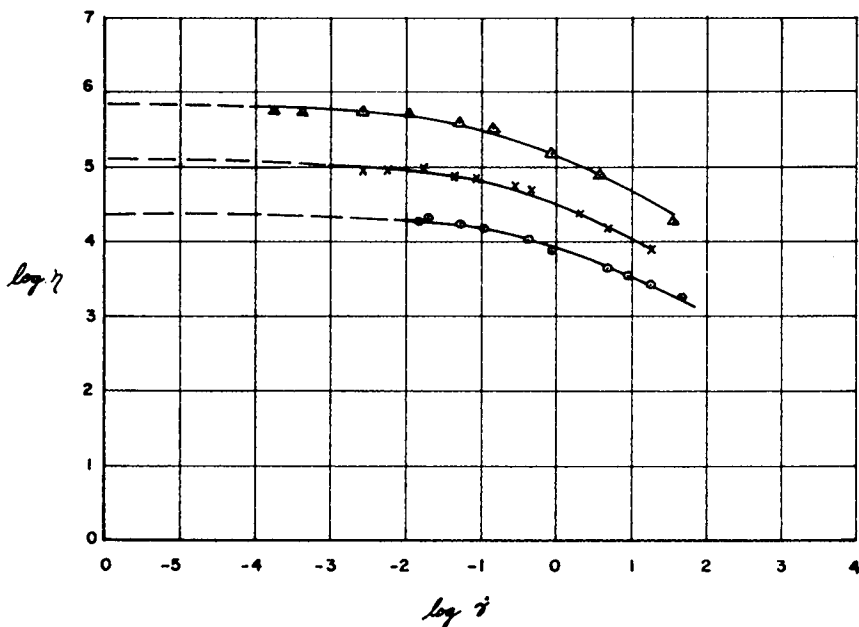
Fig. 6. Low density polyethylene. Points are experimental. Curves represent eq. (7): (△) at 125°C.; (✕) at 174°C.; (○) at 230°C.

the pressure and output per minute. For best results, one is advised to determine each shear rate with a fresh sample.

Discussion

We have attempted to relate a rheological distribution factor to conventional ratios of molecular weights. In the case of polyisobutylene, whose distribution curve was characterized by high moments of the distribution curve $(\overline{M}_z, \overline{M}_{z+1}/\overline{M}_w)$, satisfactory agreement was obtained. Polystyrenes and polyethylenes characterized by the ratio $\overline{M}_w/\overline{M}_n$ did not yield equally good results. Ten of the fifteen polyethylene samples lie close to a straight line, the others are definitely off.

The ratio $K \, \overline{M}_r/\overline{M}_w$, eq. (5), is a function of η_0 and τ. Each of these parameters is dependent on the very thing we hope to determine. Whether this is a limiting factor in determining a rheological distribution factor we cannot say. Three samples of approximately the same zero shear viscosity but differing in the rheological distribution factor are in process of being fractionated. Other fractionation data obtained by R. Horowitz at our Washington Research Center have been compared with our rheological factors and the results are considered encouraging. The role of branching ir determining the rheological distribution factor appears, at the present, the most pressing problem.

Our empirical flow equation promises to be a versatile one. Data obtained with an extrusion rheometer are not a severe enough test. To test
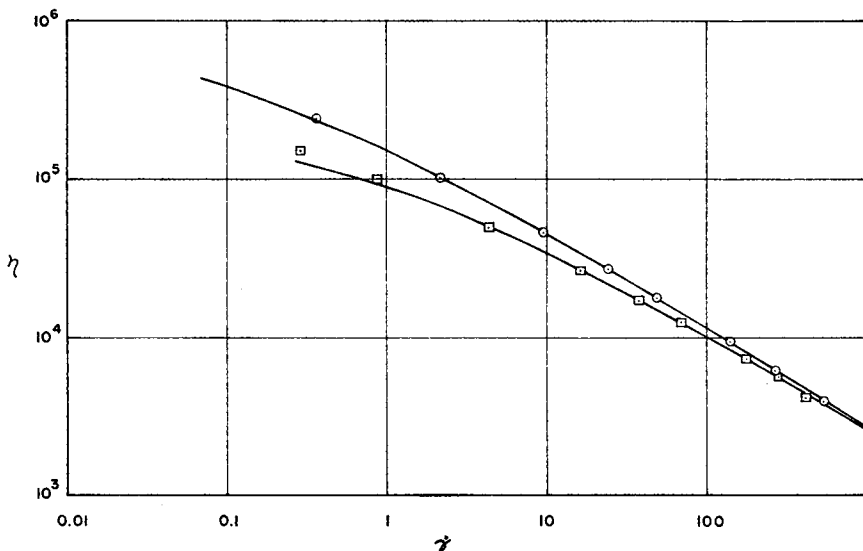
Fig. 7. High density polyethylene.   Points are experimental.   Curves represent eq. (7).

the equation truly, experimental data must extend over greater shear rate ranges.   This is necessary in the case of polyethylene of which there exist two types.   Does the same curve hold for branched and linear polyethylenes?   We hope to obtain more data on branched polyethylenes in the near future.   Over narrow ranges of shear rate the equation holds for both types.

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Synopsis

A rheological distribution factor has been derived from well-known relations. It is compared with experimental data with the use of conventional ratios of molecular weights such as $\overline{M}_w/\overline{M}_n$. Data on polyisobutylene, polystyrene, and high density polyethylene are presented. An equation of flow has also been derived from experimental data. It has been used to describe the non-Newtonian flow of various polymers.

Résumé

Un facteur de distribution rhéologique est obtenu à partir des relations bien connues. On le compare aux valeurs expérimentales au moyen des rapports conventionnels des poids moléculaires tel que le rapport $\overline{M}_w/\overline{M}_n$. On donne les résultats obtenu dans le cas du polyisobutylène, du polystyrène et du polyéthylène de densité élevée. Une équation d'écoulement est aussi obtenue à partir des données expérimentales. Elle a été utilisée pour décrire l'écoulement non-Newtonien de différents polymères.

Zusammenfassung

Ausbekannten Beziehungen wurde ein rheologischer Verteilungsfaktor abgeleitet. Er wird mit experimentellen Daten verglichen, die sich auf konventionelle Molekularge wichtsverhältnisse, wie $\overline{M}_w/\overline{M}_n$, beziehen. Daten für Polyisobutylen, Polystyrol und Polyäthylen hoher Dichte werden angeführt. Auch eine Fliessgleichung wurde aus experimentellen Daten abgeleitet. Sie wurde zur Beschreibung des nicht-newtonschen Fliessens verschiedener Polymerer verwendet.