

Melt Viscosity of Polyethylene: Shear Dependence

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Synopsis

Apparent viscosities of linear polyethylene melts may be simply related to molecular weight at various shear stresses. One gets constant slopes on a log-log scale with higher critical \bar{M}_w at higher shear stresses. The validity of Ferry's equation and the dependence of its coefficients are extensively analyzed.

Introduction

The melt viscosity of polymers has been related to molecular weight by the well-known equation:

$$\eta_0 = A \bar{M}_w^{3.5} \quad (1)$$

Equation (1) has been derived by Bueche,¹ and exponent of 3.4-3.5 appears for many linear polymer melts above a critical molecular weight (M_c). Schreiber and Bagley² summarized a list of experimental data that confirm melt viscosity-molecular weight correlations according to eq. (1).

The existence of a critical molecular weight and its value indicate a mechanism of entangled chains. The dependence of M_c on temperature and shear conditions is still in dispute. The behavior of branched polymer chains is even much more complicated. According to Tung³ (M_c) branched $>$ (M_c) linear. The difference between linear and branched polymers diminishes at lower temperatures. Tung has verified the 3.4 exponent for branched polyethylenes. With increasing temperature, linear polyethylene showed a constant slope but increasing values of M_c . Higher M_c values for higher temperatures have been claimed by Porter and Johnson⁴⁻⁷ and by Ballman and Simon.⁸

The dependence of M_c on shear has been discussed in our previous publication.⁹ We mentioned three different models as summarized by Schreiber¹⁰ and shown in Figure 1. Model A was found by various researchers.^{6-8, 11-15} Model B was suggested by Schreiber et al.¹⁶ for polyethylene fractions in a broad range of molecular weights.

Van der Vegt¹⁷ worked with polypropylene and got curves similar to those of model C. In his experiments the values of M_c increased with shear but the slopes were almost constant (3.6 ± 0.2). In this publication we shall show that our data for linear polyethylene are well described by model D (Fig. 2), which also fits Van der Vegt's¹⁷ findings.

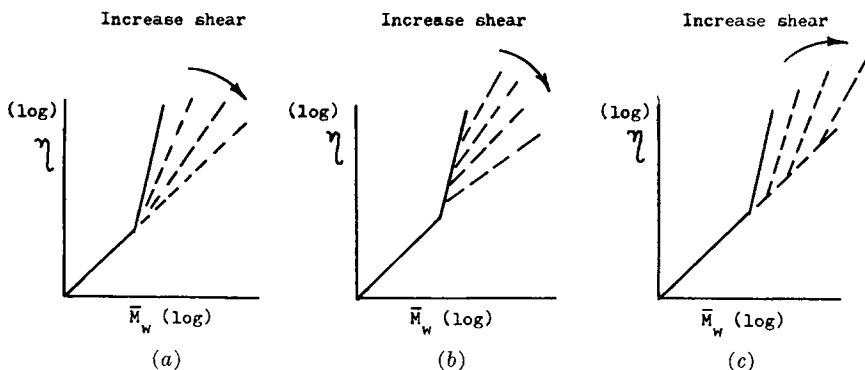


Fig. 1. Shear dependence: (a) model A; (b) model B; (c) model C.

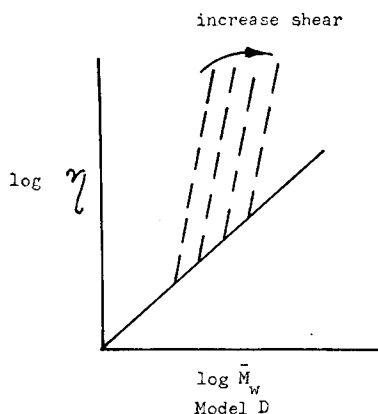


Fig. 2. Shear dependence: model D.

In order to get η_0 one has to reach the first Newtonian region at low shear. Normally it is quite difficult to work at these conditions with capillary viscometers; it also involves long times at high temperatures which cause thermal degradation. Therefore it is customary to use suitable extrapolations to zero shear stress. As stated in our previous paper,¹⁸ we have successfully adapted the equation:

$$1/\eta = 1/\eta_0 + b\tau \quad (2)$$

where τ is shear stress, which was suggested by Ferry.¹⁹ Equation (2) was also tested by Schreiber and Bagley² with excellent results. Use and analysis of eq. (2) have also been published by others.^{20,21} In our work we tried to find the dependence of b on various polymer parameters, in order to simplify the correlations.

Experimental

Both linear and branched polyethylenes have been tested in a modified melt indexer^{9,18} with a capillary of $L/R = 28$ and a set of weights that

covered shear stresses of 20,000–200,000 dyne/cm.². The values of shear stress τ_w were corrected for entrance effects by the method of Bagley.²²

$$P = 2\tau_w[(L/R) + N] \quad (3)$$

where P is the measured pressure drop and L/R is the ratio of length to radius of the capillary. In our shear range the entrance correction N amounts to 1–2 radii. The values of melt flow index (MFI) were also obtained by using standard conditions.²³ Viscosity measurements at higher shear stresses ($2 \times 10^5 - 3 \times 10^6$ dyne/cm.²) were obtained by use of the Atkinson-Nancarrow rheometer²⁴ with a capillary of $L/R = 47.3$.

Molecular weights of linear polyethylenes were calculated by measuring intrinsic viscosities in tetralin at 120°C. and using the correlations of Duch and Kuchler.²⁵ Details are given in our previous publication.¹⁸ The characteristics of the commercial linear polyethylenes used are listed in Table I.

TABLE I

Polymer	MFI	Density, g./cc.	\bar{M}_w
HD-1	0.86	0.960	100,000
HD-2	1.46	0.960	87,000
HD-3	2.6	0.960	73,000
HD-4	5.35	0.960	62,000
HD-5	9.1	0.962	48,000

Results and Discussion

Figure 3 describes flow curves for the linear polyethylenes on a log–log scale, as tested on the modified melt indexer. Both shear stress (τ_w') and rate of shear ($\dot{\gamma}_N$) were uncorrected. The straight lines in Figure 3 indicate the reliability of the power law in this range.

$$\tau_w' = K'\dot{\gamma}_N^n \quad (4)$$

The corrected apparent viscosity was calculated by use of the relationships:

$$\tau_w = PR/[2(L + NR)] = \tau_w'/[1 + N(R/L)] = \tau_w'/B \quad (5)$$

$$\dot{\gamma} = [(3n + 1)/4n]\dot{\gamma}_N = Z\dot{\gamma}_N \quad (6)$$

where n is the exponent in eq. (4).
and

$$\eta = \tau_w/\dot{\gamma} \quad (7)$$

where η is apparent viscosity. The correct power law will therefore be:

$$\tau_w = K\dot{\gamma}^n \quad (8)$$

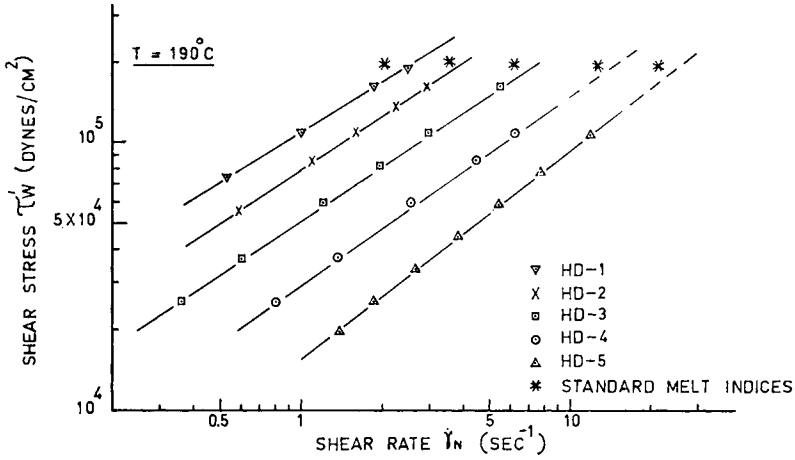


Fig. 3. Flow curves of linear polyethylenes.

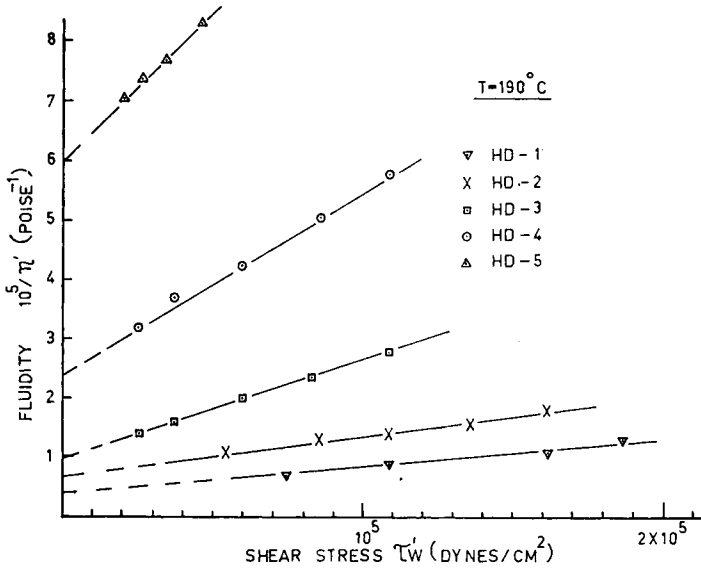


Fig. 4. Dependence of fluidity on shear stress.

and

$$K = K'/BZ^n \tag{9}$$

In Figure 3 the respective MFI values are also shown.

Figure 4 confirms the validity of eq. (2) for the same data by plotting fluidity against shear stress (both uncorrected). The correct parameters are given by eqs. (10)–(12).

$$1/\eta' = (1/\eta'_0) + b'\tau' \tag{10}$$

$$\eta_0 = \eta'_0/ZB \tag{11}$$

$$b = b'B^2Z \tag{12}$$

In our case, the difference between b and b' amounts to about 20% for typical values of $N = 2$ and $n = 0.7$.

The coexistence of the power law and Ferry's equation [eq. (2)] is surprising, because they lead to different boundaries for pseudoplastic fluids.

$$\lim_{\tau \rightarrow 0} \eta = \infty \quad \text{By power law} \quad (13)$$

$$\lim_{\tau \rightarrow 0} \eta = \eta_0 \quad \text{By eq. (2)} \quad (14)$$

It is important to describe the data in both Figures 3 and 4, because of the use of the Rabinowitsch correction as shown by eq. (6). The exact values of η_0 are therefore obtained by use of Figure 4 [eq. (2)] with the correction according to eq. (11).

It is important to verify the coefficient b of Ferry's eq. (2). It should be a function of temperature, molecular weight \bar{M}_w , and molecular weight distribution for linear polymers:

$$b = f(T, \bar{M}_w, \bar{M}_w/\bar{M}_n) \quad (15)$$

Schreiber²⁶ has recently found that the coefficient b for linear polyethylenes is mainly dependent on \bar{M}_w , but not on the distribution. In addition, Van der Vegt,¹⁷ who worked with polypropylene, did not find any sensitivity of η_0 to molecular weight distribution. It may be concluded that at constant temperatures b is roughly controlled by \bar{M}_w only, and should therefore be simply related to η_0 itself. This will enable the combination of eqs. (1) and (2) and the use of a single viscosity measurement at low shear in order to calculate \bar{M}_w .

The effect of temperature may be reduced by modifying eq. (2) as follows:

$$\eta_0/\eta = 1 + (b\eta_0)\tau \quad (16)$$

The term $(b\eta_0)$ has been titled by Ferry¹⁹ the reciprocal of an internal modulus of rigidity, G_i :

$$1/b\eta_0 = G_i \quad (17)$$

While b is strongly temperature-sensitive, G_i does not show a distinct temperature dependence.^{19,21,27} We have also some data that confirm

TABLE II

Polymer	\bar{M}_w	η_0 , poise	$b \times 10^{10}$, cm. ⁴ /dyne. ² - sec.	G_i , dyne/cm. ²
HD-1	100,000	228,000	0.68	64,500
HD-2	87,000	123,000	0.90	90,500
HD-3	73,000	83,500	2.1	57,000
HD-4	62,000	36,000	3.9	71,500
HD-5	48,000	14,500	5.9	117,000

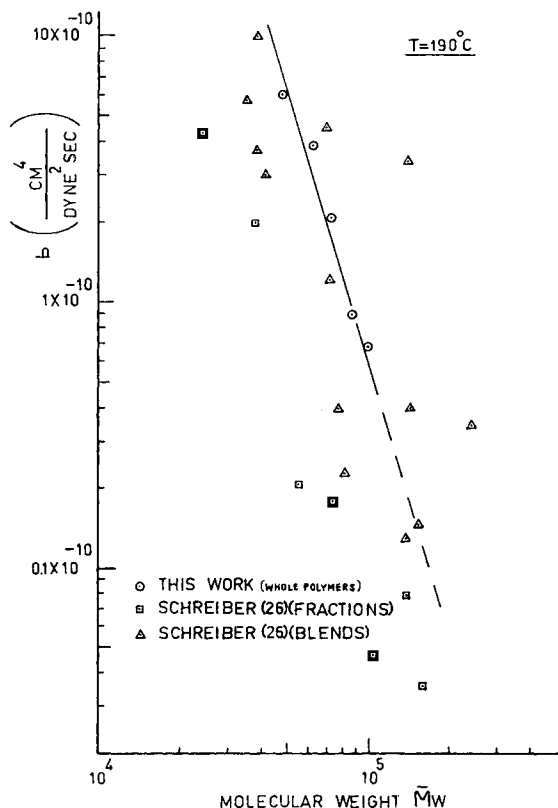


Fig. 5. Dependence of Ferry's coefficient b on M_w .

this independence for low density polyethylene. Values of b and G_i for our linear polyethylene samples are summarized in Table II.

Values of b are plotted versus \bar{M}_w on a log-log scale in Figure 5. Our data show a slope of about -3.5 , which corresponds well with the data of Schreiber²⁶ for polyethylene blends. Schreiber's data for fractions show systematically lower values of b with a slope of approximately -2.47 . On comparing Figure 5 with eq. (1) it is expected that $1/b$ should be linearly related to η_0 . This simple relationship is visualized in Figure 6 for both high and low density polyethylenes. The slopes of the lines coincide with the internal modulus of rigidity G_i , as defined by eq. (17). It seems, therefore, that for the tested polymers, G_i is about constant with \bar{M}_w for both types of polyethylene, giving higher values for the branched polymer. On comparing our data to those of Schreiber,²⁶ Leaderman et al.,²⁷ and Marker et al.,²¹ it seems that G_i does not show any systematic change with \bar{M}_w but more or less random oscillations. However a more careful look will identify a tendency for decreasing values of G_i with increasing \bar{M}_w . The exact physical meaning of G_i and its relationship to shear modulus are as yet not clear. It is well accepted that the shear

modulus G of low density polyethylene is regularly smaller than that for high density polymers. This is in contrast to the behavior of G_i , as demonstrated in Figure 6.

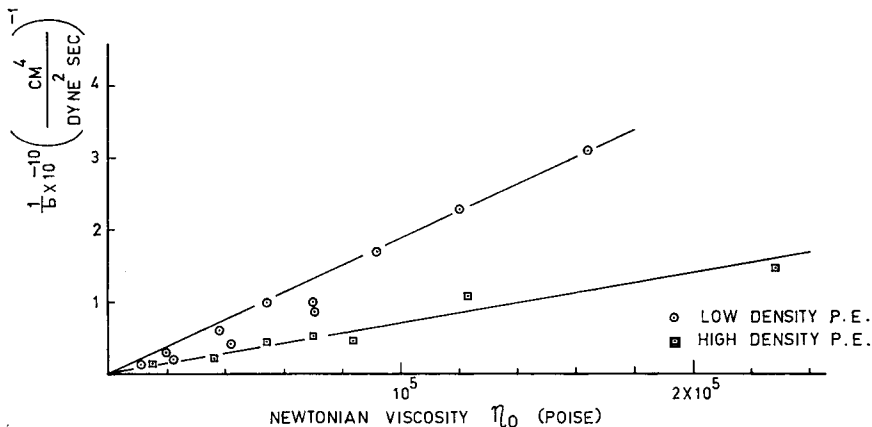


Fig. 6. Dependence of coefficient b on η_0 .

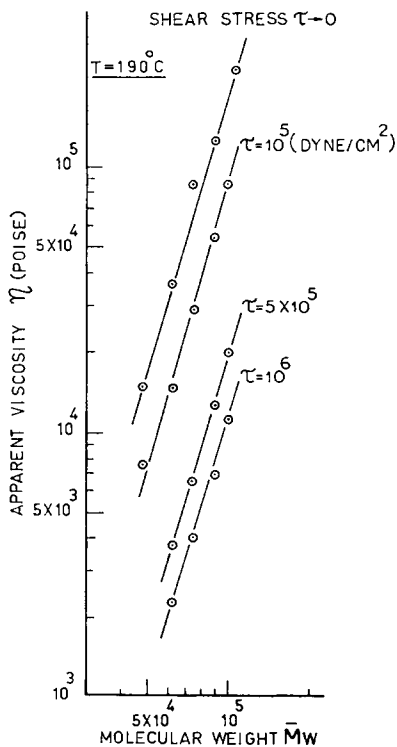


Fig. 7. Dependence of apparent viscosity on \bar{M}_w .

By using eqs. (1) and (16) one gets the following relationship for \bar{M}_w :

$$\eta = A\bar{M}_w^{3.5}/[1 + (\tau/G_i)] = A_1\bar{M}_w^{3.5} \quad (18)$$

A_1 depends mainly on shear stress τ , as G_i has been found almost constant with changing \bar{M}_w . Equation (18) predicts parallel lines when apparent viscosity is plotted against \bar{M}_w at different shear stresses on a log-log scale. This is clearly shown in Figure 7, which agrees exactly with model D as described previously (Fig. 2). Our results resemble those of Van der Vegt¹⁷ and predict that M_c increases with shear stress. Our simple correlations of η against \bar{M}_w worked well for whole linear polyethylenes of melt flow index of 1-10. However, the range of \bar{M}_w (48,000-100,000) is more limited. At higher molecular weight there might be a marked effect of distribution, and some dependence of G_i may show up. In addition one has to work at the range of shear stress in which Ferry's equation is still valid. There are findings that at higher shear stresses the effects of molecular weight distribution are no longer negligible.^{17,28} Any attempt to extrapolate our data to higher \bar{M}_w or τ must, therefore, be avoided before additional experimental results are accumulated.

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Résumé

Les viscosités apparentes de polyéthylènes linéaires fondus peuvent être reliées simplement au poids moléculaires à des tensions-élongations variables. On obtient des tangentes constantes à une échelle log-log, à un \bar{M}_w critique plus élevé, à des tensions d'élongation plus élevées. La validité de l'équation de Ferry et la dépendance de son coefficient sont analysées en détail.

Zusammenfassung

Die scheinbare Viskosität einer Schmelze von linearem Polyäthylen kann in einfacher Weise bei verschiedener Schubspannung zum Molekulargewicht in Beziehung gesetzt werden. Man erhält in einem log-log-Diagramm konstante Neigungen mit höherem kritischem \bar{M}_w bei höherer Schubspannung. Die Gültigkeit der Gleichung von Ferry und die Abhängigkeit ihrer Koeffizienten werden eingehend analysiert.

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