Simplified Correlations for Linear Polyethylene

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Synopsis

High-density polyethylenes have shown a linear relationship between molecular weight and the logarithm of melt flow index. The range of $\bar{M}_w$ was 50,000–125,000. This provides a simplified rapid tool for characterization of linear polyethylenes. Other viscometric relationships are also analyzed.

The relationships between intrinsic viscosity $[\eta]$, melt viscosity η_0, melt flow index MFI, and molecular weight have been extensively studied. Low-density polyethylenes cause difficulties in most correlations, and an additional parameter indicating the degree of long-range branching should be incorporated.[1] However, high-density (linear) polyethylenes may be properly defined by various empirical relationships. A simple correlation is here suggested between molecular weight and melt flow index of whole linear polyethylenes.

$[\eta]$–$\bar{M}_w$ correlations for linear polyethylenes (whole polymers as well as narrow-cut fractions) in various solvents and temperatures may be found in the literature.[2] The dependence of melt viscosity η_0 on $\bar{M}_w$ has been derived by Bueche[3] as follows:

$$\eta_0 = A\bar{M}_w^{3.5} \tag{1}$$

Experimental results suggest an exponent of 3.4 for many linear polymer melts, above some critical molecular weight.

If one considers the MFI as an expression for fluidity at a constant low shear stress, it may be correlated with the intrinsic viscosity of the same polymer:

$$\log \text{MFI} = A - B[\eta] \tag{2}$$

$$\log \text{MFI} = A' + (B'/a) \log [\eta] \tag{3}$$

Equations (2) and (3) were obtained by Moore[4] and Busse and Longworth,[5] respectively, under different conditions.

Equation (1) provides a good means for relating melt viscosity to molecular weight of linear polyethylenes. There are, however, some difficulties in extrapolation of viscosity data from the non-Newtonian region to the constant value of η_0. There exists also the possibility of polymer degradation

on prolonged flow at high temperatures. All this calls for more simplified correlations for linear polymers by elimination of extrapolations.

Seven high-density polyethylene samples from three different suppliers were studied. The range of MFI was 0.86–9.2.

The melt viscosity at 190°C. was found by using a modified melt indexer with a capillary having $L/R = 28$. Viscosity was measured under decreasing pressures. Non-Newtonian behavior prevailed over the whole range of shear stresses (2×10^4–10^5 dyne/cm.^{2}). The capillary end correction was found to be around $2R$. The rate of shear at the wall was corrected according to Rabinowitsch.[6] The values of the exponent n were about 0.6–0.8. A full treatment of capillary analysis has been previously published by Ram and Tamir.[7]

The extrapolation of the corrected values of viscosity to the Newtonian value of η_0 was done according to Ferry's[8] equation:

$$1/\eta = (1/\eta_0) + B\tau_w \qquad (4)$$

Equation (4) was followed well by our experimental data.

Values of intrinsic viscosity were obtained in p-xylene at 105°C. and in tetralin at 120°C. The former were related to molecular weight by Trementozzi:[9]

$$[\eta]_x^{105} = 1.65 \times 10^{-4}\bar{M}_w^{0.83} \qquad (5)$$

For the solution in tetralin, the correlation of Duch and Kuchler[10] has been used:

$$[\eta]_t^{120} = 2.36 \times 10^{-4}\bar{M}_w^{0.78} \qquad (6)$$

The polymer was directly dissolved in the Ubbelohde viscometer in order to eliminate any further transferring. The MFI was obtained at standard conditions[11] and agreed within 10% to the producers' values.

On plotting η_0 against $\bar{M}_w$, the latter being determined by intrinsic viscosity in tetralin and by using eq. (6), on a log-log scale (Fig. 1) a straight line was obtained. The slope in Figure 1 (curve 1) is 3.7, which is in excel-
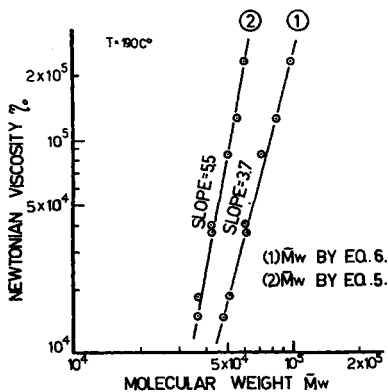

Fig. 1. Dependence of η_0 on molecular weight.

lent agreement with theory. Under similar conditions Schreiber and Bagley[12] found a slope of 4.22. However, on using the values of $\bar{M}_w$ as determined by intrinsic viscosity in xylene and eq. (5) we obtained a slope of 5.35 (Fig. 1, curve 2). The correlations for $[\eta]$ in xylene at 105°C. were originally provided for fractions, while we have worked with whole polymers. Furthermore, the temperature of 105°C. might be too low for proper dissolution of linear polyethylenes on increasing molecular weight.
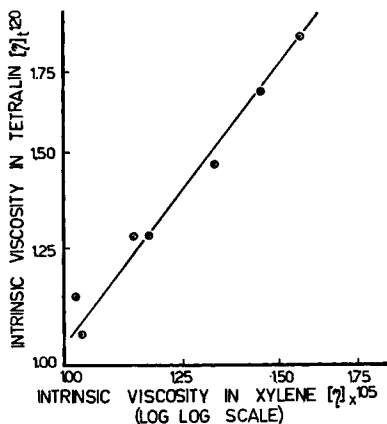

Fig. 2. Correlation between $[\eta]_t^{120}$ and $[\eta]_x^{105}$.
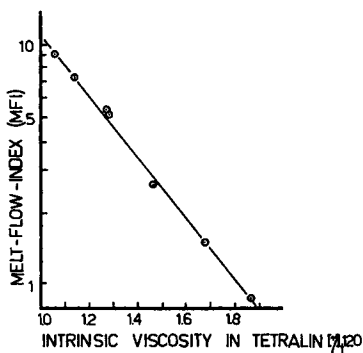

Fig. 3. Correlation between MFI and $[\eta]_t^{120}$.

We therefore preferred to use eq. (6) for our further correlations. The suitability of this equation has been confirmed by Schreiber and Waldman.[13] By plotting $[\eta]_t$ against $[\eta]_x$ on a log-log scale (Fig. 2), a straight line is shown corresponding to eq. (7).

$$[\eta]_t = 1.05 \, [\eta]_x^{1.28} \tag{7}$$

Our results of MFI were plotted on a semilog scale against $[\eta]_t$ in Figure 3. The results fit well eq. (2), principally.

In Figure 4 we show a linear relationship between log MFI and $\bar{M}_w$. This corresponds to the following equation:

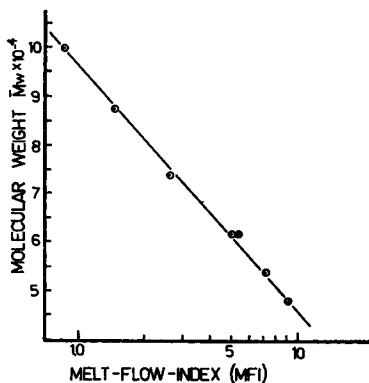$$\bar{M}_w = 96{,}500 - 50{,}500 \log \text{MFI} \tag{8}$$

Fig. 4. Correlation between MFI and $\bar{M}_w$.

Equation (8) suggests a simplified correlation between MFI and M_w. On comparing to eq. (2) one notices that there should be a linear relationship between $[\eta]_t$ and $\bar{M}_w$ in this region. In the limits of our experimental data such a linearity is shown in Figure 5 and may be expressed by eq. (9):

$$[\eta]_t = 0.34 + 1.54 \times 10^{-5}\bar{M}_w \qquad (9)$$

Equation (8) has been derived for linear polyethylene in the $\bar{M}_w$ range of 50,000–125,000 and MFI range of 0.3–9.0. The agreement with experimental data is within 3%.

The successful use of MFI as a criterion for $\bar{M}_w$ of linear polyethylene gains also from the fact that in our range of experiments the capillary end correction was fairly constant and did not interfere. In addition, Skinner[14] found a dependence of flow rate on the level of the piston above the capillary of the melt indexer. The corrected value of MFI is obtained by extrapolation to zero height of the piston. We have noticed such a sensitivity only in one case. The extrapolated value of MFI agreed well with our remaining data.

Longworth and Pieski[15] suggest for linear polyethylenes the relationship of eq. (10):

$$\log \bar{M}_w = 5.171 - 0.195 \log \text{MFI} \qquad (10)$$

There is marked disagreement in the values of $\bar{M}_w$ when calculated according to eq. (8) or eq. (10). The discrepancy lies within 50–100% in the range of MFI 1–10. Longworth and Pieski also found a slope of 5 on their log–log correlation of η_0 against $\bar{M}_w$, in contradiction with our 3.7 slope. They did not specify how $\bar{M}_w$ was measured.

It is interesting to compare our eq. (8) to the work of Mortimer et al.[16] on medium-density polyethylene of narrow distribution and low degree of branching. Their results followed eq. (11):

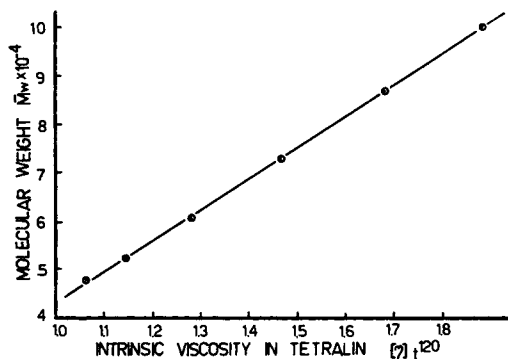$$\bar{M}_n = 37,000 - 8610 \log \text{MFI} \qquad (11)$$

Fig. 5. Linear correlation between $\bar{M}_w$ and $[\eta]_t^{120}$.

On correcting to $\bar{M}_w$ (distribution of 2.0–2.2) one gets $\bar{M}_w$ in the vicinity of our data for same MFI.

The same authors suggest correlations to intrinsic viscosity in xylene. By the use of their equations one gets values of $\bar{M}_w$ which are closer to ours [when corrected by eq. (7)] than to those of Trementozzi [eq. (5)].

When nonlinear polyethylene is considered, one must take into account the degree of branching. In addition, the role of capillary end corrections has been found to be significant. We noticed end corrections which amount to $4R$ and do depend on the molecular weight. Such corrections are severe for capillaries of $L/R = 8$ in the standard melt index. The problem of capillary end correction for branched polyethylenes will be discussed in a separate publication.

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Résumé

Les polyéthylènes de haute densité montrent une relation linéaire entre le poids moléculaire et le log de l'indice d'écoulement à l'état fondu. Le $\bar{M}_w$ était situé entre 50,000–125,000. Cela fournit une méthode simplifiée et rapide pour caractériser les polyéthylènes linéaires. D'autres relations viscosimétriques sont aussi analysées.

Zusammenfassung

Polyäthylenproben hoher Dichte zeigten eine lineare Beziehung zwischen Molekulargewicht und log (Schmelzfliessindex). $\bar{M}_w$ lag im Bereich von 50,000 bis 125,000. Damit wird eine einfache, rasche Möglichkeit zur Charakterisierung linearer Polyäthylene erhalten. Eine Analyse anderer viskosimetrischer Beziehungen wird gegeben.