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Effect of Homogeneity on Viscosity in Capillary Extrusion of Polyethylene

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Synopsis

The change in melt flow properties, as determined by melt index measurement, as a function of shear history, has been measured for linear polyethylene. It is shown that a drop in melt index occurs when a polymer sample which has had no previous shear history is melted and subjected to shear mixing. This fact is attributed to a molecular homogenization of a previously unmixed blend. An analytical model of the laminar flow in a pipe of concentric adjacent fluids with different viscosities is presented. The model indicates that the effective viscosity of this non-homogeneous system is much lower than the viscosity of an intimate blend of the same viscosity fluids.

Introduction

Several investigators[1,2] have noted a change of the viscosity of polyethylene melts extruded from a melt index apparatus with time. In general, the melt index increased with time. This was ascribed to frictional heating and changes in the segmental entanglement-disentanglement equilibrium toward a state of relative disentanglement.

It has been observed in this laboratory that the degree of mixing to which some polyethylene melts have been subjected can also have an effect on the melt index. As a polydisperse sample becomes more homogeneous, the melt index decreases. Thus, a heterogeneous sample of polyethylene powder, especially one with a broad molecular weight distribution, which has never been melted can have a higher melt index than a sample of the same material which has been subjected to heat and shear. At the same time, other molecular weight dependent properties such as intrinsic viscosity are not affected.

An analysis of the fluid mechanics of two fluids of different viscosities flowing in concentric laminae indicates that the effective viscosity of this system would be lower (and, therefore, the melt index higher) than the viscosity predicted by the experimental data of Busse and Longworth[3] of the same two fluids if they were intimately mixed.

Experimental

Experimentation involved measuring several molecular weight-dependent properties of samples of linear polyethylene powder which had not previously been subjected to heat and shear and then remeasuring the same polymers after some sort of melt-mixing operation. The mixing was variously accomplished by extrusion in a $1^3/_4$-in., 24:1 L/D single screw extruder with a polyethylene-type screw or by repeated extrusion through a melt index orifice.

Also, two polymers of widely different molecular weights which exhibited no decrease in melt index on extrusion were blended in powder form in a Waring Blendor, and this blend was then extruded in a $^3/_4$-in. single screw extruder with a polyethylene-type screw. The melt index of the blend was measured before and after extrusion.

Melt indices were determined according to ASTM procedure D1238-57T at 190°C. with a 2140 g. weight.* Intrinsic viscosities were measured at 135°C. in decalin. Flow curves were determined with an Instron capillary rheometer with a 0.030-in. diameter capillary of length 1.003 in. and a 90° entry angle at 190°C.[4]

Number-average molecular weights were determined by end-group analysis with the use of a Perkin-Elmer Model 21 double-beam spectrophotometer.[5]

Results

The characterization results for one particular polymer sample are given in Table I for the powder form and after extrusion through the $1^3/_4$-in. screw extruder.

TABLE I

Test	Powder form	Extruded form
Melt index (190°C.)	0.41	0.20
Intrinsic viscosity (in decalin at 135°C.)	2.49	2.34
Number-average molecular weight (determined from infrared measurement)	21,600	21,000
Melting point, °C.	132.5	132.0
Density of melt index extrudate, g./cc.	0.957	0.955
Volatile content, %	<0.5	<0.1

Flow curves for the two samples are shown over a wide range of shear rates in Figure 1.

On molding the powder in a compression press in which melting occurs, but without any significant shear, there was very little change from the powder melt index. For example, one sample with a powder melt index of 0.32 and an extruded melt index of 0.20 had a melt index after compression molding of the powder of 0.29.

In another experiment, powder samples were extruded through the melt indexer, and the melt indices of the extrudates were then determined. Results on several polymers are given in Table II.

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* All melt index measurements were made with constant weight samples to eliminate barrel height effects.

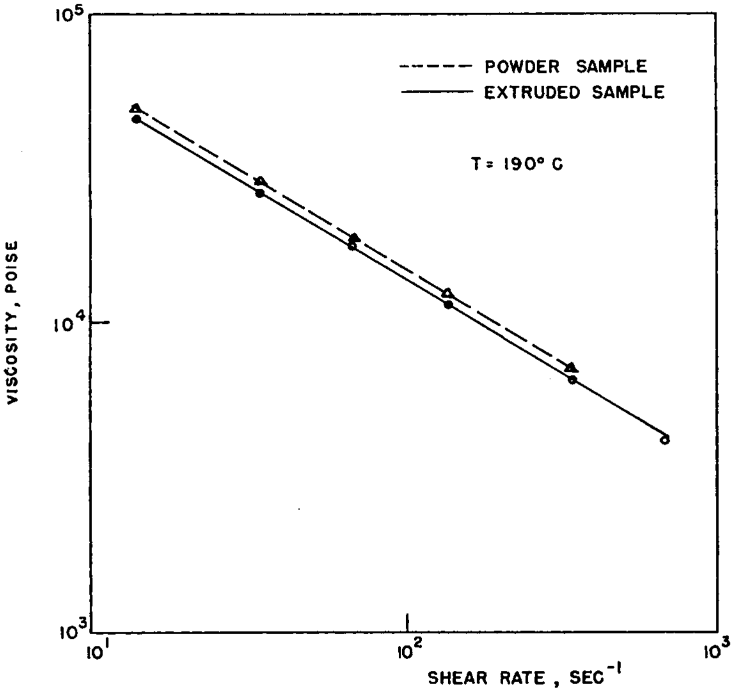

Fig. 1. Flow curve of (- -) powder and (——) extruded samples at 190°C.

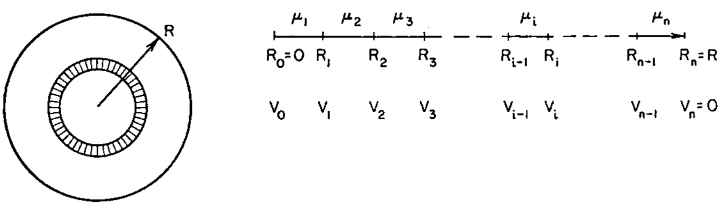

Figure 2.

Two polymer samples of widely different molecular weight were blended in powder form in a Waring Blendor. This blend was then extruded through the $^{3}/_{4}$-in. extruder. The melt index of the blend was measured before and after extrusion. It was known that the particular samples which went into the blend did not decrease in melt index on extrusion. The results of this experiment are summarized in Table III.

TABLE II

Sample	Powder melt index	Re-extruded melt index
1	0.21	0.12
2	0.21	0.16
3	0.14	0.09
4	0.14	0.07
5	0.18	0.09

TABLE III

	Melt index of powder sample	Melt index of extruded sample
Polymer A	7.4	8.0
Polymer B	0.024	0.025
Blend of 2 parts A and 1 part B	0.18	0.12

Discussion

Crosslinking was eliminated as a possible cause by melting point and density measurement, together with visual observation of solutions of the polymer. It was also determined that the samples were dry and that no significant quantity of volatile material was present.

The intrinsic viscosity and number-average molecular weights as shown in Table I indicate that, if anything, the molecular weight of the material is decreasing on extrusion. This would be expected to occur since the shear work in the extruder would tend to cause a slight amount of degradation. The decrease in melt index, on the other hand, indicates an apparent increase in molecular weight.

Howells and Benbow[6] have reported that preshearing a sample of low density polyethylene resulted in a decrease in the apparent melt viscosity of the polymer by a factor of about two. At the same time, light-scattering molecular weight values were unchanged. The effect was interpreted molecularly as a result of a reduction in the amount of chain entanglement on shearing of the material.

The effect observed and reported in this paper is an increase in the melt viscosity of the polymer by some initial shearing action. It is felt that in this case the nonhomogeneous unsheared material is in a state of relative disentanglement, and that the homogenization brought about by extrusion or some other shearing operation results in a greater degree of chain entanglement and, therefore, an increase in low shear melt viscosity.

Since a wide spectrum of molecular weights is contained in a given sample, it is likely that two or more species would be segregated prior to some sort of homogenization of the polymer. The application of shear in the extruder and the dissolution of the polymer in a solvent as in an intrinsic viscosity determination would tend to homogenize the polymer and cause its behavior to be indicative of its true molecular weight.

In the melt indexer, a nonhomogeneous mixture of high and low molecular weight entities could flow with a viscosity which was characteristic of a molecular weight other than that of the whole polymer. As homogenization took place, the zero shear viscosity or the melt index would tend toward the value which is characteristic of an intimate blend of all the molecular weight species present.

As an approximation of this system, we studied analytically a model of the laminar flow in a pipe of concentric adjacent fluids having different

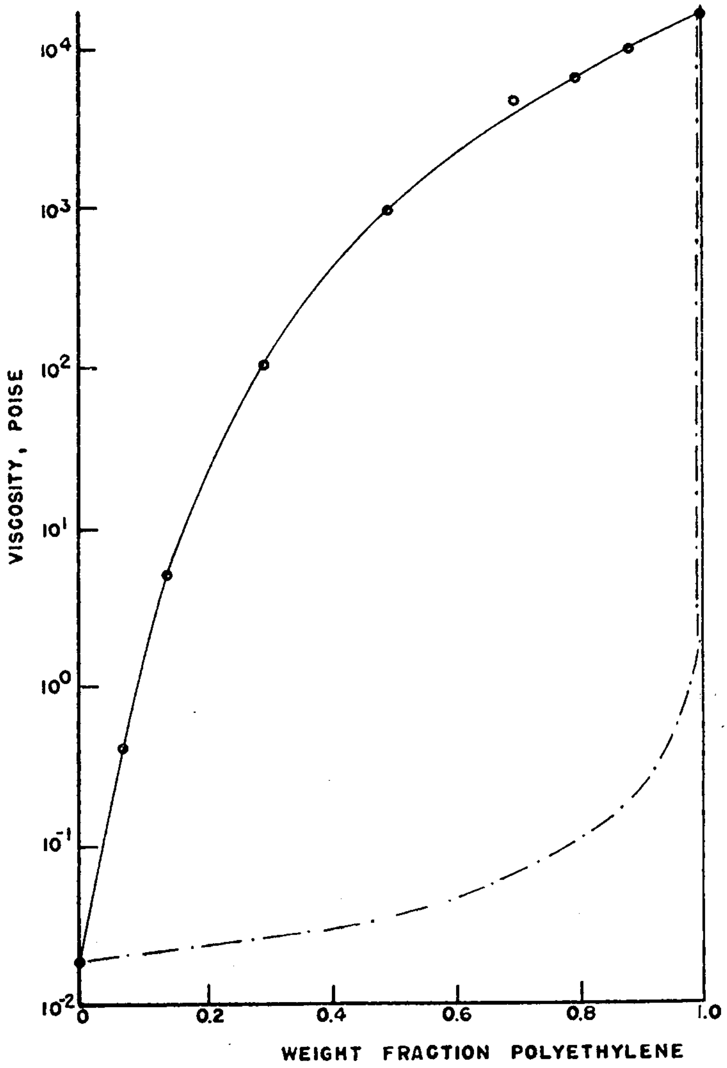

Fig. 3. Viscosities of polyethylene–wax blends: (———) experimental data of Busse and Longworth;[3] (·—·) calculated from eq. (5) for same polymer–wax blend.

viscosities. It was assumed that the fluids were Newtonian and had the same density, but that they had different viscosities μ_i. The "effective" or "equivalent" viscosity μ_E, of this system was defined as the viscosity of that single fluid (of the same density) which flowing through the same pipe, under the same pressure gradient, gives the same volume flow rate. The effective viscosity for a system of the two fluids was compared to the viscosities of intimate blends of polymers. For that purpose we used the experimental data of Busse and Longworth.[3]

The derivation of the mass flow rate for the system of fluids follows the same lines as the derivation of the Poiseuille equation. Analogous derivations are given in the literature.[7] The boundary conditions chosen in our derivations were zero velocity at the wall, and continuity of shearing stress and velocity at the liquid interfaces. A sketch illustrating the symbols used appears in Figure 2.

Under the circumstances the balance of forces on a cylinder of radius r where $R_{i-1} < r < R_i$ leads to

$$-\Delta P/L = 2\tau/r$$

where $\Delta P/L$ is the pressure drop across the tube and τ is the shearing stress on the surface of the cylinder. Since

$$\tau = \mu_i dv/dr$$

we have

$$dv = (-\Delta P/2L\mu_i)\, rdr$$

Integrating between the limits r and R_i we have for the velocity in layer i:

$$V - V_i = (\Delta P/4L\mu_i)\,(R_i^2 - r^2)$$

For $r = R_{i-1}$ we have $V = V_{i-1}$. Knowledge of V presupposes knowledge of V_i. This can be evaluated using iterative procedures, starting from layer n (where $V_n = 0$).

The value of V_i is thus found to be

$$V_i = \frac{\Delta P}{4L} \sum_{j=i+1}^{j=n} 1/\mu_j\,(R_j^2 - R_{j-1}^2)$$

and the velocity in layer i is:

$$V = \frac{\Delta P}{4L\mu_i}\,(R_i^2 - r^2) + \frac{\Delta P}{4L} \sum_{j=i+1}^{n} \frac{1}{\mu_j}\,(R_j^2 - R_{j-1}^2) \tag{1}$$

The volume flow rate in element i is

$$Q_i = \int_{R_{i-1}}^{R_i} 2\pi V r dr$$

and the volume flow rate through the tube is:

$$Q_T = \sum_{i=1}^{n} Q_i$$

Carrying out the integration and evaluating the summations we have finally:

$$Q_T = \frac{\pi \Delta P}{8L} \sum_{i=1}^{n} \frac{1}{\mu_i}\,(R_i^4 - R_{i-1}^4) \tag{2}$$

The volume flow rate Q_E for a fluid (of the same density) of viscosity μ_E

flowing through the same tube under the same pressure gradient is given by

$$Q_E = (\Delta P/8L\mu_E)R^4$$

Setting $Q_E = Q_T$, we can solve for μ_E, the effective or equivalent viscosity:

$$\mu_E = \frac{R^4}{\sum_{i=1}^{n} \frac{1}{\mu_i} (R_i^4 - R_{i-1}^4)} \tag{3}$$

This can also be written

$$\frac{R^4}{\mu_E} = \sum_{i=1}^{n} \frac{(R_i^4 - R_{i-1}^4)}{\mu_i}$$

and shows that the effective viscosity depends on the reciprocal average of the viscosities of the different layers.

The general case was particularized for a system of two fluids A and B each occupying in an alternating manner $n/2$ layers. The weight or volume fractions of the fluids were assumed to be variable, i.e., w for A, $(1-w)$ for B, but it was assumed that all annuli of a given fluid had the same area. Thus, for the tube of radius R, A occupies $n/2$ layers, each of area $2\pi w R^2/n$, and B occupies $n/2$ layers, each of area $2\pi(1-w)R^2/n$.

By using eq. (3), the two components, A and B, are separated, and the summation sign expanded. By using the identity

$$(R_i^4 - R_{i-1}^4) = (R_i^2 - R_{i-1}^2)\,(R_i^2 + R_{i-1}^2)$$

it is seen that $(R_i^2 - R_{i-1}^2)$ is constant and equal to the annulus area, while the terms $(R_i^2 + R_{i-1}^2)$ form an arithmetic progression. The following expression for μ_E is arrive at:

$$\mu_E = \frac{1}{\frac{w\,(n - 2 + 2\,w)}{n\mu_A} + \frac{(1 - w)(n + 2w)}{n\mu_B}} \tag{4}$$

For values of n large compared to 1, eq. (4) reduces to the simple expression

$$\mu_E = \frac{1}{\frac{w}{\mu_A} + \frac{1 - w}{\mu_B}} \tag{5}$$

Equation (5) gives the effective viscosity of a system of two liquids, divided into a large number of layers and flowing adjacently without mixing. To compare this effective viscosity to the viscosities of intimately mixed blends, we used the data of Busse and Longworth[3] for high density polyethylene. Busse and Longworth experimentally determined the viscosities of intimate blends of linear polyethylenes with wax. By using eq. (5) the effective viscosity of the two polymers flowing in adjacent laminae was calculated and compared to that of the intimate mixture. The results are plotted on Figure 3, and it can be seen that the predicted viscosities for adjacent flow are much lower than those experimentally determined.

These results further support the hypothesis that homogeneity of a polymer sample is necessary to get a true indication of molecular weight by use of a melt index determination.

Although the model used in the calculations is a simplification of the actual flow in the melt indexer, it is believed that in a qualitative manner the actual conditions are approached, and the model should certainly indicate the direction in which the viscosity is affected.

Conclusion

The degree of mixing of samples of polymers having widely different molecular weights or of a given polymer sample which is very heterogeneous with regard to molecular weights affects significantly the melt viscosity of the mixture especially at low shear rates. For example, erroneously high melt index values can be obtained from such mixtures if the polymer melts are not first subjected to some homogenization process. A simplified fluid model can be used to present a qualitative explanation of the observed phenomenon.

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Résumé

On a étudié dans le cas du polyéthylène linéaire les changements des propriètés d'écoulement à l'état fondu, tels qu'on les détermine par mesure de l'indice de fusion, en fonction du cisaillement éventuel préalable. On a montré qu'une diminution de l'indice de fusion se présente lorsqu'un échantillon polymérique n'ayant subi aucun traitement préalable est fondu, et soumis à mélange sous cisaillement. On attribue de fait à l'homogéneisation moléculaire du mélange préalable. Un modèle analytique de l'écoulement laminaire dans un tube de liquides concentriques adjacents de différents viscosités en est présenté. Le modèle indiqué que la viscosité effective de ce système non-homogène est fort inférieure à la viscosité d'un mélange intime de fluides de même viscosité.

Zusammenfassung

Die Änderung der Fliesseigenschaften der Schmelze von linearem Polyäthylen wurde durch Messung des Schmelzindex in Abhängigkeit von der vorhergehenden Scherungsbeanspruchung gemessen. Wird eine keiner voehergehenden Scherung unterworfene Polymerprobe geschmolzen und durch Scherung durchgemischt, so nimmt der Schmelzindex ab. Dies wird auf eine molekulare Homogenisierung der vorher unvermischten Probe zurückgeführt. Es wird ein analytisches Modell für das laminare Fliessen in einer Röhre mit konzentrischen benachbarten Flüssigkeitsschichten verschiedener Viskosität angegeben. Wie das Modell zeigt, ist die effektive Viskosität dieses nicht homogenen Systems viel kleiner als die Viskosität einer gut durchmischten Probe der die Schichten bildenden Flüssigkeiten.

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