

Effects of Molecular Weight Distribution and Branching on Rheological Parameters of Polyethylene Melts. Part I. Unfractionated Polymers*

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Synopsis

It is well known that the rheological behavior of polyethylene melts is affected by at least four variables: (1) molecular weight, (2) molecular weight distribution, (3) long-chain branching and its distribution, and (4) short-chain branching. Of these, the first three appear to have the largest effects. In the present paper an attempt is made to determine the effect of molecular weight distribution by rheological studies of polymers having similar molecular weights and degrees of branching, but varying considerably in their molecular weight distributions as determined by fractionation. The rheological parameters studied were melt recovery, non-Newtonian behavior, critical shear rate, and melt strength. It is shown that the melt recovery increases uniformly as the molecular weight distribution broadens. The degree of non-Newtonian behavior, as measured by the exponent n of the power law, also increases with distribution breadth and is particularly affected by the amount of low molecular weight polymer present. Melt strength increases in a similar manner. Critical shear rate is inversely related to the breadth of the molecular weight distribution and is particularly dependent on the molecular weight of the highest fractions. The log of the critical shear rate is inversely proportional to the melt index recovery.

INTRODUCTION

It is now well established that high pressure polyethylene may vary considerably in molecular structure, depending on the conditions used in its preparation. It may contain both short and long branches, and the length and frequency of these branches may vary considerably. In addition to this, high pressure polyethylene has a relatively broad distribution of molecular weight which is due, at least in part, to the long-chain branching mechanism.¹ The actual breadth of the distribution, however, has been the subject of considerable dispute. Light-scattering studies, for example,

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indicate values of \bar{M}_w/\bar{M}_n in excess of 10–20, which depend to a certain degree on the sample preparation.² Fractionation results, on the other hand, indicate considerably narrower distributions.^{3,4} Actually, the results of the two methods can be reconciled only if the methods are sensitive to different parts of the same distribution curve.

It is well known that the rheological properties of polymer melts are profoundly affected by relatively small changes in both molecular structure and molecular weight distribution. The study of rheological properties of polyethylene may therefore give considerable insight into structural variations between polymers.

In the present study, an attempt was made to evaluate the effect of molecular weight distribution on the following main characteristics of polyethylene melts: (1) melt recovery, (2) critical shear rate, (3) melt strength, and (4) non-Newtonian behavior. In order to minimize the effects of structural changes, polymers were selected in three groups having similar densities (and hence, similar degrees of short-chain branching). The melt indices of all polymers were between 1 and 2.4. The amount of long-chain branching was not determined but the samples were chosen so that a relatively constant frequency could be expected within each group, based on a knowledge of the preparation conditions. The distributions of the polyethylenes were determined by a chromatographic fractionation method.³ These results were plotted as inherent viscosity distribution curves because there was insufficient information about the frequency of long-chain branching to convert these to molecular weight distribution curves by the procedure described by Guillet.⁵

EXPERIMENTAL

Melt Indexer

An extrusion Plastometer, Model 3 (Tinius Olsen Testing Machine Co.) with a Thermodyne temperature controller was used to determine the following properties.

Melt Index (MI). This is the melt flow in g./10 min. at 190°C. with a load of 2160 g.⁶ The average deviation was 4.6% of the measurement, using 2σ limits.

Melt Flow, 10 Kg. (MF₁₀). This is the melt flow in g./10 min. at 190°C. with a load of 10 kg. The average deviation was 2% of the measurement, using 2σ limits.

Melt Index Recovery (MIR). This is the melt recovery of the extrudate measured during the determination of the melt index (190°C., load 2160 g.). The average deviation was 12.4% of the measurement, using 2σ limits. Three to five measurements of the diameter of the extruded cord were made at a distance $1/4$ in. from the end. The average of these was the value used. Melt index recovery is the percentage increase in the diameter of the extrudate over the diameter of the orifice, $10_0 (d - d_0/d_0)$, where $d_0 = 0.0825$ in.

Melt Strength (MS). When a molten plastic is extruded from the orifice of the melt indexer, the diameter of the extrudate changes because of the stress applied to the melt by the weight of the material which has preceded it. By measuring the change in diameter of the extruded cord over the first $\frac{1}{2}$ in. of length (230°C., load 2160 g.), a melt viscosity at extremely low shear rates (0.1–0.01 sec.⁻¹) can be calculated. The melt viscosity calculated in this manner has been named melt strength (MS), since it indicates how well the melt can support its own weight. The equation used to calculate the melt strength (in poises) was

$$MS = 3.54 \times 10^5 \Delta l^2 r_0^2 / MF_{230} \quad (1)$$

where Δl is the length of cord (inches) required for a 50% decrease in diameter of the cord, r_0 is the radius (inches) of the cord as it first emerges from the die (measured by extrapolation of measurements at $\frac{1}{16}$, $\frac{1}{4}$, and $\frac{1}{2}$ in.), and MF_{230} is the melt flow in g./10 min. at 230°C. and 2160 g. load on the melt indexer.

High Pressure Melt Indexer

The high pressure melt indexer is a gas rheometer in which the shear stress on the melt can be easily and quickly changed by varying the pressure of the nitrogen used from 40 to 2000 psig. The barrel containing the molten polymer is 0.625 in. in diameter and 5 in. long. A stainless steel ball bearing is used as a piston. The extrusion die has a capillary diameter of 0.0197 ± 0.0003 in. and a land length of 0.0394 ± 0.0003 in. The entrance to the capillary is tapered at an angle of 60°. This apparatus was used to determine the following properties.

High Pressure Melt Index (HPMI). This is the melt flow in grams/min. at 190°C. and 1450 psi, as determined with the high pressure melt indexer. The average deviation was 13% of the measurement, using 2σ limits.

HPMI/MI Ratio. This ratio is an arbitrary parameter indicating the relative change in viscosity with shear stress. Multiplication of this ratio by a factor of 74 gives the ratio of apparent viscosity at a shear stress of 43.2 psi to the viscosity at 1450 psi.

Critical Shear Rate (CSR). This is the shear rate at which roughness first occurs on the extruded rod. The average deviation was 26% of the measurement, using 2σ limits.

Critical Shear Stress (CSS). This is the stress at which roughness first occurs on the extruded rod.

Power Law

For non-Newtonian fluids, the ratio of shear stress S to shear rate $\dot{\gamma}$ is no longer a constant. Over certain ranges of shear stress, a suitable expression for the relation between S and $\dot{\gamma}$ is given by eq. (2):

$$S = K\dot{\gamma}^n \quad (2)$$

where n is a constant which is a measure of the divergence of the flow from the Newtonian law. When n is unity, the equation becomes Newton's law, and K becomes equal to the Newtonian viscosity, η . If n is not equal to unity, K is the viscosity at a shear rate of 1 sec.⁻¹ The smaller the value of n , the greater will be the change in apparent viscosity with shear rate. K and n may be calculated from either HPMI/MI or MF₁₀/MI, but the values will be different because of the difference in shear stress ranges covered by the two ratios.

Fractionation

The fractionation method used was a modification of the Baker and Williams method described by Guillet and co-workers.³ Measurements of the inherent viscosity $[\eta]$ of the samples were made in tetralin at 100°C. and at a concentration of 0.10 g./100 ml. An integral plot was made of the viscosity of each fraction as a function of the summation of the weight per cent of polymer removed.

RESULTS AND DISCUSSION

Melt Recovery

Typical distribution curves for a series of intermediate-density polyethylenes are shown in Figure 1. The most striking correlation is immediately evident—the direct relation between the melt recovery and the breadth of the distribution as indicated by the viscosity of the highest fractions. Almost without exception this has been found to be true for polymers having similar degrees of long-chain branching. For correlation it is convenient to characterize the distribution curves by the viscosity at Σ wt.-% = 5, 50, and 95. Rheological and fractionation data in this form for low, intermediate, and medium density polyethylenes are shown in Tables I, II, and III, respectively. The polymers are listed in order of increasing viscosity at Σ wt.-% = 95. It is clear that the melt recovery in-

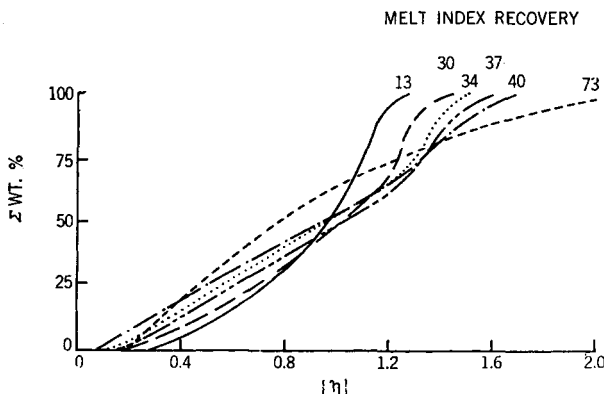


Fig. 1. Fractionation curves for intermediate density polyethylene.

creases as the distribution broadens. The experimental error in the melt recovery measurement could explain the one reversal observed in Table III.

Another parameter which can be abstracted from the actual distribution curve is the ratio $[\eta]_{95}/[\eta]_{50}$, which is proportional to the breadth of the

TABLE I
Properties of Low Density Polyethylenes^a

Sample	MI, g./10 min.	MIR, %	CSR, sec. ⁻¹	CSS, dynes/ cm. ² × 10 ⁻⁶	MS at 230°C., poises × 10 ⁻⁴	Power law parameters ^b		
						n_1	K_1 , poises × 10 ⁻⁴	$[\eta]_{95}$
A-1	2.10	25	1340	6.69	2.9	0.675	7.0	1.43
A-2	2.17	43	376	3.88	6.5	0.642	7.6	1.53
A-3	1.54	58	91	2.42	18	0.598	9.7	0.90
A-4	2.38	69	37	1.29	—	0.625	9.1	1.98
A-5	1.56	71	34	1.98	110	0.596	10.5	2.11

^a Annealed density 0.919–0.921 g./ml.

^b Using MF₁₀/MI ratio.

TABLE II
Properties of Intermediate Density Polyethylenes^a

Sample	MI, g./10 min.	MIR, %	CSR sec. ⁻¹	CSS, dynes/ cm. ² × 10 ⁻⁶	MS at 230°C., poises × 10 ⁻⁴	Power law parameters ^b		
						n_1	K_1 , poises × 10 ⁻⁴	$[\eta]_{95}$
B-1	1.98	13	556	4.14	7.0	0.668	6.9	1.17
B-2	1.68	30	696	4.91	12	0.644	8.5	1.35
B-3	1.91	34	649	4.83	25	0.614	8.1	1.42
B-4	1.71	37	465	4.40	17	0.625	8.3	1.44
B-5	1.75	40	430	3.88	42	0.617	7.9	1.52
B-6	2.08	73	107	2.33	40	0.614	8.0	1.88

^a Annealed density 0.924–0.926 g./ml.

^b Using MF₁₀/MI ratio.

TABLE III
Properties of Medium Density Polyethylenes^a

Sample	MI, g./10 min.	MIR, %	CSR, sec. ⁻¹	CSS, dynes/ cm. ² × 10 ⁻⁶	MS at 230°C., poises × 10 ⁻⁴	Power law parameters ^b		
						n_1	K_1 , poises × 10 ⁻⁴	$[\eta]_{95}$
C-1	1.51	34	250	3.71	17	0.637	8.6	1.21
C-2	1.69	37	605	5.09	8.7	0.637	8.1	1.43
C-3	1.35	59	147	2.94	27	0.603	9.8	1.78
C-4	1.54	59	102	2.33	65	0.602	9.0	1.82
C-5	1.61	47	101	1.98	60	0.593	8.9	1.95

^a Annealed density 0.934–0.937 g./ml.

^b Using MF₁₀/MI ratio.

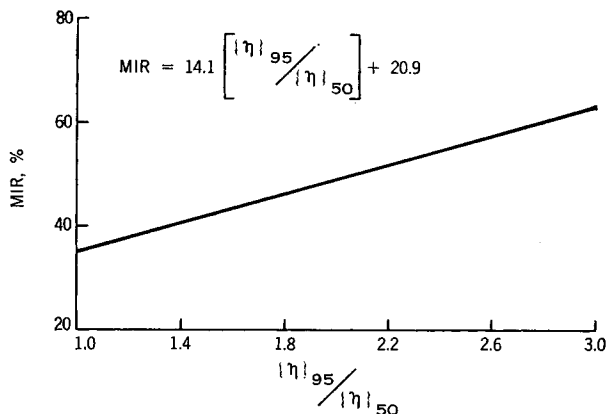


Fig. 2. Relationship of $[\eta]_{95}/[\eta]_{50}$ and MIR.

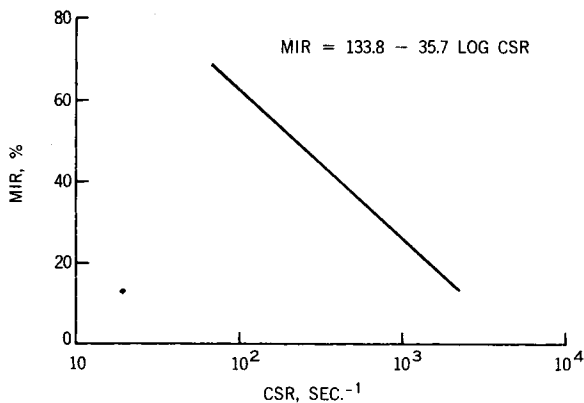


Fig. 3. Relationship of CSR and MIR.

molecular weight distribution and is particularly sensitive to changes in the high end of the distribution. The study of fractionation data on over 100 samples of polyethylene showed that the melt recovery was correlated with this ratio at higher than 99.9% confidence level. A linear regression equation for the data gave the curve shown in Figure 2. Comparison of the equation given in Figure 2 with the data presented in Figure 1 indicates that the equation does not hold at the extreme values of melt index recovery, but that it does hold in the middle range of values.

Critical Shear Rate

Inspection of the data in Tables I-III shows that the critical shear rate decreases as the molecular weight distribution broadens. This is also true for critical shear stress. It has been shown^{7,8} that critical shear stress is a unique function of \bar{M}_w :

$$(\text{CSS}) (\bar{M}_w) = K \quad (3)$$

These polymers all have nearly the same low-shear melt viscosity, as indicated by their melt indices, which also should be related to \bar{M}_w by the equation prepared by Bueche.⁹

$$\eta = K\bar{M}_w^{3.5} \quad (4)$$

In view of these experimental results it must be assumed that one or the other relation is incorrect or that a different average molecular weight must be used in the two relations.¹⁰ The observed change in critical shear rate with distribution shows that there should also be a strong relation between critical shear rate, or shear stress, and the melt recovery. This also proves to be true. Figure 3 shows the regression line obtained by analysis of critical shear rate measurements on 38 samples of polyethylene. By using this regression equation, 77.5% of the variance was removed. Considering the percentage errors in the measurements of MIR and CSR, this is in excellent agreement with the experimental data.

Melt Strength

As the molecular weight distribution broadens, melt strength increases, as indicated in Tables I-III. It should be noted that the melt viscosity, as measured in the melt indexer (shear rate 5 sec.⁻¹) and as indicated by K in the power law (shear rate 1 sec.⁻¹) is nearly the same for all samples, whereas the melt strength measured at shear rates of 0.1-0.01 sec.⁻¹ is greatly different for these samples.

Change in Apparent Viscosity with Shear Rate

The degree of change in apparent viscosity with increasing shear rate (non-Newtonian behavior) is indicated by the deviation of n in the power law from unity. As shown in Tables I-III, the value of n decreases as the breadth of distribution increases for each of these series. This is probably related to the greater degree of chain entanglement which occurs with a broad distribution of molecular weights at low shear rates.

CONCLUSION

In view of these experimental results, it is concluded that the melt recovery of polyethylene samples with similar degrees of long-chain branching is directly related to the breadth of their molecular weight distributions. The melt recovery can therefore be used as a convenient index of the breadth of molecular weight distribution for polymers of known degrees of long-chain branching. Since this measurement is sensitive to relatively small changes in the high end of the distribution, for polydisperse samples, the weight-average molecular weight should correlate more quantitatively with the melt recovery than would the number-average molecular weight.

The critical shear stress and shear rate increased significantly when the breadth of the distribution was decreased. Further, there is a high inverse correlation between melt recovery and critical shear rate. The degree of

non-Newtonian behavior also increases with breadth of distribution, so that among polymers having the same low-shear melt viscosity the ones with broad distributions have lower viscosities at high shear rates. This leads to obvious advantages in processability of the polymer in equipment using high shear stresses.

Melt strength appears to be closely related to viscosity at extremely low shear rates. As the molecular weight distribution broadens, the melt strength for polymers of similar-melt indexes increases.

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Résumé

Il est très connu que le comportement rhéologique des polyéthylènes fondus est affecté par quatre variables au moins: (1) le poids moléculaire, (2) la distribution du poids moléculaire, (3) la longue ramification des chaînes et sa distribution et (4) la courte ramification des chaînes. Parmi ceux-ci les trois premiers semblent avoir les effets les plus importants. Le présent article marque un essai pour déterminer l'influence de la distribution des poids moléculaires sur les propriétés rhéologiques des polymères qui ont un poids moléculaire similaire et un degré de ramification comparable, mais qui diffère considérablement par la distribution du poids moléculaire, ainsi que cela a été déterminé par fractionnement. On a étudié les paramètres rhéologiques suivants: le recouvrement du polymère fondu, le comportement non-Newtonien, la vitesse de cisaillement critique et la force de rupture du polymère fondu. On a montré que le recouvrement du polymère fondu augmente d'une manière uniforme à mesure que la distribution des poids moléculaires s'élargit. L'écart par rapport à un comportement Newtonien qui a été mesuré à partir de l'exposant n de la loi de la viscosité augmente également lorsque la distribution du poids moléculaire s'élargit et est très affecté par la quantité des polymères de bas poids moléculaires présents. La force de rupture du polymère fondu augmente d'une manière similaire. La vitesse de cisaillement critique varie en fonction inverse de la largeur de la distribution du poids moléculaire et est particulièrement affectée par le poids moléculaire des fractions les plus hautes. Le logarithme de la vitesse de cisaillement critique est inversement proportionnel à l'indice de recouvrement du polymère fondu.

Zusammenfassung

Es ist bekannt, dass das rheologische Verhalten von Polyäthylenschmelzen von zumindest vier Variablen beeinflusst wird: (1) Molekulargewicht, (2) Molekulargewichtsverteilung, (3) Langkettenverzweigung und ihre Verteilung und (4) Kurzkettenverzweigung. Davon scheinen die ersten drei den grössten Einfluss zu haben. In der vorliegenden Arbeit wird ein Versuch zur Bestimmung des Einflusses der Molekulargewichtsverteilung durch rheologische Untersuchungen von Polymeren mit ähnlichem

Molekulargewicht und Verzweigungsgrad, aber verschiedener durch Fraktionierung bestimmter Molekulargewichtsverteilung angestellt. Die untersuchten rheologischen Parameter waren Schmelzrückbildung, Nicht-Newton-Verhalten, kritische Schergeschwindigkeit und Schmelzfestigkeit. Die Schmelzrückbildung nimmt einheitlich mit der Verbreiterung der Molekulargewichtsverteilung zu. Der Grad an Nicht-Newton-Verhalten, gemessen durch den Exponenten n des Potenzgesetzes, nimmt auch mit der Verteilungsbreite zu und hängt insbesondere vom Gehalt an Polymerem mit niedrigem Molekulargewicht ab. Die Schmelzfestigkeit nimmt in ähnlicher Weise zu. Die kritische Schergeschwindigkeit verhält sich zur Breite der Molekulargewichtsverteilung reziprok und hängt speziell vom Molekulargewicht der höchsten Fraktionen ab. Der Logarithmus der kritischen Schergeschwindigkeit ist der Schmelzindexrückbildung umgekehrt proportional.

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