

Determination of the Molecular Characteristics of Commercial Polyethylenes with Different Architectures and the Relation with the Melt Flow Index

M. Teresa Rodríguez-Hernández, J. L. Angulo-Sánchez, A. Pérez-Chantaco

Centro de Investigación en Química Aplicada, Saltillo, Coahuila, México 25100

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ABSTRACT: The molecular weight distribution curves of several commercial polyethylene samples were evaluated by high-temperature gel permeation chromatography with two detectors (a refractive-index detector and a viscometer) to determine the molecular sizes and architectures (branching). The polymer samples included high- and low-density polyethylenes with different molecular weight distributions (wide, medium, unimodal, and bimodal) from nine producers. The results were tested against the melt flow index and zero-shear melt viscosity to find correlations. The data for high-density polyethylene correlated well with the molecular weight, whereas the data for low-density polyethylene did not correlate. However, when the weight-average molecular weight was corrected by the branching parameter and a factor form, all the polyethylene

samples fit a single equation. These results indicate that the melt flow index is dependent not only on the molecular weight but also on the molecular shape, including branching. The relation accounted for samples of different resin producers, molecular weights (65,000–638,000), and polydispersities (2.9–20). The use of the branching parameter for the correction of the molecular weight allowed the correlation of these parameters despite differences in the technologies, molecular weights, and molecular architectures. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 1572–1578, 2007

Key words: melt; molecular weight distribution/molar mass distribution; polyethylene (PE); structure-property relations; viscosity

INTRODUCTION

There are virtually thousands of polyethylene commercial grades with specific solid-state and flow properties that depend on molecular characteristics such as the average molecular weight, molecular weight distribution (MWD) curve, and branching. The melt flow index (MFI) is the most used parameter in industry as an indicator of the molecular weight and processability and is preferred over other parameters because of its rapid and simple determination (ASTM D 138-190/2.16). However, two polymers with the same MFI values often show different performances during processing or in the final product. There have been attempts to correlate the molecular weight data with the MFI,^{1–9} including the presence of nonpolymer compounds such as oils and monomers such as styrene. Wooden et al.⁵ reported the following equation:

$$\ln \text{MFI} = 22.15 - 3.79 \ln M_w + 0.255 (\text{Oil}) \\ + 0.189 (\text{Low}) + 0.495 (\text{Monomer}) \quad (1)$$

where M_w is the weight-average molecular weight. However, Todd and Enos⁸ reported the following:

$$\bar{M}_v = -8480.6 \times \ln \text{MFI} + 62,836 \quad (2)$$

$$\text{MFI} = C_i (M_w)^{C_j} \quad (3)$$

where M_v is the viscosity average molecular weight and C_i and C_j are constants determined by the catalyst technology. For polymers with bimodal MWD curves, a better fit was obtained with

$$\text{MFI} = 1.85E + 18 \left(\frac{M_w}{\text{PI}^{0.202}} \right)^{-3.65} \quad (4)$$

where PI is the polydispersity index. The reported equations are adequate only for polymers of equivalent architectures with similar polydispersity values and synthesis technologies. However, they do not account for changes found in polymers from different producers (technologies) and molecular architectures, such as linear and randomly branched polyethylenes. Chain branching affects the polymer melt and solution viscosities by promoting entanglements or reducing the radius of gyration; this modifies the flow characteristics and hence the MFI.

Most previous publications reported relationships between M_w and MFI for linear polyethylene and

Correspondence to: M. T. Rodríguez-Hernández (tere_rdz@ciqua.mx).

metallocene-catalyzed, branched structures. Some results for branched structures^{10–16} have shown that the MFI depends on the branching density and frequency for metallocene polyethylene with a narrow MWD. However, when commercial polymers are analyzed, the polydispersity can be broad. The use of gel permeation chromatography (GPC) coupled with a viscometer allows the simultaneous determination of the MWDs and branching characteristics,^{17–24} and in principle, these parameters can be correlated with the MFI. This article reports on the molecular architecture and data of the molecular weight averages and distributions, as well as results of long-chain branching degree, for 18 commercial polyethylene samples from 10 producers. The molecular characteristics were related to the MFI with the branching parameter determined by GPC for the correction of the molecular weight data.

THEORY REVIEW

Relation between the melt viscosity and molecular weight

The polymer melt viscosity is extremely dependent on the molecular weight; there are two regions²⁵ in a plot of the viscosity versus the molecular weight. Below a certain critical value, there are no entanglements, and the viscosity is dependent on the molecular weight; the slope of the line is 1.0. For very long chains, entanglements are important and increase the viscosity; there is an empirical relation between the zero-shear melt viscosity $[\eta(0)]$ and M_w :

$$\eta(0) \propto M_w^{3.4} \quad (5)$$

This is the well-known power law. A correlation between the MFI and M_w with a power-law equation has been obtained for linear (high-density) polyethylene for a given catalyst system in a single reactor and with a unimodal MWD but does not fit a multiple-stage reactor process with polymers exhibiting multimodal MWDs that change from product to product.

Modification of the viscosity by branching

Chain branching affects the melt viscosity, but its effect is difficult to quantify because the length and number of the branches, as well as their geometrical arrangement (stars, comb, or random), can vary. The branches long enough to form entanglements yield a higher zero-shear melt viscosity for the branched molecules compared with linear chains,^{14,26} although the solution viscosity decreases. Bueche²⁷ explained the solution viscosity reduction in terms of the ratio of the mean-square radius of gyration ($\langle s^2 \rangle$) for the

branched molecules over the linear molecules with the same molecular weight. From dilute solution theory, the branching parameter (g) is defined as follows (such that $g \leq 1$):

$$g = \langle s^2 \rangle_b / \langle s^2 \rangle_l \quad (6)$$

where subscript b represents branched molecules and subscript l represents linear molecules. The effect of branching on the intrinsic viscosity ($[\eta]$) is accounted in the following equation:

$$[\eta]_b = g[\eta]_l \quad (7)$$

That is, the viscosity of the branched structure is lower than that of the linear structure. In general, $[\eta]$ and the molecular weight²⁸ are related through either the following equation

$$[\eta] = 6^{3/2} \Phi_0 \frac{\langle s^2 \rangle_0^{3/2}}{M} \quad (8)$$

where M is the molecular weight, or the Mark–Houwink (M–H) relation:

$$[\eta] = KM^\alpha \quad (9)$$

where Φ_0 is a constant and K and α are constants for a given polymer–solvent pair. Moreover, the M–H relation is not valid for broad ranges of molecular weights as the slope changes. This is important particularly if multimodal polymers with broad molecular weight limits are studied. Accordingly, the determination of the branching characteristics of the molecules is important for a correct interpretation of the flow characteristics and differences.

Branching determination by GPC

Presently, the branching characteristics and MWD curves can be simultaneously obtained from the GPC data if a viscometer and refractive-index detector are used. The method is based on the Zimm–Stockmayer model.¹⁷

For linear polymers, the two constants of the M–H equation justify the $[\eta]$ law along the whole MWD. Molecules with short-chain branching can be described with the same α value used for the linear chain but with lower K values. For long-chain-branching molecules, a more elaborated model is required. The Zimm–Stockmayer model describes the relation of the mean-square radius of gyration of long-chain-branched or nonbranched polymers. This model can be combined with semiempirical relationships of the type $g' - g^\varepsilon$ [where ε is the form factor (structure) with values between 1/2 and 3/2] to produce the following equation:²⁹

TABLE I
Commercial Polyethylene Producers that Supplied the Polymer Samples

No.	Producer
1	Chemtex (subsidiary of the M&G group, Milan, Italy)
2	Chevron (Phillips Chemical)
3	Equistar Chemical Co.
4	Exxon Mobil Corp.
5	Paxon
6	Pemex SA de CV
7	Petrothene
8	Repsol YPF Chemical Division
9	Total Fina Elf

$$[\eta] = [\eta]_l(\lambda M/C_1 + \sqrt{1 + \lambda M/C_2})^{\varepsilon/2} \quad (10)$$

where C_1 is equal to $9\pi/4$ and C_2 is 7 for branching points with functionality $f = 3$, C_1 is equal to $3\pi/4$ and C_2 is 6 for $f = 4$, and λ is the branching density along the chain (Dalton branching probability) obtained by the division of the total number of branching points by the polymer molecular weight. Branching randomness makes λ independent of the molecular weight, and this is the main assumption in the model. With the M–H relation, the $[\eta]$ law for randomly branched polymers can be obtained:

$$\log[\eta] = \log K + \alpha \log M - \frac{\varepsilon}{2} \log(\lambda M/C_1 + \sqrt{1 + \lambda M/C_2}) \quad (11)$$

This equation is applied at each slice in the MWD of the polymer. From Eq. (10), $[\eta]$ is defined by four parameters: K , α , λ , and ε . According to this model, the low-molecular-weight (LMW) chains are essentially linear, and $[\eta]$ is asymptotic in this region.

Molecular weight/MFI relationship

Molecular weight data from GPC have been tested for correlation with the MFI, the parameter commonly used for the classification and selection of commercial polyethylene. In principle, the MFI is related to the melt viscosity because it corresponds to the amount of the polymer melt that passes through a die, under standard conditions of the length/diameter ratio, temperature, and weight, in 10 min. However, only the molecular weights of linear polymers with low or moderated polydispersity [weight-average molecular weight/number-average molecular weight (M_w/M_n)] have been properly correlated with the MFI. When viscosity data are obtained in line, even polymers with multimodal MWDs synthesized in multireactor equipment can be correlated. In this case, the MFIs predicted by

the molecular weight data are adequate even for samples with $PI = 25$. However, when this approach has been used for branched polymers, no correlation has been obtained.

EXPERIMENTAL

Materials

Commercial samples of polyethylene from 10 different resin producers were obtained and characterized. The reported architectures and nominal MFI values for the polymers are presented in Table I.

Molecular weight and branching determination

Molecular weight distributions were determined in a high-temperature Waters GPC2000 gel permeation chromatograph (Milford, MA) coupled with two detectors, a differential refractometer and a viscometer. A set of Styragel columns included one mixed linear bed column and one 10^3 -Å column. The analysis conditions were 145°C with 1,2,4-trichlorobenzene at a rate of 1.0 mL/min; the solution concentration was 1 mg/mL. Polyethylene samples were placed in a volumetric flask and heated to 170°C for 1 h to dissolve properly³⁰ and afterwards were filtered through metallic filters (0.5 μ) and injected (219.5 μL) into the chromatographic system.

Molecular weight determinations were carried out with a universal calibration curve with the reported values of the M–H constants for linear polyethylene ($K = 0.0003230$ and $\alpha = 0.735$).³¹ The determination of the branching parameters for low-density polyethylene (LDPE) was carried out on the basis of the Zimm–Stockmayer model with Millennium 32 software in the chromatograph. The averages M_n , M_w , M_z , and $M_z + 1$ (where M_z is the z -average mole-

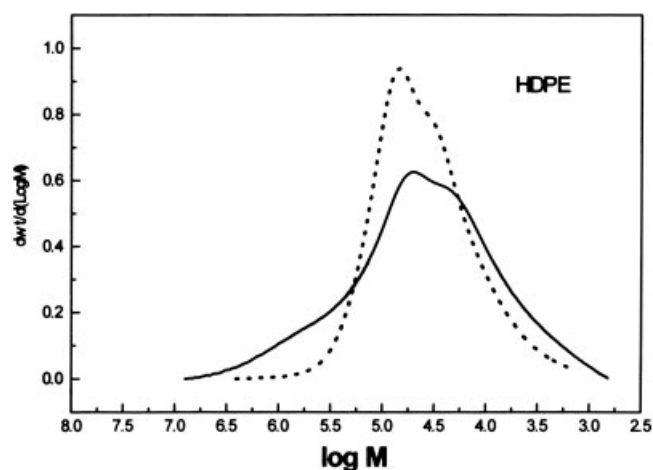


Figure 1 MWD of HDPE obtained by GPC for two samples.

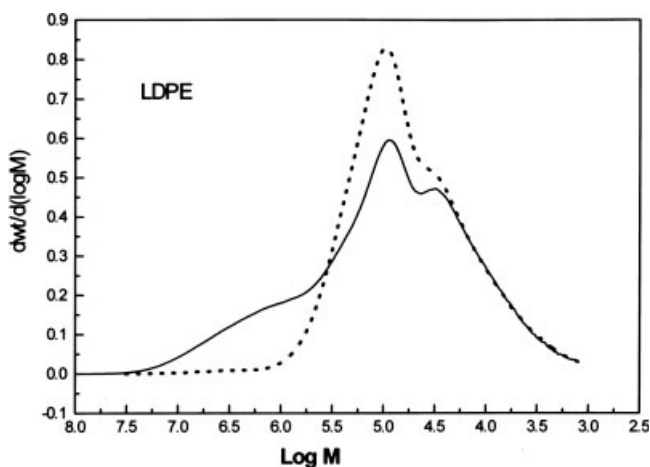


Figure 2 MWD of LDPE obtained by GPC for two samples.

cular weight) were obtained with the definition equations and are presented in the figures with the MWD.

Melt viscosity

The melt viscosity as a function of the shear rate was measured in a Instron 3211/138 capillary rheometer with a conical die (1.55 cm long, length/diameter = 31.1) at 190°C. The velocities of the piston were 0.03, 0.1, 0.3, 1.3, and 10 cm/min. The values at zero shear were obtained by the extrapolation of the curves obtained with these data.

MFI

The MFI measurements were carried out with a Kayeness, Inc., model 7053 plastograph with 2.16 kg at 190°C according to ASTM D 138-190/2.16. The reported values are the averages of five independent measurements.

RESULTS AND DISCUSSION

The MWDs of the polymers, determined by GPC with refractive-index and viscometer detectors, were unimodal or bimodal. Multimodal MWDs are obtained with two-stage reactors or different catalysts such as Ziegler–Natta or metallocene catalysts, and they are presently designed to obtain specific physical properties. Two MWDs are presented for high-density (Fig. 1) and low-density (Fig. 2) samples; these were selected in terms of the maximum and minimum polydispersities. The maximum in the MWD curves was around 100,000 g/mol, but the limit for high-molecular-weight (HMW) species was approximately 7.72×10^6 g/mol, although these species were found only in the low-density samples. On the LMW side, the curves showed molecular species down to 1000 g/mol, and some samples showed a small signal around 300 g/mol, corresponding to a wax. This is important because later results showed behavior modifications that might be associated with these extreme values. The branching factors were obtained directly from the GPC data; in Figure 3, the plot shows the MWD, viscosity, and branching factor for an LDPE sample.

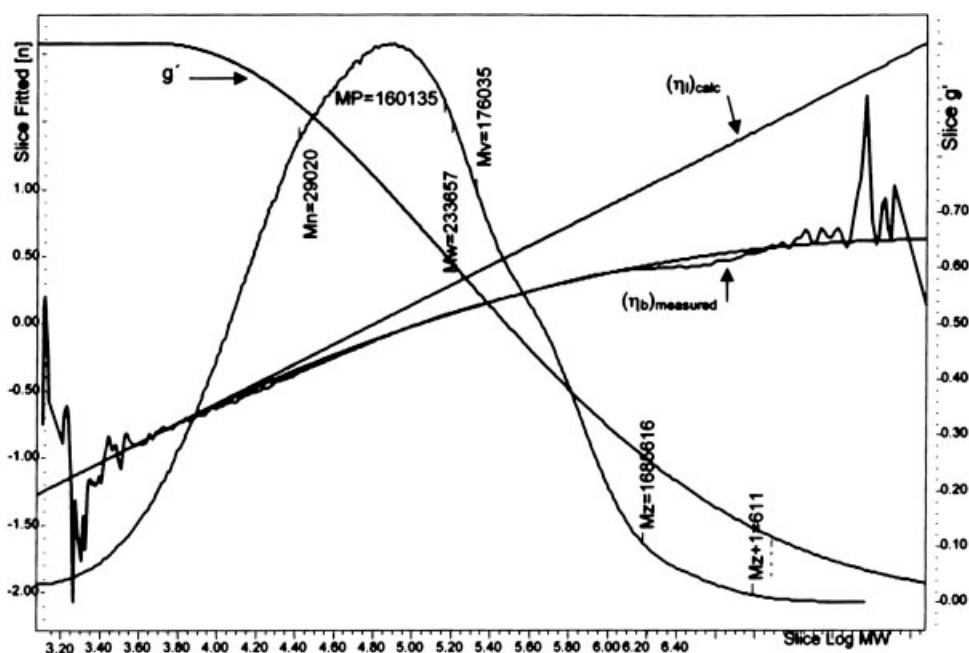


Figure 3 Molecular weight and branching parameter data for LDPE samples.

TABLE II
Molecular Characteristics of the Commercial Polyethylene Samples from the Nine Different Producers

Sample	MWD	MFI	M_w (g/mol)	g'	PI	η_0 (P)	Density (g/cm ³)
HDPE1	Multimodal	0.196	158,094	1	13.2	176,929	0.961
HDPE2	Unimodal, skewed to LMW	0.292	122,608	1	4.6	145,245	0.955
HDPE3	Unimodal, skewed to LMW	0.3	136,936	1	5.7	150,453	0.955
HDPE4	Unimodal, skewed to HMW	0.32	135,637	1	4.6	147,130	0.947
HDPE5	Unimodal	0.344	117,121	1	4.3	191,602	0.955
HDPE6	Unimodal, skewed to LMW	0.74	104,037	1	4.5	102,141	0.950
HDPE7	Unimodal, skewed to LMW	0.765	109,887	1	5.16	162,517	0.955
HDPE8	Unimodal	6.23	69,935	1	3.4	13,624	0.955
HDPE9	Bimodal	5.14	96,000	1	7.3	75,666	0.96
HDPE10	Unimodal	13.8	64,874	1	3.2	6,799	0.947
LDPE1	Bimodal	0.22	380,000	0.48	11.0	202,116	0.918
LDPE2	Unimodal	0.373	523,000	0.37	17.53	206,253	0.922
LDPE3	Unimodal	1.83	138,193	0.60	4.7	71,664	0.921
LDPE4	Unimodal, skewed to LMW	2.15	155,700	0.65	5.1	106,611	0.920
LDPE5	Bimodal	2.07	203,998	0.52	6.3	69,008	0.921
LDPE6	Bimodal	6.4	638,538	0.24	20.2	87,398	0.918
LDPE7	Bimodal	0.323	225,498	0.6	11.7	214,092	— ^a
LDPE8	Unimodal	2.381	113,630	0.7	6.3	57,465	— ^a

^a Not determined.

The measured molecular characteristics of the studied polymers are presented in Table II. The values for the molecular weight averages (M_w and M_n) as well as the polydispersities were different for the samples because of the MWD differences. M_w ranged from 70,000 to 649,000, and PI was 3.3–20.2. The branching parameters for the low-density polymers varied from 0.24 to 0.76, and the polymer densities varied from 0.918 (LDPE) to 0.96 [high-density polyethylene (HDPE)]. The MFIs were in the range of 0.2–6.4, whereas the melt viscosity ranged from 6102 to 80,205 P. These data show, as expected, broad differences in the structures (branching) and molecular weights for the polymers; this is related to the synthesis process and conditions. Both the polydis-

persity and branching were dependent on the molecular weight, as shown in Figure 4; for low-density polymers, the branching and polydispersity increased with the molecular weight.

Correlation between the molecular weight and MFI

The variation of $1/\text{MFI}$ as a function of M_w for (linear) HDPE is presented in Figure 5. There is a general tendency for the MFI to decrease as the molecular weight increases, which is the expected behavior and agrees with other authors' reports.⁵ In our case, the equation for the linear relationship was

$$1/\text{MFI} = -4.04114 + 0.00006 M_w \quad (12)$$

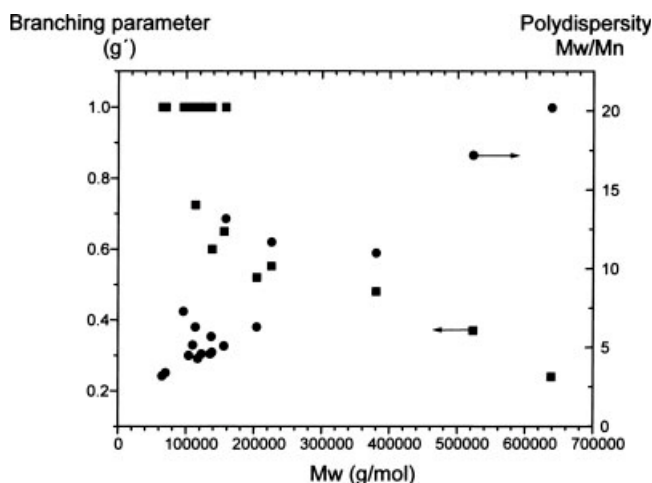


Figure 4 Branching parameter and polydispersity as functions of the molecular weight for commercial LDPE and HDPE.

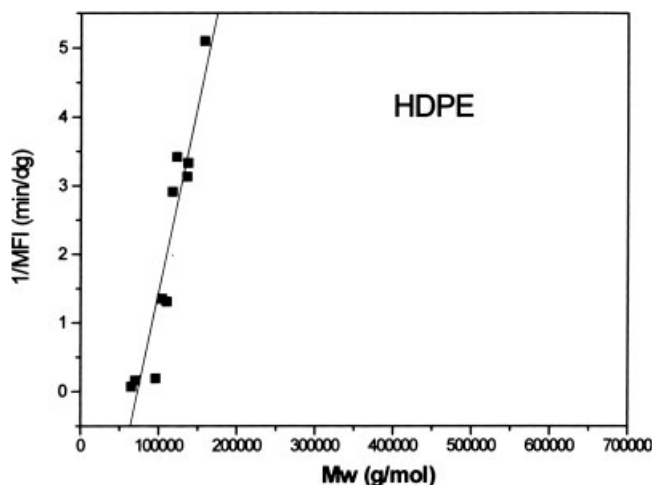


Figure 5 MFI as a function of the molecular weight for commercial HDPE.

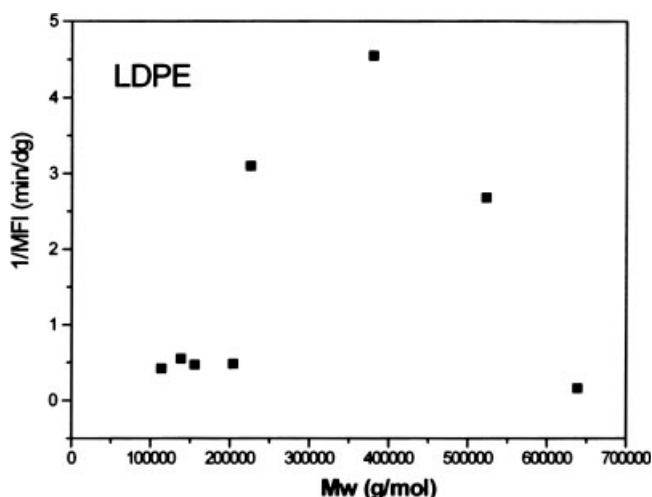


Figure 6 MFI as a function of the molecular weight for commercial LDPE.

This equation is valid for linear samples with polydispersities in the range of 3.2–13.2. However, when the data for LDPE were plotted (Fig. 6), there was no correlation. This is a common problem when data are compared from different polymers and indicates that other parameters apart from the molecular weight affect the MFI and have not been considered. The basic difference between LDPE and HDPE is the branching produced during the polymerization process by free radicals due to back-biting and chain transfer. Branching may be short- or long-chain; the first affects the polymer density, whereas the second modifies the viscosity and hence the flow characteristics and MFI. The main effect of branching is a reduction of the molecular size measured as the radius of gyration²⁷ because of the reduction of available freedom degrees; hence, the free volume is also reduced.²⁸ The molecular shape may also be modified when the number of branching points is increased and their position within the polymer molecule is changed. Accordingly, we believe that the reduction of the radius of gyration promoted by branching and a factor form are required to correlate the molecular weight and MFI for LDPE.

To consider the branching characteristics associated with low density, we modified the molecular weight, multiplying it by the branching factor (g') obtained by GPC, and we elevated the product to the 3/2 power, considering a structure factor as in Eq. (11). All data were plotted again as a function of the branching-corrected M_w (Fig. 7). The correction effect is evident as all points were close to the line; this indicates that the assumption that the branching and shape sensitively affect the MFI is adequate. The obtained equation is

$$1/\text{MFI} = -3.4066 + 0.00005 M_w g'^{3/2} \quad (13)$$

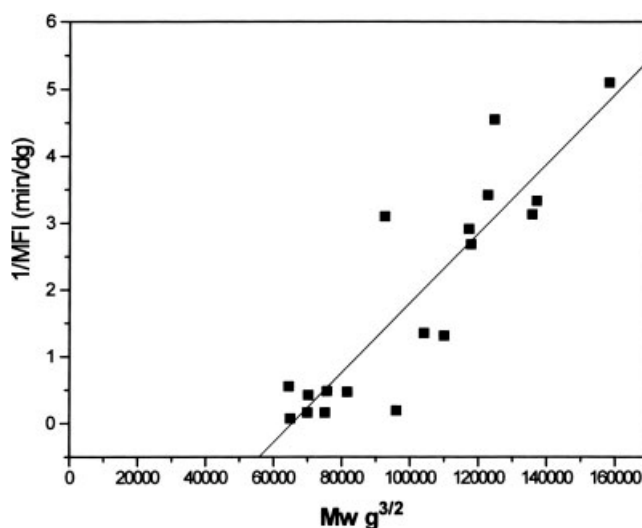


Figure 7 MFI as a function of the branching-corrected molecular weight for commercial LDPE and HDPE.

To corroborate the relation between the molecular weight and viscosity mentioned in eq. (5), the data were plotted and are presented in Figure 8. Again, the high-density data correlate well, but the low-density data do not. In the plot, the arrows indicate points that lie far off the limit. The equation for HDPE is

$$\eta_0 = 46,751.55 + 3.4482 \times 10^{-13} M_w^{3.4} \quad (14)$$

where η_0 is the zero-shear melt viscosity.

This equation is similar to that reported by Raju et al.,³² $\eta_0 = 3.3 \times 10^{-15} M_w^{3.6}$, for narrow-MWD HDPE polymers. However, our equation is valid for linear and branched polymers. When the branch-corrected molecular weights were used, it was not

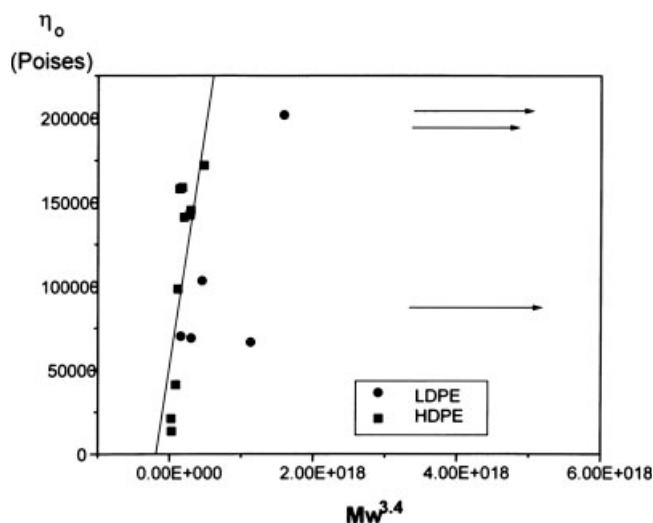


Figure 8 Zero-shear viscosity versus the molecular-weight power-law plot for commercial LDPE and HDPE.

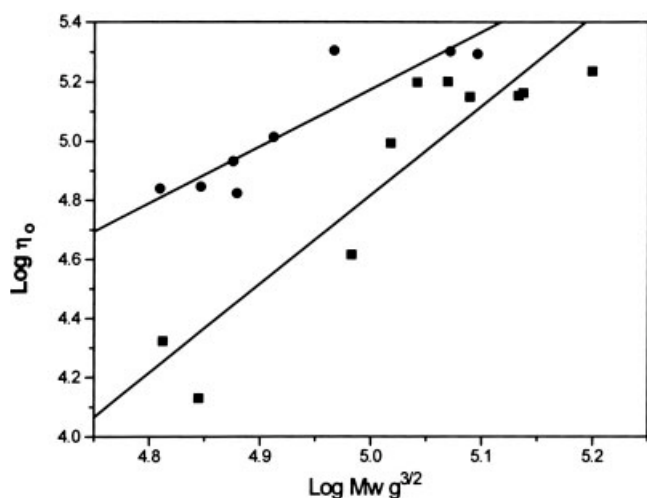


Figure 9 Zero-shear viscosity versus branching-corrected M_w for commercial LDPE and HDPE.

possible to obtain a single relation as with the MFI (Fig. 9), but two lines were obtained, one for the high-density polymers and another for the low-density polymers. The following equations were obtained:

$$\text{HDPE: } \log \eta_0 = -4.19501 + 1.9489[\log(M_w g^{3/2})] \quad (15)$$

$$\text{LDPE: } \log \eta_0 = -4.443 + 1.9239[\log(M_w g^{3/2})] \quad (16)$$

The polydispersity of the samples ranged from 3.3 to 20.2. It has been reported that the presence of branches in the polymer induces an increase in the zero-shear viscosity.^{14,15,27} Gabriel et al.¹⁵ reported higher viscosities for narrow-MWD, branched, metallocene-catalyzed ethylene copolymers. Our results are in agreement with their report as the branched polymers showed higher viscosity than the linear polyethylenes.

CONCLUSIONS

The commercial LDPE and HDPE studied had very different molecular weight averages and distributions as well as branching characteristics besides the linear and branched structures. This led to severe differences in the viscosity and MFI data, particularly for LDPE.

The MFI of the linear (HDPE) polymers correlated well with the molecular weight averages despite differences in the polydispersities, which ranged from 3 to 13. For branched (LDPE) polymers, it was not possible to define a direct correlation.

When the molecular weight was corrected by the consideration of the branching parameters obtained by GPC and a form factor, the MFI data correlated with the MFI despite structural and molecular weight differences.

The zero-shear viscosity was correlated with the molecular weight, but the chain-structure differences generated two lines, one for linear molecules and another for branched molecules.

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