

Investigation of the Molecular Weight of Polyethylene Using Rheological Techniques

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ABSTRACT: The zero shear viscosity (η_0), relaxation time, relaxation spectrum index (RSI) of 20 metallocene-catalyzed, and conventional polyethylenes are presented. The effect of molecular weight (M_w) determined by gel-permeation chromatography on rheology parameters was analyzed. The dependence of zero shear viscosity or relaxation time on molecular weight allowed the polyethylene samples to be separated into three different groups and different values of parameter in $\eta_0 = K(M_w)^\alpha$ were obtained, respectively. Two groups of polymers display viscosity deviation from linear relationship and the reason was attributed to different level of long-chain branching and high-molecular weight

tails. The intrinsic reason was disclosed when relaxation spectra at frequencies between 1 s and 10 s were involved and RSI was used for quantitative analysis. Thus, an alternative single rheological method, based on the effect of molecular structure on dynamic rheological behaviors, was proposed to evaluate the molecular weight of polyethylene. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 000: 000–000, 2012

Key words: polyethylene; rheology; molecular weight; zero shear viscosity; relaxation spectrum

INTRODUCTION

The uniqueness of a polymer is most frequently measured and expressed in terms of molecular weight (M_w), molecular weight distribution (MWD), and degree of branching. It is important to elucidate these aspects of molecular structure of polyolefins both in the production of polymers and their end-use properties. It is well known that besides the dependence of the rheological behavior on external parameters such as shear rate and temperature, the rheological properties of polymer melts are strongly affected by the molecular structure.^{1–3} Since the rheological testing has its own advantage compared with gel permeation chromatography (GPC), temperature rising elution fractionation (TREF), ¹³C-NMR, etc, it is necessary to get some insight into the relationship between rheological properties and molecular characteristics of polyolefins.⁴

Using molecules structure parameters and dynamic rheological data correlation to assess the molecular characteristics of polyethylenes is a practicable

method to avoid complicated computation based on various models if right samples are analyzed. The influence of M_w on the zero shear viscosity (η_0) has been a subject of many investigations. Most of these investigations are based on equation $\eta_0 = K(M_w)^\alpha$, but different values for the parameters have been reported in the literature. Garcia-Franco et al. mentioned of a equation for linear polyethylene (PE) without branches that had been found not only from extensive experimentation but also from some simulations⁵: $\eta_0 = 6.04 \times 10^{-14} M_w^{3.33}$. The correlation proposed by Raju et al. is $\eta_0 = 3.4 \times 10^{-15} M_w^{3.60}$. This equation has been shown to be valid for conventional high-density polyethylene (HDPE), which due to the nature of Ziegler–Natta catalysts does not present long-chain branching (LCB).⁶ Based on the investigation of nine commercial metallocene linear low-density polyethylenes (four ethylene–butene copolymers and five ethylene–octene copolymers), Hussein et al. obtained equation $\eta_0 = 2 \times 10^{-15} M_w^{3.7}$. It was also referred that the data for the different metallocene polyethylenes (mPEs) with different branch chain were somewhat scattered.⁷ Although method was also employed to deal with this problem by introducing the molecular weight per backbone bond as a normalizing variable of weight-average molecular weight⁵ or by model calculation,⁸ generalized formulation was still required concerning the relationship between zero shear viscosity and molecular weight of polyethylenes.

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TABLE I
Characterization of Conventional and Metallocene Polyethylene Samples

Sample ID ^a	Resin type	MI (g/10 min)	Density (g/cm ³)	M_w	M_w/M_n	BC ^b (CH ₃ /1000 C)
LDPE ^c	LDPE	1.90	0.9218	84,700	4.25	13.5
HDPE ^c	HDPE	0.05	0.9536	138,700	18.55	5.1
LLDPE ^c	LLDPE	0.71	0.9250	83,700	3.89	10.1
mPE1 ^c	mLLDPE	0.98	0.918	107,400	2.77	11.1
mPE2 ^c	mLLDPE	1.06	0.9178	134,000	3.29	11.6
mPE3 ^c	mLLDPE	2.6	0.9183	96,600	2.16	11.5
mPE4 ^c	mLLDPE	0.96	0.9174	131,700	2.85	10.5
mPE5 ^c	mLLDPE	0.98	0.9155	98,000	2.80	13.4
mPE6 ^c	mLLDPE	3.12	0.9280	84,000	2.37	8.9
LM1 ^e	mLLDPE	1.08	0.9326	113,000	4.0	8.6
LM2 ^e	mLLDPE	0.375	0.9339	109,000	2.6	3.9
LM3 ^e	mLLDPE	1.37	0.9204	101,000	2.9	10.7
LM4 ^e	mHDPE	6.48	0.9481	67,000	6.2	4.6
LM5 ^e	mHDPE	0.073	0.9439	173,600	3.16	2.4
LM6 ^e	mHDPE	0.053	0.9444	209,700	2.83	2.5
LM7 ^e	mLLDPE	0.37	0.9353	143,000	2.7	–
LM8 ^e	mLLDPE	1.34	0.9390	111,000	1.9	3.2
LM9 ^e	mHDPE	3.44	0.9417	88,000	3.4	4.5
LM10 ^e	mLLDPE	2.86	0.9297	99,000	2.0	5.7
LM11 ^e	mLLDPE	5.12	0.9284	84,000	2.8	7.3

^a c represents commercial polymer; e represents experimental polymer.

^b Short chain branching content by means of FTIR.

Misleading observations regarding the influence of different structure parameters on the rheological behavior of polyethylenes was proved a hindrance to a successful result. The influence of branching or MWD on the viscoelastic behavior of polyethylenes is always observed, as reported by Wood-Adams et al.^{9,10} So the central problem in the rheological characterization is how to separate the effects of molecular weight, MWD, and LCB.

In this study, we would like to investigate the correlation between molecular parameters and the rheology of polyethylenes. First, The weight-average molecular weights (M_w) as well as MWD were obtained by GPC. Then the viscoelastic behavior was studied and correlated with M_w .

EXPERIMENTAL

Materials

Twenty polyethylenes were studied in this work. Nine samples are commercial blown film grades in pellet form, including six mPE, produced by Exxpol technology in gas phase process using metallocene catalyst, one low-density polyethylene (LDPE), produced by Basell's Lupotech T technology using peroxide initiator, one HDPE, produced by Basell's Hostalen technology in slurry process using Ziegler-Natta catalyst, and one linear low-density polyethylene (LLDPE), produced by Unipol technology in gas phase process using Ziegler-Natta catalyst. In addition, eleven laboratory-produced metallocene polyethylenes (LM) provided by Mr. Wang Xiong were

also used. These samples were prepared via a metallocene catalyst system of silica gel supported (1-Me-3-*n*-BuCp)₂ZrCl₂/methylaluminoxane (MAO) following the method reported in Ref. ¹¹. Polymerization was done in 10-L kettle under slurry process at 70°C, 0.8 MPa, and hexane was used as solvent. All of these noncommercial samples are copolymers of ethylene and hexene except for LM6 and LM7, which were homopolymers of ethylene. Reactor powders were stabilized with adequate amount of antioxidants (2500 ppm Irganox B561) and pelletized with a HAAKE PolyLab QC extruder, where the temperature was 220°C in the barrel and 200°C at the die, except for polymers LM6 and LM7, which were extruded at higher temperature (barrel, 240°C, and die, 210°C). Properties of the resins such as the melt index (MI), density, weight-average molecular weight, MWD, and short-chain branching content (BC) are given in Table I.

Measurements

The MI was measured in accordance with ISO-1133 using a 2.16 kg load, at a melt temperature of 190°C. Density was determined according to ISO-1183 in a density gradient column, consisting of a water-isopropyl alcohol mixture, at a constant temperature of 22°C. The weight-average molecular weights (M_w) as well as MWD which represents by the ratio of molecular weight by weight (M_w) and molecular weight by number (M_n) were obtained by GPC. GPC data were collected using 1,2,4 trichlorobenzene as solvent at 150°C in a WATERS GPC2000 instrument

equipped with four mixed-bed columns (Waters Styragel HT5, HT4, HT3, HT2) and refractive index detector. Calibration was performed against narrow MWD polystyrene standards purchased from Polymer Laboratories and a broad linear polyethylene standard (Phillips Marlex BHB 5003). An injection volume of 220 μL was used with a nominal polymer concentration of 0.3 g/L, and the flow rate was 1 mL/min. In addition, all the PE samples were characterized by FTIR for short-chain branching content ($\text{CH}_3/1000 \text{ C}$) in accordance with ASTM D6645, which determines the methyl content of a polyethylene based on the absorbance at 1378 cm^{-1} from a pressed plaque. Details of the characterization results are presented in Table I.

Rheological measurements were made using the dynamic rheometers AR-G2 (TA Instruments). The geometry used was parallel plates with diameter 25 mm. The gap was set at 1 mm. A circular disk of PE specimens was prepared by compression molding at 180°C . Experiments were conducted at 190°C and small-amplitude oscillatory shear flow functions, dynamic viscosity, η^* , storage modulus, G' , and loss modulus, G'' , were obtained in the frequency range 0.01–100 Hz (0.0628–628 rad/s). The strain was 1%, which belongs to the linear viscoelastic region, located by the aid of a previous dynamic strain sweep test. Zero-shear viscosity was determined by using the TA Data Analysis software to fit complex viscosity data to cross models. Steady-state shear measurement was also done for comparison using AR-G2 and same geometry was used. Testing was also conducted at 190°C and the viscosity was obtained in the shear rate range $0.001\text{--}10 \text{ s}^{-1}$.

RESULTS AND DISCUSSION

Nascent polyethylene resins are sensitive to crosslink or degradation reaction at high temperature, and remarkable viscosity drop may be observed at low frequency.⁷ To minimize thermally induced chemical changes, the experimental specimens were kept in a nitrogen atmosphere during the rheological test and antioxidant should be added. Normally, 0.1% (1000 ppm) of primary and secondary antioxidants is used commercially for polyolefin stabilization and result was found that 1000 ppm was sufficient to protect the resin from degradation.⁷ Here, adequate amount of antioxidant (2500 ppm) were added to laboratory-produced metallocene polyethylenes resins used in this study. The presence of antioxidant caused the rheology of sample resins to show the typical Newtonian plateau in the viscosity curve.

To get zero shear viscosities, the dependence of dynamic complex viscosity (η^*) on frequency (ω) for polyethylene samples was firstly transformed to the dependence of apparent shear viscosity (η_a) on shear

rate (γ) through the Cox–Merz relationship ($|\eta^*(\omega)| = \eta_a(\gamma)|_{\gamma=\omega}$), and secondly by fitting the dependence of apparent shear viscosity (η_a) on shear rate (γ) to Cross model ($\eta_a = \frac{\eta_0}{1+(\lambda_0 \bullet \gamma)^{1-n}}$). Model parameters such as zero shear viscosity, η_a , and relaxation time, λ_0 , are given for different resins in Table II.

Curves of complex viscosity vs. shear viscosity were given for some samples (Fig. 1), so as zero shear viscosity obtained by fitting data of steady-state shear measurement to Cross model (Table II). Based on these curves, we can see that the zero shear viscosities were well reached by oscillatory shear tests. Comparison of zero shear viscosity values calculated from steady-state shear measurement with oscillatory shear testing not only validate the accuracy of the Cross model for these materials, but also help convince us that the Cox–Merz relationship applies to these materials at lower shear rates.

Figure 2 shows the zero shear viscosity (η_0) of these commercial and experimental polyethylene samples as a function of the weight-average molecular weight (M_w) as well as the η_0 (M_w) relationship based upon the linear model polyethylenes ($\eta_0 = 3.4 \times 10^{-15} M_w^{3.60}$).

As can be seen in Figure 2, the dependence of η_0 on M_w force us to classify the materials in three groups taking as reference the correlation proposed by Raju et al. Viscosities of the materials gathered in Group I of Table II approach to the values given by $\eta_0 = 3.4 \times 10^{-15} M_w^{3.60}$ (continuous line in Fig. 2), whereas for Group II a clear viscosity deviation, which is even more remarkable for Group III, can be observed. These three groups, which cannot be distinguished attending to MWD and short-chain branching level, are also defined by the dependence of relaxation time on M_w , as can be noticed by the remarkable differences found for each group in Figure 3.

The following facts must be taken into consideration to explain the differences found in η_0 and λ_0 for polyethylenes of apparently the same molecular architecture⁶: (a) depending on the conditions used in polymerization, single-site catalysts can give rise to LCB¹²; (b) experimental results obtained with conventional HDPEs and LLDPEs, which have been irradiated or treated with peroxides to promote very small levels of LCB, show an increase of linear viscosity; (c) high values of zero shear viscosity and the relaxation time for the onset of nonlinear behavior have been found in metallocene-catalyzed polyethylenes having small amounts of LCB, with respect to non-LCB polyethylenes; and (d) from a theoretical point of view it has been considered that the increase of zero shear viscosity found for branched polymers is caused by a slowing of the reptation along a backbone contour when long arms are present.

TABLE II
Rheological Parameters of Different Polyethylene Samples

Sample ID	η_0^a (Pa s)	η_0^b (Pa s)	λ_0^b (s)	RSI ^c	LCBI ^d
Group I ^e					
LM8	5238	5308	1.268	3.0	0.117
LM10		3756	0.00956	7.7	0.163
LM11	2094	2090	0.00864	6.7	0.208
mPE2		8954	0.02409	7.2	0.221
mPE3		3779	0.01167	6.8	0.172
mPE4		7919	0.02391	7.9	0.122
mPE6		2627	0.007672	5.4	0.164
Group II ^e					
mPE5		8768	0.02393	17.6	0.114
LM9	5149	5073	0.01693	16.4	0.179
mPE1	8591	8643	0.02809	15.3	0.144
LM1		9674	0.1456	22.2	0.462
LM3		8504	0.1445	20.1	0.493
LM4		1956	0.04028	19.2	0.434
LM7		27190	0.07901	19.0	0.498
Group III ^e					
LDPE		11220	1.083	121.0	1.021
HDPE	135670	135600	3.749	157.6	0.938
LLDPE		13260	0.1494	79.8	0.444
LM2	42860	42900	0.01602	53.4	0.742
LM5		207400	10.76	62.7	1.110
LM6		380600	28.2	75.9	1.151

^a Zero shear viscosity obtained by fitting data of steady-state shear measurement to Cross model.

^b Zero shear viscosity and relaxation time, λ_0 , calculated from oscillatory shear and Cross model.

^c RSI represents relaxation spectrum index calculated by TA Orchestrator software.

^d LCBI represents long chain branching index.

^e Different groups of samples which were classified according to the dependence of zero shear viscosity on molecular weight, and can be defined by RSI values.(Group I: RSI value below 10; group II: RSI value above 10 but below 30; group III: RSI value above 30.)

The approach of Group I materials to the viscosity data of non-LCB conventional HDPEs, given by $\eta_0 = 3.4 \times 10^{-15} M_w^{3.60}$ in Figure 2, allows us to assume that in these metallocene-catalyzed samples

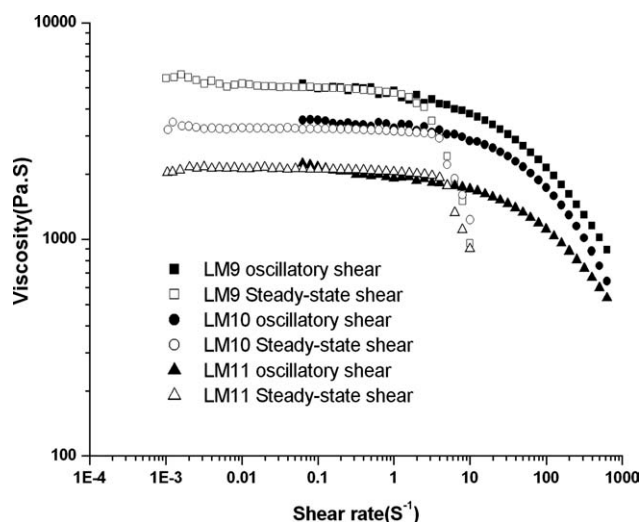


Figure 1 Curves of complex viscosity vs. shear viscosity for different polyethylene samples.

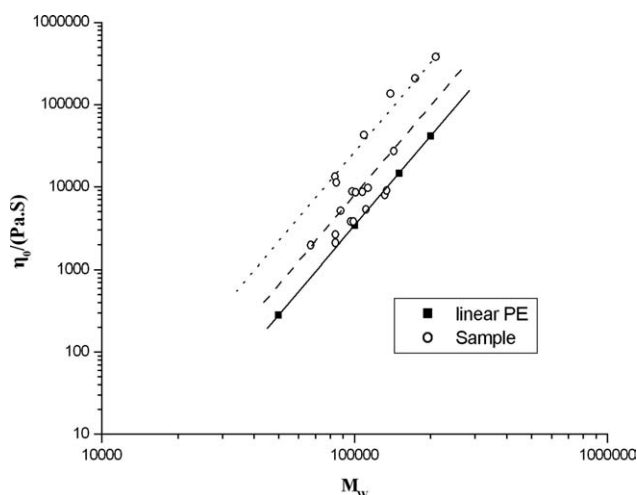


Figure 2 The zero shear viscosity dependence of molecular weight, M_w for different polyethylene samples. Group I: LM8, LM10, LM11, mPE2, mPE3, mPE4, mPE6, RSI value below 10; Group II: LM1, LM3, LM4, LM7, LM9, mPE1, mPE5, RSI value above 10 but below 30; Group III: LDPE, HDPE, LLDPE, LM2, LM5, LM6, RSI value above 30. The continuous line corresponds to equation $\eta_0 = 3.4 \times 10^{-15} M_w^{3.60}$. The other lines were drawn parallel to the continuous line to guide the eye and to define the groups of Table II.

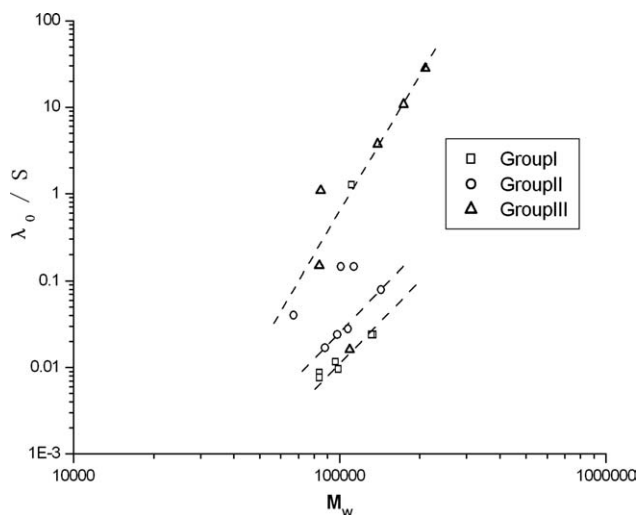


Figure 3 The relaxation time dependence of molecular weight, M_w for different polyethylene samples. See Figure 2 and Table II for definition of groups. Dashed lines were drawn to guide the eye.

LCB does not occur. The aforementioned both experimental and theoretical considerations lead also to the suggestion that probably different levels of LCB are present in Groups II and III, respectively.

According to the model developed by Bersted and coworkers,^{13,14} that considers the opposing effects of branching concentration and the reduction of the radius of gyration, the level of LCB of both Groups II and III samples must be below the branching level from which a decrease of the viscosity with respect to non-LCB is predicted. This model forecasts a maximum of the viscosity with LCB level at approximately 0.25 long branches/1000 C atoms and lower values of the viscosity with respect to non-LCB samples starting from approximately 1–2 long branches/1000 C atoms.

It is interesting to find that four out of six commercial metallocene polyethylenes belong to Group I, while laboratory-produced samples fall into three groups. From these facts we may deduce that processes of laboratory polymerization were not well controlled compared with those of commercial processes in terms of the absence of LCB. All three conventional polyethylenes belong to Group III, but the reason differs. For LDPE sample, reason may be attributed to LCB that occur during the free-radical polymerization of ethylene, and for HDPE and LLDPE sample, high-molecular weight tails and broad MWD due to polymerization processes employing Ziegler–Natta catalyst systems may be the causation.

Result can be found from the data in Tables I and II that which resins fall into each of the few group cannot be defined according to MWD values. The MWD values of most samples were at close range

due to the metallocene-catalyzed sample we chose. MWD was obtained by GPC, and the accuracy of integral calculation depends on the area selected to a certain extent. So, the high-molecular tails is much more important than the MWD values, which can be seen from LLDPE data. The MWD value of LLDPE is slightly larger than that of all samples in Group I, but their rheological behaviors are apparently different.

Since density is directly influenced by short-chain branching, which have little effect on rheological behaviors, no obvious conclusion can be drawn on which resins fall into each of the few group according to density. However, it can be observed that resins with medium density fall into three groups, while metallocene-catalyzed resins with low density belonged to Groups I and II. The possible reason is that LCB or high-molecular tails is easier to come into being when the comonomer concentration is low during polymerization, which may be testified by the fact that homopolymers of ethylene, LM6, and LM7, belonged to Group III.

To quantify the levels of LCB, method proposed by Garcia-Franco was used. Long-chain branching index (LCBI) was obtained from equation $LCBI = 2.5085 - 2.8178 \times 10^{-2}\delta$, in which δ is phase angle measured from Van Gorp–Palmen plot at ($|G^*| = 10$ kPa).¹⁵ Values of LCBI were shown in Table II. LCBI values are low for samples in Group I and rather high for samples in Group III, revealing different content of LCB in these samples. It is interesting to observe that LCBI values differ for samples in Group II. Three samples such as mPE5, LM9, and mPE1 have low LCBI similar to that of samples in Group I.

The objective of this article is to propose a generalized $\eta_0(M_w)$ formulation for polyethylene. Although papers have reported polyethylene with different molecular structures have different $\eta_0(M_w)$ relationship, they did not outline any method for correcting the problem.^{5–7} It is well known that linear viscoelastic results are closely related to the molecular architecture of polymers, namely to molecular weight, MWD and chain branching. Physical models give a discrete relaxation spectrum that may be expressed by different decay time functions. The Maxwell model assumes that the relaxation modulus can be conveniently expressed as a set of exponential decays: $G(t) = \sum_{i=1}^n g_i \exp(-t/\lambda_i)$, where each relaxation mode is defined by a relaxation strength, g_i , and a relaxation time, λ_i . Using this equation and the constitutive equation of linear viscoelasticity theory, the dynamic moduli become^{6,12}:

$$G'(\omega) = \sum_{i=1}^n g_i \left[(\omega\lambda_i)^2 / (1 + (\omega\lambda_i)^2) \right] \quad (1)$$

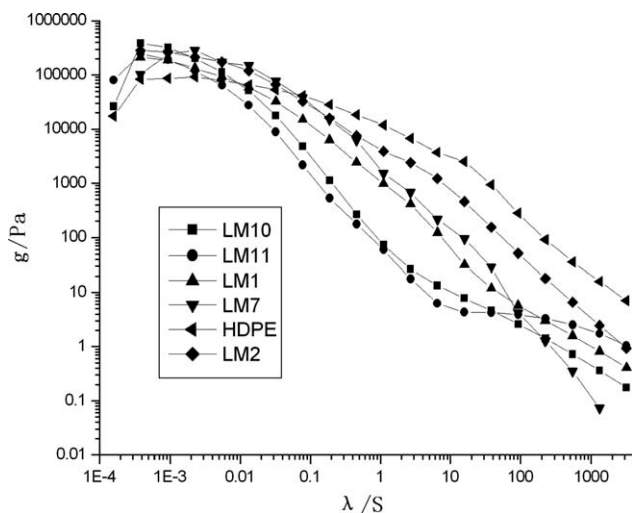


Figure 4 The relaxation spectrum of different polyethylene samples (twenty points per curve).

$$G''(\omega) = \sum_{i=1}^n g_i \left[\frac{\omega \lambda_i}{1 + (\omega \lambda_i)^2} \right] \quad (2)$$

By adjusting eqs. (1) and (2) to G' and G'' data, values of g_i and λ_i can be obtained. In our case, parameters of a discrete relaxation spectrum were calculated using the TA Orchestrator software, which transforms, by a nonlinear spectrum calculation method, G' and G'' data collected from the dynamic frequency sweep test. Number of points in spectrum was selected as 20. Relaxation time distributions of six materials, two of each group of Table II, are presented in Figure 4.

We observe that in the short-time region the spectra are similar, which suggests that the properties associated to high frequencies or short times are not affected by LCB or high-molecular weight tails, while relaxation strengths of different PEs in the long-time region trended diversely, that cannot be labeled according to their groups. On the other hand, relaxation strengths of different PEs in relaxation time between 1 and 10 s differed with each other. In general, resins in Group III showed highest values of relaxation strengths in comparison to the resins in Groups II and I in relaxation time between 1 and 10 s. The relaxation strength of modes on the narrow range 1–10 s is determined mainly by the limited molecular mechanisms. This may be attributed to the molecular entanglement on the relaxation behavior of these resins, which is because of LCB or high-molecular weight tails. Either LCB or high-molecular weight tails increase the intermolecular or intramolecular entanglement, which would inhibit each molecule to relax and high-relaxation strengths were observed in molten state. This difference cannot be distinguished from molecular characterization

of polymers, whether it is molecular weight, MWD, or chain branching, and additional rheology tests, such as nonlinear rheology may be performed for further study.

It would be interesting to see how the discrete relaxation spectrum look if the interval is 1–2 point per decade, so number of points in spectrum was selected as 10 for comparison (Fig. 5). Results can be found that spectrum curves with different number of points have the same trend.

The relaxation spectrum index (RSI) can be used for quantitative analysis of discrete relaxation spectrum and values are presented in Table II. This rheological index was introduced by Wasserman to take into account the effect of the breadth of the MWD and LCB level on the relaxation time distribution.¹² It is defined as the ratio of the second moment g_{11} to the first moment g_1 of the relaxation time distribution: $RSI = g_{11}/g_1$, where the respective moments are:

$$g_1 = \frac{\sum g_i}{\sum g_i/\lambda_i} \quad (3)$$

$$g_{11} = \frac{\sum g_i \lambda_i}{\sum g_i} \quad (4)$$

where the values of g_i and λ_i were obtained by adjusting the experimental G' and G'' data to the generalized Maxwell model, eqs. (1) and (2).

Report had been published which indicated the RSI constituted a measure of the elasticity.¹² The elasticity of polymer melt is related to entanglement of molecular chain, which can be enhanced by LCB and high-molecular weight tail, so RSI values can be used to define the groups in Table II to take into account the influence of LCB or high-molecular weight tail on zero shear viscosity.

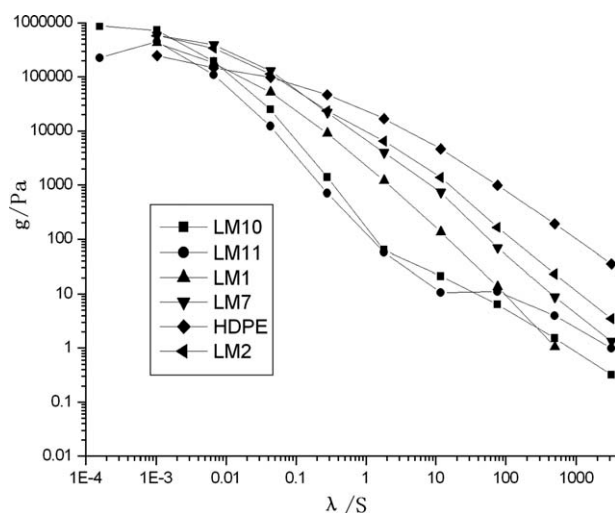


Figure 5 The relaxation spectrum of different polyethylene samples (ten points per curve).

As can be seen from Table II, the RSI values of samples in Group I are all below 10, while RSI values of samples in Group II are between 10 and 30, and RSI values of samples in Group III are all above 30 due to the aforementioned reason. Then different group can be defined according to their RSI values although the RSI value used to define the boundary of different group, such as 10 and 30 is empirical to some degree.

The zero shear viscosity data of PEs in Table II and molecular weight data of PEs in Table I were fitted to the well known equation $\eta_0 = K(M_w)^\alpha$ by regression analysis using excel software which indicate that PEs in Group I (low RSI value, below 10) are well adjusted to the equation $\eta_0 = 5 \times 10^{-11} M_w^{2.7729}$ (correlation coefficient is 0.9797), while PEs in Group II (medium RSI value, above 10 but below 30) are well adjusted to the equation $\eta_0 = 1 \times 10^{-13} M_w^{3.3453}$ (correlation coefficient is 0.9742). On the other hand, the data of PEs in Group III (high RSI value, above 30) are correlated by the equation $\eta_0 = 2 \times 10^{-15} M_w^{3.8341}$ (correlation coefficient is 0.9770). The calculated values of the exponent cover that reported for different PEs as referred before. Therefore, the feasibility of characterization the M_w of polyethylene by rheological method was proved.

It should also be point out that, before widely application, large numbers of data from polyethylene with different structures are needed to validate the RSI criterion of group definition as well as to amend the proposed empirical equations of zero shear viscosity vs. molecular weight.

CONCLUSIONS

Linear rheological behaviors of metallocene and conventional polyethylenes were successfully investigated and correlated to M_w . The increase in M_w has increased the zero shear viscosity, and different trends were observed for polyethylenes in different groups. Relaxation spectrum was very helpful in classifying samples. These facts are presumably due

to the presence of very small amounts of LCB in metallocene-catalyzed samples and high-molecular weight tails in Ziegler–Natta catalyst samples.

Furthermore, this work provides scaling relationships between the molecular weight and zero shear viscosity, and samples can be classified according to their RSI values. If these relationships holds true universally, the molecular weight of polyethylene can be demonstrated by robust and relatively fast experimental techniques suited for a high throughput experimentation environment as well as the manufacturing plant.

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