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New aspects on the rheological behaviour of metallocene catalysed polyethylenes

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Abstract

In this article, the linear viscoelastic properties of a family of metallocene-catalysed ethylene homopolymers and ethylene/1-hexene copolymers near the 'plateau' and in the terminal regions have been measured. The zero shear viscosity and relaxation time both scale to 3.41 power of the molecular weight, as is observed for most of the linear polymers. At the same time, no rheological signs associated with the presence of long chain branching are detected. However, an unexpected low value of the plateau modulus has been found. This result is discussed in terms of a possible decrease in the entanglement density and/or an increase in chain flexibility with respect to other model polymers. A simple method, previously tested in the literature, based on simplified molecular dynamics, enables a correct description of the dynamic modulus from the knowledge of the form of the molecular weight distribution and the material rheological constants G_N^o and η_o. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Viscoelastic properties; Newtonian viscosity; Plateau modulus

1. Introduction

The successful application or testing of fundamental rheological principles to polymers are closely linked to the degree of accuracy in the description of the molecular architecture of the system under study. Among the polyolefin group, polyethylene (PE) family constitutes a good example of how the understanding of the viscoelastic response of the material parallels to the progress in the description of the molecular population involved. Indeed, industrial polymerisation of PE has constantly evolved following the needs of the products market by incorporating the current knowledge on new catalyst systems to the technological process. The overall result is a spectrum of more or less complex molecular population with one end defined by the commercial high-pressure low density PE (LDPE). In good sense, the other end of the spectrum should correspond to PE models obtained in selected labs either by fractionation of existing Ziegler–Natta products [1–4] or by hydrogenation of anionically polymerised polybutadiene [5–10]. Obviously, the latter are only available in small amounts to a few research groups and hence, the public scientific information disclosed is much more limited. Besides the difficulties associated to molecular complexity as described above, nowadays, rheology faces another threat linked to the technological demand in processing speed which requires the control of flow instabilities generated at the high deformation rates employed in the processing industry. Consequently, extrusion studies that involve relatively large amount of material are needed.

During the last decade, huge advances in the polymerisation mechanism took place with the use of single-site catalysts as an alternative route for the polymerisation of α-olefins [11]. Indeed, various types of organometallic-based catalysts were, and even now continue to be, the subjects of numerous studies. Particular attention needs to be given to the metallocene-based catalysts that have been successfully scaled to industrial plant production for the polymerisation of various degrees of PE and polypropylenes [12,13]. The existence of a single type of active centre in the catalyst leads to a high degree of molecular regularity as reflected in the case of PE by a relatively low dispersity number, the absence of long chain branching (LCB) and a homogeneous distribution of short chain branching (SCB) when a co-monomer is introduced [14]. Furthermore, LCB can be introduced in a controlled manner without broadening the MWD [15], as in the case of constrained geometry catalysts [12]. Due to the limitations on preparing monodisperse samples of polyethylene by fractionation or by

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hydrogenation of polybutadiene (PB), single-site catalyst has been proposed as a good alternative to obtain model polymers. Furthermore, various steps of the polymerisation reactions associated with this type of catalyst can be adequately computed by modern quantum mechanics tools. The results provide, in many cases, valuable initial information for the experimental work promoting the development of new catalyst systems as compared to other Ziegler–Natta catalysts [16,17].

Most of the rheological studies in the literature deal with the analysis of the possible presence of LCB [18,19] and its effect in viscoelastic or viscometric functions and in processability [20–22]. Linear polymers have also been studied. For the latter, the expected correlations between Newtonian viscosity, η_o, and molecular weight, M_w, have been found to hold. A power law exponent of 3.6 in η_o–M_w relationships has been repeatedly reported in mPE [18–21]. In the case of fractionated linear polyethylene (LPE) and linear monodisperse hydrogenated polybutadiene (HPB), values ranging from 3.36 to 3.64 has been found [1–8]. In general, these results have been considered to agree with the expected behaviour predicted by the reptation theory for linear, long chain branchless, monodisperse polymers [23,24], and with the predicted behaviour for the loss modulus, G'', in the terminal zone ($G'' \propto \omega$) by the linear viscoelastic model [25]. However, some rheological variables of major importance for the validation of theories such as the terminal relaxation time, λ_o, and the plateau modulus, G_N^o, are difficult to determine experimentally.

The linear viscoelastic model allows one to approach the value of the main relaxation time, λ_o, by the longest relaxation time of the generalized Maxwell model [25]:

$$\lambda_o = \lim_{\omega \to 0} \frac{G'}{\omega G''} = \eta_o J_e^o \tag{1}$$

where J_e^o is the recoverable steady-state compliance defined in a constrained recoil experiment. In general, the scaling laws predicted by both the general viscoelastic model and the de Gennes–Doi–Edwards theory [23,24], $G' \propto \omega^2$ and $G'' \propto \omega$, do not fully hold for PE in the usual frequency range [19]. For this reason, Newtonian viscosity and relaxation time are commonly estimated from viscosity experimental data by fitting to a given function and extrapolating to low frequencies. Different models are available in literature to obtain these characteristic values of the terminal zone [25,26]. For dynamic viscosity data, the various models take a general form given by:

$$\eta(\omega) = \frac{\eta_o}{\left[1 + \left(\frac{\omega}{\omega_o}\right)^A\right]^B} \tag{2}$$

with the parameters η_o, ω_o, A and B, where ω_o is the inverse of a relaxation time, τ_o, related to the main relaxation time, λ_o. Linear correlations between τ_o and η_o have been found for linear mPE [18,19,21], according to theoretical considerations by the reptation model for polymer melts containing linear molecules with narrow molecular weight distribution.

In the case of G_N^o values ranging from $1.4–1.9 \times 10^6$ for fractions of linear PE [4], conventional high-density polyethylene (HDPE) and linear low-density polyethylene (LLDPE) [27,28], and mPE obtained through constrained geometry metallocene catalysts [20], to $1.9–2.7 \times 10^6$ Pa for monodisperse HPB [5,9,10,29], can be found in the literature. The application of the theory of rubber elasticity yields a relationship between the characteristic value of the modulus and the critical length between entanglement points, M_e, and is most commonly described by the expression:

$$M_e = \frac{K\rho RT}{G_N^o} \tag{3}$$

where R is the universal gas constant, ρ the density, T the absolute temperature, and K is a constant with a value of 1 [30] or 4/5 [24] depending upon convention. Moreover, the entanglement molecular weight is related to the critical molecular weight and it is determined by the onset of the effect of entanglements in the viscosity function, $M_c = 2M_e$ [30]. Above this critical molecular weight, the Newtonian viscosity follows the power law relation $\eta_o \propto M_w^\alpha$ with $\alpha =$ 3.4–3.6. It has been suggested in literature that G_N^o is independent of polydispersity [31,32] and LCB [10,33–35]. However, these molecular features may cause a large extension of the terminal zone shifting it to higher frequencies and causing then, some uncertainty in the estimation of G_N^o. This parameter is also insensitive to temperature for linear polymers and to chain length for long chains, and varies with polymer chemical nature. A universal law seems to exist between this viscoelastic property and molecular dimensions [10,29]. Recently, it has been proposed a very simple power law equation relating entanglement parameters (plateau modulus, G_N^o, and entanglement molecular weight, M_e) with melt density, ρ, and chain dimensions [36,37].

In the present paper, a series of metallocene ethylene homopolymers and ethylene/1-hexene copolymers have been studied by rheological methods. Due to the characteristics of the polymerisation process, relatively homogeneous molecular features can be obtained and almost ideal rheological behaviour is expected for these materials. Newtonian viscosity, relaxation time and ‘plateau’ modulus have been obtained for the materials in the temperature range 130–190°C. The use of these rheological parameters together with the molecular features obtained by GPC allow us to explain the viscoelastic response of the materials by the use of a relatively simple molecular model [38]. This model is based on a chain relaxation time composed with an average molecular weight that establishes the effect of the environment where the molecule reptates.

Table 1
Molecular parameters of the polyethylenes studied

Sample	$[\eta]$ (GPC) (dl g^{-1})	M_w (g mol^{-1})	M_w/M_n	CH_3/1000C
mPEL1	0.87	65,000	3.6	0.0
mPEB1	1.39	109,000	2.0	7.30
mPEB2	–	129,000	2.0	12.0
mPEL2	1.79	152,000	2.3	0.0
mPEL3	1.83	170,000	2.2	0.0
mPEL4	2.00	173,000	2.1	0.0
mPEL5	2.05	185,000	2.2	0.0

2. Experimental

2.1. Materials characterization

The PE materials studied has been supplied as nascent powder by Repsol-YPF. The molecular parameters of the materials, M_w, M_w/M_n, were obtained by Size Exclusion Chromatography (SEC) using a 150 CV Waters GPC equipment coupled with differential refractive index and viscometer. The set up used to measure the polymer intrinsic viscosity was composed of an on-line 150R model high-temperature viscometer. For the SEC evaluation, the universal calibration procedure was applied using a set of polystyrene standards dissolved in TCB at 145°C. The level of SCB and the double bond content of the samples were determined by ^{13}C NMR in a Bruker DPX-300 NMR Spectrometer operating at 75 MHz and 100°C. Sample solutions of 20% (v/v) were prepared using deuterated benzene and 1,2,4-trichlorobenzene (TCB) with trimethylsilane as an internal standard. All this molecular and physical parameters are listed in Table 1.

2.2. Dynamic measurements

Small amplitude oscillatory measurements were carried out in a Polymer Laboratories MKII Torsion System Viscosimeter in the frequency range 10^{-2}–10^{2} Hz. The deformation was set around 10%, which belong to the linear viscoelastic region, located by the aid of previous amplitude sweeps. For all the samples, the measurements were performed at temperatures between 145 and 190°C for homopolymers, and between 130 and 190°C for copolymers. The experiments were carried out with test specimens of 30 mm of diameter and 1 mm of thickness moulded in a Schwabenthan Polystat 200T for 5 min at 160°C and at a nominal pressure of 150 bar. All samples have been stabilized against oxidation by adding 1% antioxidant Irganox 1010. Thermal stability of the samples has been tested by means of time sweeps at low frequencies (0.1–1 Hz) in the temperature range of study.

Table 2
Rheological properties of the polyethylenes studied

Sample	E_{ah}	E_{av}	η_o(Pa s)	τ_o (s)	$G_m \times 10^{-5}$ (Pa)	$G_N^o \times 10^6$ (Pa)
mPEL1	5.7	0.0	650	0.0076	–	–
mPEB1	6.9	0.9	4100	0.014	1.69	0.67
mPEB2	6.9	0.6	5500	0.018	1.62	0.65
mPEL2	5.4	0.0	16,000	0.050	2.60	1.01
mPEL3	4.6	0.0	22,500	0.083	2.60	1.00
mPEL4	4.3	0.0	27,000	0.094	2.50	1.03
mPEL5	4.8	0.0	33,000	0.117	2.50	1.09

3. Results and discussion

3.1. Time–temperature superposition principle

The data obtained at different temperatures have been shifted at 190°C using the method developed by Mavridis and Shroff [39] defining the shift factors, a_T and b_T, for the frequency and the modulus, respectively, obtained from different temperatures through an Arrhenius-type equation. The superposition of the data is excellent in all cases and no signs of thermorheological complexity have been observed. The corresponding values for the activation energy of flow, E_a, are listed in Table 2. The average value is 5.0 Kcal mol^{-1} for the homopolymers and 6.9 Kcal mol^{-1} for the copolymers. It is worthwhile to mention that the former value of the activation energy is somewhat lower than those previously reported for LPE (6.3 Kcal mol^{-1}). This relatively low value approaches the E_a level of very flexible chain polymers such as polydimethylsiloxane (3.5 Kcal mol^{-1}) [40]. As far as copolymers are concerned, they exhibit similar values to those reported for conventional LLDPE, decreasing with respect to the linear, generally attributed to the presence of SCB. The activation energy is known to be extremely sensitive to the presence of long branches in the polymer chain. For instance, in highly branched polyethylene (LDPE), an increase in E_a up to 18 Kcal mol^{-1} has been reported [39–41]. For long chain branched mPE, values ranging from 7 to 15 Kcal mol^{-1} has been observed [19,42,43]. The above low values of the activation energy of flow ought to be considered as a strong argument in favour of linearity as it has been pointed out by the majority of the numerous studies on this subject [39–41]. Only a recent work suggests the presence of LCB without a noticeable increase of E_a [44].

3.2. Newtonian viscosity and relaxation time

Complex viscosity master curves at 190°C for the samples studied are shown in Fig. 1. The superposition of the data collected at different temperatures was excellent in all samples. As it is well known, the values of zero shear viscosity, η_o, can be obtained from the curves of complex viscosity at low frequencies providing that the linear viscoelastic model is applicable [25]:

$$\eta_o = \lim_{\omega \to 0} \eta' = \lim_{\omega \to 0} \eta^* \qquad (4)$$

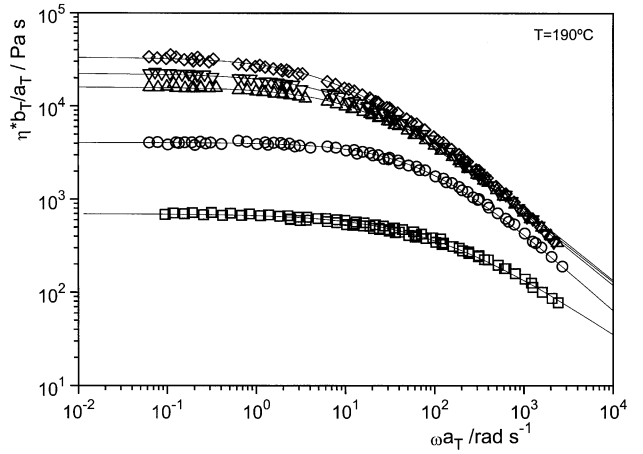

Fig. 1. Reduced dynamic viscosity against reduced frequency at $T_o = 190°C$ for the polymers studied. (□) mPEL1, (○) mPEB1, (△) mPEL2, (▽) mPEL3, (◇) mPEL5. The solid lines represent the fitting of experimental data to Eq. (5).

In general, as it has been indicated in Section 1, the scaling laws predicted by the general viscoelastic model and by the de Gennes–Doi–Edwards theory, $G' \propto \omega^2$ and $G'' \propto \omega$ do not completely hold for PE in the usual frequency range. Among the various available models, the Cross approach describes, quite well, our experimental results. Consequently, we have stuck to this fitting, since it contains the lower number of parameters. Thus, the general form of Eq. (2) takes the particular expression here:

$$\eta^*(\omega) = \frac{\eta_o}{1 + (\omega\tau_o)^A} \tag{5}$$

where η_o is the Newtonian viscosity and τ_o the relaxation time related to the longest relaxation time λ_o as defined in Eq. (1). The fitted values of η_o and τ_o are included in Table 2. In order to test the validity of the η_o values, a parallel creep experiment has been carried out in the highest viscosity sample. The result is coincident with that obtained by the application of Eq. (5).

Although most of metallocene catalysts yield strictly linear molecules, the high versatility of these catalysts permits under certain polymerisation conditions to incorporate small amounts of LCB [15,42,43]. Though the rheological consequences of incorporating small amounts of LCB are remarkable [18–22], there exist serious difficulties to evaluate them by direct measurements. Recently, Shroff and Mavridis [18] have developed a simple method to establish the presence of low amounts of LCB in polyethylenes. Following their argument, the representation of η_o vs. intrinsic viscosity, $[\eta]$, should give a qualitative measurement of the level of LCB. The fundamental principle of this method is related to the melt viscosity enhancement due to low amounts of LCB, which, in contrast, does not affect the value of $[\eta]$. The results obtained for our materials and the data of Shroff and Mavridis obtained by GPC are plotted in Fig. 2. The agreement between the two sets of data is

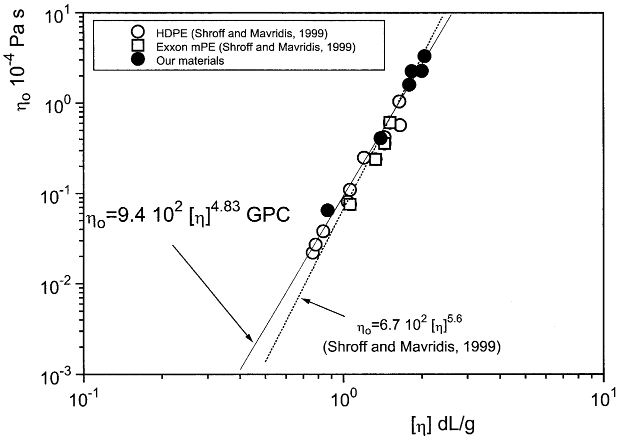

Fig. 2. Newtonian viscosity at 190°C vs intrinsic viscosity at 145°C obtained by GPC for PE samples: (□) Conventional HDPE and (○) mPE in Shroff and Mavridis [18]; (●) mPE in this work; the solid line represents the best fitting for all the results; the dash line represent the fitting given in Ref. [18].

excellent and it points towards the total absence of LCB in our samples providing that the linear nature of Shroff and Mavridis polyethylenes is accepted. The correlation found between η_o (Pa s) and $[\eta]$ (dl g^{-1}) can be described by the following power law:

$$\eta_o = 9.4 \times 10^2[\eta]^{4.83} \tag{6}$$

It is worthwhile to mention that Eq. (6) slightly differs from that published in Ref. [18]. We will come back later on to this point. On the other hand, the most usual plot between η_o and M_w is depicted in Fig. 3 for our set of data. Data for fractions of linear PE, monodisperse HPB and metallocene linear PE [1–8] have also been included in the plot. All data seem to follow a power-law correlation with a critical

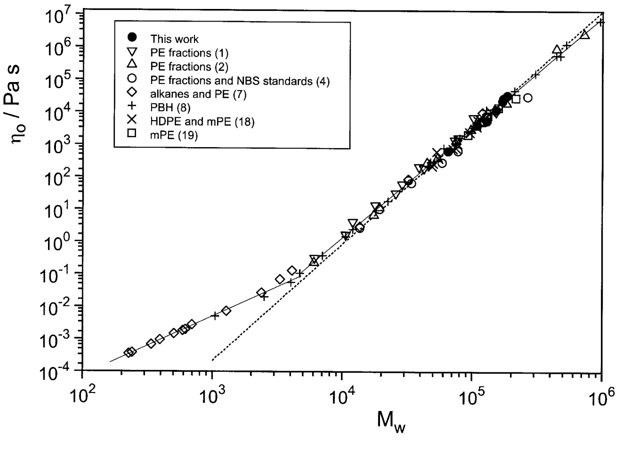

Fig. 3. Newtonian viscosity vs weight average molecular weight at $T = 190°C$ for a set of different PE. (●) mPE of this work; solid line represents the fit to a power law function, $\eta_o \propto M_w^a$ Eq. (7) similar to those found in literature [1–3,6]; the dash line and the other symbols represent the behaviour observed in the literature for PE fractions, monodisperse linear HPB and other mPE [1,2,4,7,8,18,19].

exponent of 3.41:

$$\eta_o = 3.17 \times 10^{-14} M_w^{3.41} \tag{7}$$

The exact values of the exponent and pre-exponent have been a controversial issue for many years. Indeed, values of the pre-exponent constant in the η_o–M_w correlation at 190°C between 3.40×10^{-15} and 2.39×10^{-14} can be extracted from the literature while values from 3.36 to 3.64 can be found for the exponent. In general, limited molecular weight intervals have commonly been studied in each case. This fact and the uncertainty in the measurement of the MWD and/or in the estimation of η_o could be the cause of the deviations found in the pre-exponent and exponential constants. On the other hand, Eq. (7) recalls us that obtained in the 1970s by Mendelson et al. [1], Saeda et al. [2] and Locatti and Gargani [3] for fractions of PE and by Arnett and Thomas for model HPB [6]. The dotted line in the figure represents the nowadays accepted η_o–M_w relationship for PE [5]. Since Eq. (7) has been obtained for a wide range of molecular weights of nearly monodisperse or narrow molecular weight distribution materials, we can state that it could represent better the general behaviour of linear polyolefins at 190°C. The 3.41 value pull through again the old published data by Berry and Fox [45]. In fact, its value can be directly read from the combination of the Mark–Houwink–Sakurada (MHS) relationship and Eq. (6). The MHS exponent for PE lies between 0.69 and 0.73 in TCB at 145°C and the exponent β in Eq. (6) goes from 4.80 till 5.60 [1,2,4,5,7,18,20]. The value 3.41 would correspond to a MHS exponent of 0.707, which is pretty close to our experimental GPC value. On the other hand, the 3.6 value would correspond to the same MHS exponent but a β value of 5.10 [4,5].

Linear PE shows relaxation times proportional to $M_w^{3.4-3.6}$, with the exponent varying in a similar way as η_o. This would imply a linear correlation between τ_o and η_o, a conclusion easily attainable from the linear viscoelastic model assuming a single exponential relaxation modulus $G(t)$ in the terminal zone [25]. In Fig. 4, the values of τ_o against η_o have been plotted. Indeed, a clear linear correlation is obtained:

$$\tau_o = 3.09 \times 10^{-6} \eta_o \tag{8}$$

The solid line in the figure represents the results on linear PE taken from literature [18] and clearly coincides with our samples fitting. It can also be observed in the figure that the most polydisperse sample deviates upwards of the general τ_o–η_o correlation, whereas it fits quite well to the η_o–M_w power law (see Fig. 3). This effect, which is commonly exhibited by polydisperse samples, has been generally explained as a direct consequence of a broadening in the time relaxation spectrum [25].

3.3. The 'plateau' modulus

In Fig. 5, the viscoelastic response of the highest molecular weight sample in an oscillatory shear experiment at a reference temperature of 190°C is depicted. All the materials studied follow a similar trend: a strong viscous behaviour at low frequencies ($G'' \gg G'$) and a well developed maximum value in G'' at high frequencies. As it is known, G_N^o is usually obtained by means of the following expression [30]:

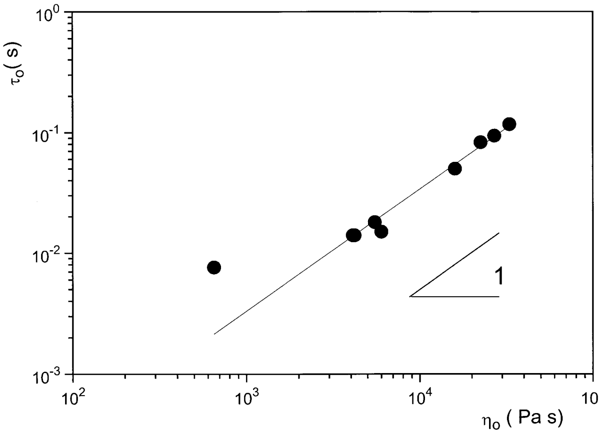

Fig. 4. Relaxation time against Newtonian viscosity at $T = 190$°C for the materials studied. The line represents the results given in Ref. [18].

$$G_N^o = \frac{2}{\pi} \int_{-\infty}^{\infty} G''(\omega)\, d \ln \omega \tag{9}$$

where the integral extends only over the terminal (low angular frequency, ω) peak of the loss modulus. The application of expression 9 requires that the terminal and transition response are well resolved. The extrapolated high-frequency end of the terminal peak in the loss modulus, G'', is shown inside the figure by the continuous line for both the highest molecular weight homopolymer and one of the copolymers. The calculated values of G_N^o for all the polymers studied are listed in Table 2. G_N^o takes a value of around 1.0×10^6 Pa for the homopolymers and of 6.6×10^5 Pa for the copolymers. These values are much lower than those quoted for linear and low-content 1-butene HPB (which always has been considered as LPE) [10], and than those accepted for conventional Ziegler–Natta HDPE and LLDPE [27,28] and mPE obtained through DOW-metallocene catalysts [20]. As it has been previously observed, broad MWD and LCB both contribute to a shift in the maximum of G'' towards higher frequencies, a fact that can be understood by a broadening effect of the transition frequency region. This fact usually leads to uncertainties in the extrapolation procedure and, consequently, to lower values of G_N^o than those expected. However, the materials studied here are characterised by their narrow MWD and the absence of LCB, i.e. the maximum in G'' is well defined as it can be seen in Fig. 5.

Recently, a re-examination and extension of Graessley and Edwards studies [29] has proposed a very simple power law equation relating entanglement parameters

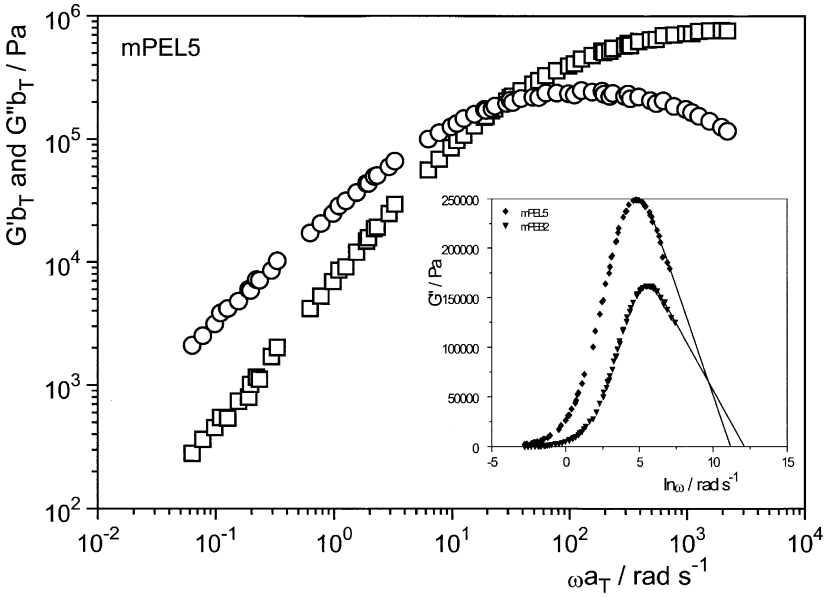

Fig. 5. Reduced viscoelastic response at the reference temperature of 190°C for the highest molecular weight material mPEL5: (○) G', (□) G''. The figure inside shows the extrapolation of G'' curve for G_N^o calculation in mPEL5 and mPEB2.

(plateau modulus, G_N^o, and entanglement molecular weight, M_e), melt density, ρ, and the packing length, p [36,37]:

$$G_N^o \propto \frac{1}{M_e} \propto p^{-3} \tag{10}$$

The packing length can be linked to the 'thickness' of the chain, and it can be defined as the volume occupied by a chain of molecular weight M, $M\,(\rho N_a)^{-1}$, divided by the mean-square end-to-end distance $\langle R^2 \rangle_o$:

$$p = \frac{M}{\langle R^2 \rangle_o \rho N_a} \tag{11}$$

Taking into account the relations in Eqs. (10) and (11), a decrease in G_N^o can be explained by a decrease in the concentration of entanglement couplings or by an increase in chain flexibility (a decrease in chain dimensions) of the mPEs studied here with respect to other PEs. A lower entanglement density implies a lower value of the entanglement molecular weight, M_e, which is, in fact, related to G_N^o by means of Eq. (1). The use of Eq. (3) with $K = 4/5$ for the homopolymers leads to a value of $M_e = 2400$. The correlation of Pearson et al. [8] for low molecular weight PE (alkanes) and the correlation for Newtonian viscosity for high molecular weight PE given by Eq. (7) intersect at a value of M_c of approximately 4200. This yields to a value of $M_e = M_c/2$ of 2100, which is in good agreement with the previous result from the value of G_N^o. There exists a dichotomy of results in the values of M_e and M_c depending of the experimental method used. The value of M_c for PE has been calculated to be in the range 3400–5200 from the dependence of viscosity on molecular weight [2,8,30,46]. The entanglement spacing calculated from integration of loss modulus range from 830 to 1850 [4,5,36,37], giving values of the calculated $M_c = 2M_e$ from 1700 to 3700.

We can suspect a certain lowering in the degree of entanglement density in our samples with respect to other linear PEs, due to the use of a different catalyst system. This probable lower entanglement density comes from the polymerisation method and may remain 'frozen' in the nascent powder. It is interesting to note that for similar linear polymers synthesised with the same catalyst system ($M_w = 3,00,000$ and $M_w/M_n = 2$) similar results in the values of G''_m, G_N^o and M_e have been obtained [47].

On the other hand, the lower value of E_a found in the metallocene homopolymers ($E_a \approx 5.0$ Kcal mol^{-1}) could be a symptom of an increase in flexibility with respect to LPE and HPB ($E_a = 6.4$–7.2 Kcal mol^{-1}). In fact, general correlations for rheological properties–temperature behaviour has been developed using molecular conformational parameters for fixed valence angles and free internal rotation [40]. For example, in the case of amorphous polystyrene (PS) and polypropylene (PP), higher flow activation energies than in HDPE or LLDPE have been reported. The result has been explained by an increase in the height of the rotational potential barrier [41].

The instrument compliance at high frequencies may also affect the determination of G_N^o. For these reasons, polydisperse polydimethylsiloxane (PDMS), polystyrene (PS), and conventional PE samples have also been analysed. The same calculation procedure has been applied for these samples. A very good agreement with the literature values ($G_N^o = 2 \times 10^5$ Pa) has been found for the former [36,37]. For PE, a value of 1.3×10^6 Pa, in

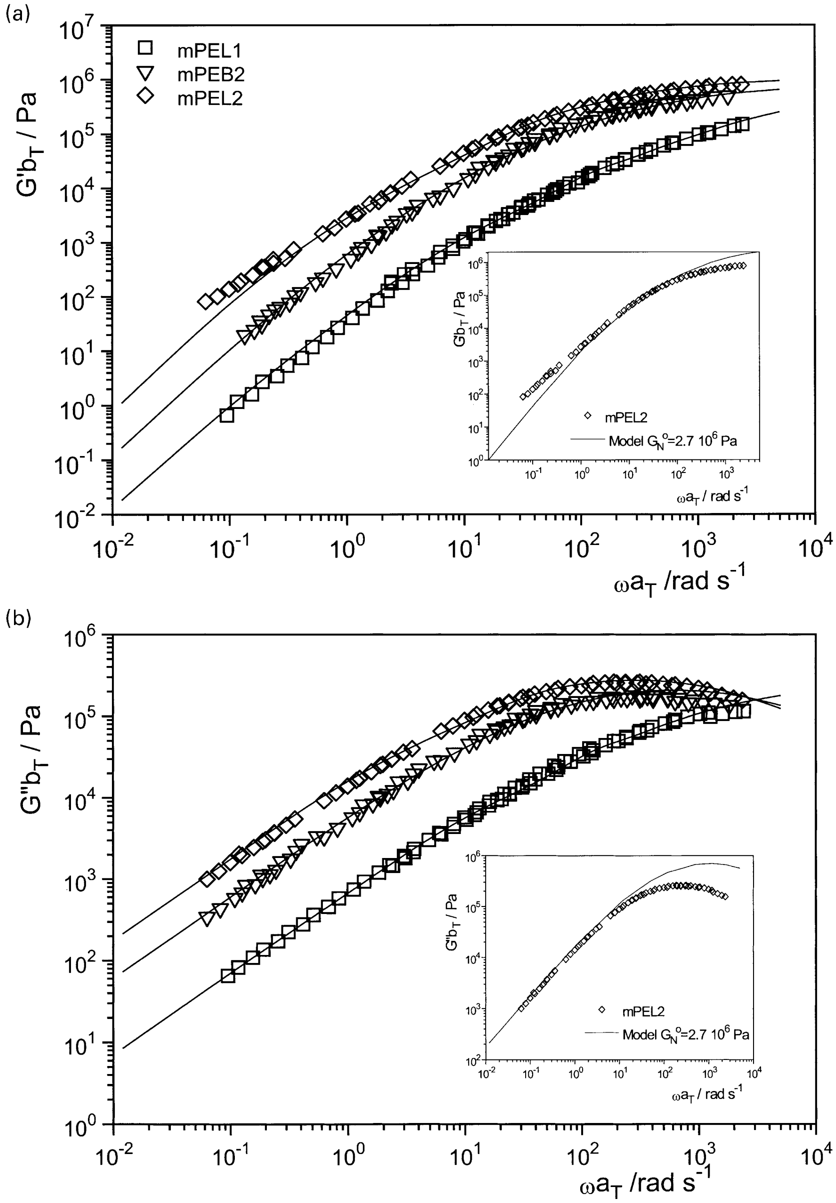

Fig. 6. Experimental storage (a) and loss modulus (b) at 190°C for some of the materials studied here. The solid line represents the fitting curve to Eqs. (12)–(14) using the molecular and rheological parameters given in Tables 1 and 2 (see Ref. [38] for details). The plot inside the box in each of the figures represents the fitting curve of the corresponding function (G', G'') but using a G_N^o value of 2.7×10^6 Pa for one of the samples.

agreement with literature values for conventional PEs [27,28] has been measured.

The lower value of G_N^o obtained in the copolymers is in agreement with the results obtained by Carella et al. [10] and Fetters et al. [36,37] in model HPB. They observe a decrease of 15% in G_N^o for a model PE with 20 branches per thousand backbone carbon atoms. However, there is still some controversy about this particular subject. Another recent study yields to the conclusion that there is not significant differences between the linear viscoelastic behaviour of linear and short chain branched poyethylenes of narrow MWD [20]. Obviously, more work on this particular subject is clearly needed.

3.4. Relaxation spectrum and molecular weight distribution

The relationship between rheological properties of polymer melts and MWD is another topic of increasing interest. All the current models are based on the classical reptation theory of de Gennes [23] lately implemented by Doi–Edwards [24]. The monodisperse model assumes that the surrounding species of a polymer molecule constitute a time invariant matrix that can be figured out as a fixed tube where the polymer chain reptates. Different available models allow one to test the ability of the boundary viscoelastic properties of the transition zone, i.e. η_o and G_N^o, to describe the viscoelastic behaviour of linear polymers. A good summary about the state-of-the-art on this particular subject can be found elsewhere [48]. A relatively simple model has been recently developed by Llorens et al. [38]. This model provides a good description of linear polymers having molecular weight distribution with polydispersity index around two. The model is based on a chain relaxation time convoluted with an average molecular weight distribution that describes the effect of the environment where the molecule reptates. The G values can be then expressed by:

$$G'(\omega) + G''(\omega) = \frac{G_N^o}{c\pi^{1/2}} \int_0^\infty \exp\left[-\left(\frac{1}{c}\ln\frac{M}{M_0}\right)^2\right] \times \left[\frac{A^2 + A}{1 + A^2}\right]\frac{\mathrm{d}M}{M} \tag{12}$$

$$A = \omega\left(\frac{\eta_o}{G_N^o}\right)\frac{[M_n]^{1.25}M^{2.15}}{[M_w]^{3.4}} \tag{13}$$

where the M_0 and c values depend on the type of MWD. In our case, the MWD may be approximated by a log-normal distribution and then the above can be expressed by the equation:

$$M_0 = M_w \exp\left(\frac{-c^2}{4}\right) = M_n \exp\left(\frac{c^2}{4}\right) \tag{14}$$

The application of the above equations connects directly the rheological response of the material with the MWD without using the relaxation spectrum. The GPC measurements in our samples present, in all cases, a bell-shaped form, thus the Eq. (14) is applicable. The model has been applied using the molecular parameters collected in Table 1 together with the values of G_N^o and η_o listed in Table 2. The solid lines in Fig. 6 represent the results of the model. For the most polydisperse polymer with the lowest molecular weight, we choose an average value of the plateau modulus of 1.0×10^6 Pa. This is acceptable since it is well established that this viscoelastic feature is independent of molecular weight. A reasonable accuracy between the experimental results and those obtained by application of the model can be observed in all the cases. The use of the characteristic plateau modulus of HPB (2.7×10^6 Pa) yields a poor reproduction of the experimental values as can be seen in Fig. 6 for one of the materials studied.

4. Conclusions

Zero shear viscosity is found to vary with the weight-average molecular weight to the 3.41 power for a set of different LPEs in a broad range of molecular weight. This result contradicts the most recent accepted value of 3.60. The main relaxation time and the Newtonian viscosity are clearly connected through a linear correlation. These two results confirm that the materials studied in this work are essentially linear. Indeed, very low amounts of long chain branches would be enough to provoke a clear deviation from the observed behaviour. At the same time, the samples yield unexpected low values of the 'plateau' modulus. The average value ranges from 6.6×10^5 Pa for the copolymers up to 1.0×10^6 Pa for the homopolymers. This observation could be of great importance in view of the adhesive properties dependence on this viscoelastic parameter. The application of a simple model for polymers with bell-shaped MWD reproduces the viscoelastic response of the materials in the whole range of frequencies studied. This result allows us to demonstrate that the values obtained for the rheological parameters η_o and G_N^o are well determined and opens up the question of what is causing the difference observed between mPE and other model PE.

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