

## Rheological features and molecular architecture of polyethylenes

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### Summary

Compared to other polymers, highly increased melt viscosity, elasticity, and flow activation energy were observed in several chromium-based polyethylenes. Findings reported in the literature suggest that these effects could, at least theoretically, be accounted for by the polydispersity of these polyethylenes. However, the data presented here would appear to indicate a much stronger, evident connection with long chain branching than with polydispersity.

### Introduction

Within the large polymer group of polyolefins, the polyethylene (PE) family constitutes a good example of how the molecular architecture is related to the viscoelastic response and processing. Low-density polyethylene (LDPE) is widely used in many applications due to ease of its processing. This polydisperse polymer has also been attributed the characteristics of a high degree of long chain branching (LCB) and complex topology. In contrast, it is claimed that high-density polyethylene (HDPE) and linear low-density polyethylene (LLDPE) are of linear molecular structure, with no LCB, though some degree of short chain branching (SCB) is expected. These materials cannot be easily processed, yet most of their physical properties are improved over those of LDPE. Notwithstanding, the possible presence of LCB in some of these essentially linear PEs has always been suspected [1-6]. The rheological properties of polymer melts are known to be strongly dependent on LCB [7]. Unfortunately, along with molecular weight distribution (MWD), this molecular feature is very difficult to control using conventional polymer synthesis technology. Indeed, better-controlled branched structures are now being obtained by single-site catalyst systems [8]. Among a polymer's rheological properties, its linear viscoelastic response and the non-linear extensional flow are known to offer most clues as to the presence and effects of such structures [5-11].

The main aim of this study was to try to account for the differences observed in the viscoelastic response shown by a family of chromium-based PEs and that shown by linear and branched polydisperse PEs.

## Experimental

### Materials

Table 1 shows the molecular properties of PE samples determined by GPC. Samples were supplied by *Repsol-YPF* (Spain). A LDPE and a metallocene HDPE (mHDPE) were included for comparative purposes. The viscoelastic data of the latter are already published elsewhere [12]. All samples were stabilised against oxidation by adding 1% of Irganox 1010.

**Table 1.** Molecular parameters of the polyethylenes

Sample	$M_w$	$M_w/M_n$
PE1	160700	9.5
PE2	135500	11.4
PE3	137600	8.8
PE4	143500	15.5
PE5	182000	9.5
LDPE	225000	9.5
mHDPE	152000	2.0

### Rheological Measurements

Creep measurements in the linear regime were performed in a controlled-stress CVO Bohlin rheometer with 25 mm parallel plates and cone-and-plate geometries. A temperature of 145°C was chosen to avoid degradation since this materials show broad relaxation and retardation spectra, and long duration experiments are needed. Incomplete creep tests were conducted according to the method of Meissner [13,14]. From these experiments, Newtonian viscosity,  $\eta_0$ , and steady-state compliance,  $J_e^0$ , were estimated. Linear dynamic oscillatory measurements were also made in the temperature range 130-190°C and frequency range 0.001-100 rad·s<sup>-1</sup>. To check possible degradation effects during experiments, measurements were repeated several times on the same and on fresh samples. In all cases, variations among measurements were negligible. The variables storage and loss moduli  $G'$  and  $G''$ , the complex viscosity  $\eta^*$ , and flow activation energy  $E_a$ , were determined according to the time-temperature superposition principle (TTSP), at a reference temperature of  $T_0=145^\circ\text{C}$ .

## Results and discussion

### Temperature dependence of viscoelastic properties

At temperatures above 140°C, corresponding to those at which most polyolefin melts are processed, a close approximation of the temperature dependence shift factor through application of TTSP can be made using an Arrhenius-type equation [15]:

$$a_T = \exp\left[\frac{E_{aT}}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right)\right] \quad (1)$$

where  $R$  is the gas constant,  $T$  is the experimental temperature,  $T_0$  is the

reference temperature and  $E_{aH}$  is the “horizontal activation energy”. Similarly, a vertical shift factor,  $b_T$ , can be defined in terms of a “vertical activation energy”,  $E_{aV}$  [16]. In the case of chromium-based PEs and LDPE,  $E_{aV}$  values ranged from 7.5 to 22.2 KJ·mol<sup>-1</sup> (see Table 2). For linear PEs,  $E_{aV}$  has been reported to be null or negligible. In contrast, polymers with LCB are thermorheologically complex, and if we neglect vertical shifts then the TTSP is not fulfilled [9,16]. As in the case of LDPE, high  $E_{aH}$  values, in the range 39.7 to 73.6 KJ·mol<sup>-1</sup>, were also calculated for the present materials. In contrast, the linear mHDPE presented a low value of  $E_{aH}$  (20.8 KJ·mol<sup>-1</sup>) and a null  $E_{aV}$  value.  $E_{aV}$  and  $E_{aH}$  showed good correlation; the higher the vertical shift needed, the higher the  $E_{aH}$  value obtained. These values are consistent with those cited in the literature for LCB materials, although linear polydisperse polymers have been reported to show slightly higher  $E_{aH}$  values. Applying the polydispersity index 3.3 to 12.7, an increase in  $E_{aH}$  from 25.5 to 36.8 KJ·mol<sup>-1</sup> has been reported [9]. However, unlike our samples, these linear polymers were not observed to be thermorheologically complex. The presence of SCB also causes enhanced  $E_{aH}$  values. However, the materials studied here are HDPE, then they should present low SCB content. It is well-known that the characteristic  $E_{aH}$  value for HDPE is 27.0 KJ·mol<sup>-1</sup> [6]; a lower value than those obtained for the present materials.

#### *Creep properties and viscoelastic moduli.*

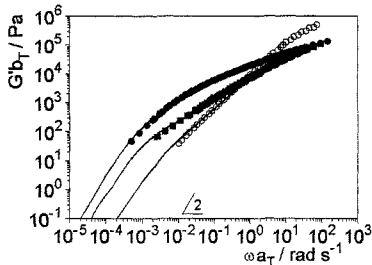
From creep measurements corresponding to the change in deformation over time  $\gamma(t)$ , we can calculate the linear viscoelastic shear compliance  $J^\circ(t)$ . This function comprises the recoverable elastic portion  $J_e^\circ(t)$ , and the irrecoverable viscous portion,  $t/\eta_o$ :

$$\frac{\gamma(t)}{\sigma} = J^\circ(t) = J_e^\circ(t) + \frac{t}{\eta_o} \quad (2)$$

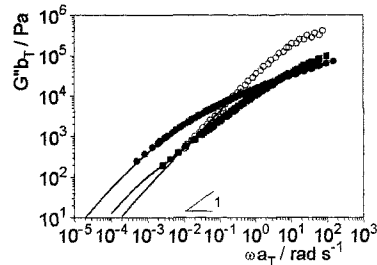
$\sigma$  being the applied stress. When the strain  $\gamma(t)$  starts to follow a straight line, the compliance  $J^\circ(t)$  does the same. Since the slope of the line is  $1/\eta_o$ , it follows that  $J_e^\circ(t)$  has reached its final equilibrium value  $J_e^\circ$ . The materials under study showed different  $J_e^\circ$  and  $\eta_o$  values, despite presenting a similar  $M_w$ , and  $M_w/M_n$ . The resulting equilibrium quantities were reached after long periods of 30 minutes to 6 hours (see Table 2). These quantities are higher than those corresponding to the linear mHDPE. It may thus be concluded that the linear viscoelastic behaviour of the materials may be attributed to their highly prolonged relaxation time, i.e., to their broad relaxation time spectrum, indicating the presence of very high  $M_w$  molecules and/or LCB.

The creep recovery and oscillatory tests results can be combined. The time and frequency dependent linear viscoelastic functions need to be converted into a retardation or relaxation spectrum. To this end, we followed the procedure described by Kraft and co-workers [14,17]. The plots in Figures 1 and 2 show the resultant data, along with the experimental values of  $G'$  and  $G''$  obtained in the oscillatory shear test for some of the materials studied. Excellent agreement was shown between the calculated and the experimental results. Moreover, by combining the data, the viscoelastic response was extrapolated to a wide range

of frequencies.



**Figure 1.** Master curve of  $G'$  vs.  $\omega$  of some of the materials at  $T_0=145^\circ\text{C}$ . Symbols: shear oscillation (■) PE5, (●) LDPE, (□) mHDPE. Solid curves: creep [13,14,17].



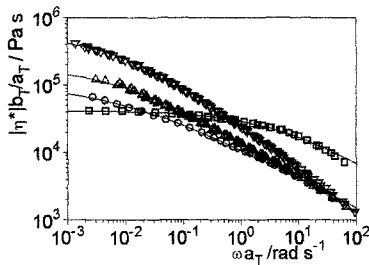
**Figure 2.** Master curve of  $G''$  vs.  $\omega$  of the materials at  $T_0=145^\circ\text{C}$ . Symbols: shear oscillation (the same than in Figure 1). Solid curves: creep [13,14,17].

**Table 2.** Rheological properties of the polyethylenes

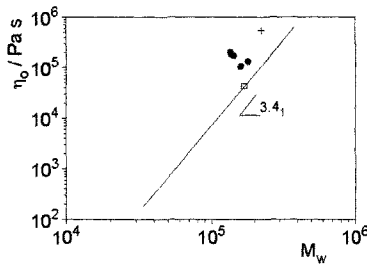
Sample	$\eta_0$ (KPa·s)	$J_e^0$ (KPa <sup>-1</sup> )	$E_R$	$G_x$ (KPa)	$E_{aH}$ (KJ·mol <sup>-1</sup> )	$E_{aV}$ (KJ·mol <sup>-1</sup> )
PE1	104	9.0	3.9	70.8	$39.7 \pm 1.9$	$10.5 \pm 0.6$
PE2	190	2.0	4.8	42.6	$73.6 \pm 3.3$	$22.2 \pm 1.3$
PE3	175	2.6	5.2	45.0	$66.1 \pm 3.6$	$20.5 \pm 1.3$
PE4	170	4.5	4.1	43.1	$61.5 \pm 2.6$	$17.2 \pm 1.0$
PE5	130	4.0	3.4	74.1	$38.5 \pm 1.5$	$7.5 \pm 0.5$
LDPE	540	1.0	2.1	9.9	$75.0 \pm 3.0$	$18.8 \pm 1.2$
mHDPE	43	0.20	0.10	160	$20.8 \pm 0.0$	0.0

*Viscosity curve and zero-shear viscosity*

Figure 3 shows changes in the modulus of the reduced complex viscosity with the frequency for materials with similar  $M_w$ .



**Figure 3.** Master curves of  $|\eta^*|$  vs.  $\omega$  at  $T_0=145^\circ\text{C}$  for some of the materials. (○) PE1, (△) PE2, (▽) LDPE and (□) mHDPE.



**Figure 4.**  $\eta_0$  vs.  $M_w$ , for the materials  $T_0=145^\circ\text{C}$ . (line) linear PEs [12], (●) chromium-based PEs, (+) LDPE, (□) mHDPE.

The plots show that neither the chromium-based PEs nor the LDPE reach the limiting  $\eta_0$  value at low frequencies. This behaviour contrasts with that shown by the linear mHDPE. In addition, the degree of shear thinning is also enhanced with respect to the observed in the linear polymer. These features are characteristic of polydisperse and/or LCB polymers [9]. Figure 4 shows plots of the  $\eta_0$  values listed in Table 2 versus  $M_w$  for the materials under study. Also included in the figure, are data for linear mPEs shifted at  $145^\circ\text{C}$  obtained from

the literature[12], which follow the well-known correlation  $\eta_o \propto M_w^{3.4}$ . The values of  $\eta_o$  are clearly higher for the chromium-based polymers than for the linear polymers of similar  $M_w$ . This increase can be attributed to the presence of LCB [5-9]. However, similar increases have been found in polydisperse, supposedly-linear polymers obtained by blending different LLDPEs, with polydispersity indices between 3.3 and 12.7 [9]. In contrast, other HDPEs and blends ( $M_w/M_n$  ranging from 5.0 to 16) do not show this enhancement in  $\eta_o$  but present the typical 3.4 power law exponent for its dependence with  $M_w$  [18]. Considering the conflicting results reported in the literature along with the present  $\eta_o$  data, one can only suspect the presence of LCB in our polymers. However, the high values of  $E_{aH}$  and the complex thermorheological character (see preceding section), strongly suggest that the enhanced  $\eta_o$  values reflect the presence of LCB. In several investigations on near monodisperse star model polymers, this parallel enhancement in  $E_{aH}$  and  $\eta_o$  was also noted [19,20]. The authors of these studies demonstrated that this enhancement was exponentially dependent on arm  $M_w$ , irrespective of the number of arms shown by stars of the same total  $M_w$ . Owing to the method of preparation, these model samples are uniformly branched. Hence, our result could be accounted for by increased branch lengths, provided branching distribution in the samples examined was uniform. However, in our samples, branching would be expected to randomly occur such that, at low levels of branching, not every molecule will contain a branch point. Our findings are consequently more consistent with the analysis performed by Bersted [21]. This author proposes that increases in  $\eta_o$  and in  $E_a$  can be explained by treating the materials as blends of branched and linear species. Thus, at low levels of branching, the increases would indicate a higher fraction of branched species in the polymer. Similar conclusions were recently drawn in connection with branched mPEs [22,23].

### *Elasticity*

Several rheological indices can be extracted from dynamic mechanical measurements on linear polymer melts for characterise polydispersity [24]. MWD and LCB are specific molecular features that affect these indices. One such index is denoted  $E_R$ :

$$E_R = C \cdot G' \Big|_{G''=500Pa} \quad (3)$$

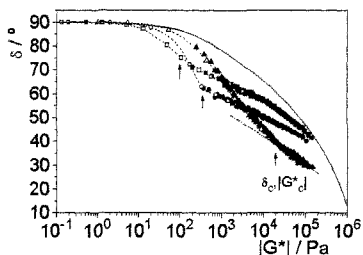
where  $C$  is an arbitrary constant chosen so that  $E_R$  lies between 0.1 and 10.  $E_R$  is actually a measure related to  $J_e^o$ , and accounts for the effect of polydispersity (the high- $M_w$  tail) and/or LCB. Table 2 lists the indices calculated. These values are higher than those obtained for linear PEs of similar polydispersity index ( $E_R \leq 2$ ) [18]. The good correlation observed between  $E_R$ , and the  $\eta_o$  and  $E_{aH}$  increases would appear to suggest that the higher the LCB content, the greater the elastic nature of the polymer. This might appear as a challenge, but we must accept that the increases observed in  $\eta_o$  and  $E_{aH}$ , along with the thermorheological complexity, are LCB polymers' specific features [9]. In principle the enhanced  $E_R$  values of the materials examined could also be ascribed to the no-symmetric character of the relaxation time spectra; a tail of high relaxation times corresponding to large molecular species. However, SEC

results clearly indicate a lognormal MWD for these polymers. It has also been established that branched molecules in symmetric MWD give rise to similar increases in the values of  $E_R$  [18]. Moreover, similar results have been reported for other measures of the rheological polydispersity, such as the cross-point modulus,  $G_x$ , between  $G'$  and  $G''$  [24]; the more elastic a material (lower  $G_x$ ) the higher the increase in  $\eta_0$  and in  $E_{aH}$ . If we focus our attention in the values of  $J_e^\circ$  obtained in creep measurements, the expected correlation between elastic indices and this terminal variable is not observed. In Table 2, the polymer assumed to be most highly branched (higher values of  $E_a$  and  $E_R$ ), showed the lowest  $J_e^\circ$ . Indeed, it has been recently found that branched polydisperse polymers show lower values of  $J_e^\circ$  than less branched ones. This decrease in  $J_e^\circ$  could be explained by a different entanglement state provoked by higher degree of branching [25]. The dilution concepts proposed by McLeish et al. [26] also provide an explanation for this behaviour: thus the relaxation of polymer chains with long relaxation times will be accelerated by surrounding chains or chain segments with shorter relaxation times that act as diluents. In highly branched materials (high volume fraction occupied by the branches), the branches may relax more rapidly than the entire molecules, thus they could dilute the surrounding of the latter leading, to an overall reduction of elasticity.

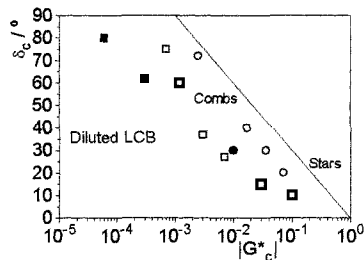
#### *The MWD-rheology conversion and branching morphology*

The relationship between the rheology of polymer melts and MWD is a topic of increasing interest. Most current models are based on the reptation theory [27,28]. This theory applied to the monodisperse case assumes that the surrounding species of a polymer molecule constitute a time invariant matrix that can be considered as a fixed tube, along which the polymer chain reptates. Llorens et al. recently developed a relatively simple model which has been confirmed for linear polymers with a lognormal MWD [12,29]. These authors derived an direct analytical relationship between the relaxation time spectrum and the MWD. In the present samples, the MWD always took the form of a bell-shape and thus the model is applicable. Llorens' model was applied to the polymers using the molecular and rheological properties listed in Tables 1 and 2 (average  $M_w/M_n=10$ ), together with an average  $G_N^\circ$  value of  $1.5 \times 10^6$  Pa for PE obtained from the literature [12] (see references 12 and 29 for details). The solid line in Figure 5 represents the result of the model for the loss angle  $\delta$  (note that this plot is independent on  $M_w$ ). The materials present enhanced elastic character (lower values of  $\delta$ ) and a broader transition between the terminal ( $\delta=90^\circ$ ) and plateau zones ( $\delta=0^\circ$ ) than the predicted from the MWD-rheology conversion scheme. All the chromium-based PEs examined showed similar behaviour. The abrupt "bump" in  $\delta$  function suggests a different relaxation mechanism than that corresponding to a linear polymer of the same MWD. In branched molecules, since terminal relaxation involves movement of the entire molecule, well-entangled arms suppress longitudinal motion at low frequencies. Moreover, a further mechanism at higher frequencies is needed to allow translation of a branched molecule. Arm retraction of all branches to a more compact structure has been proposed as such a mechanism [30]. In a recent study of Larson, these mechanisms were further explored, and the whole

viscoelastic response was found to depend, not only on the branching content, but also on branching structure and topology [31]. Further, Trinkle et al. [32] claim that plots such as those of Figure 5 are extremely useful for assessing, not only the presence of LCB, but also their topology. These authors defined the coordinates of the "bump" in the  $\delta$  function as  $\delta_c$ , where  $|G^*_c| = |G^*|_{\text{bump}}/G_N^\circ$  (arrows in Figure 5). Through the systematic study of these coordinates for model branched polymers and branched mPEs, these authors drew up a topology map in which characteristic branched morphologies cover distinct areas. Figure 6 shows a plot of the results obtained for our materials and those cited for linear and branched blends [32], and branched mPEs [33]. The materials examined here appear in the zone corresponding to diluted branched polymers, i.e., to mixtures of linear and branched molecules, as suggested above. It should also be mentioned, that the values of  $\delta_c$  obtained for our materials are lower than those corresponding to the polymers and blends studied by Trinkle et al. [32]. This is most likely due to the heterogeneous MWD and branching structure of the present materials.



**Figure 5.** Loss angle  $\delta$ , vs. complex modulus  $|G^*|$ , for (■□) PE5, (●○) PE2 and (▲△) LDPE. Closed symbols: oscillatory shear. Open symbols: creep. The solid line represents MWD-rheology conversion results.



**Figure 6.** LCB topology map [32]. (■) Chromium-based PE1 and PE5, (●) LDPE, (□) Linear/branched blends [32] (○) branched mPEs [33].

## Conclusions

In an attempt to relate viscoelastic functions to molecular architecture, several rheological variables were determined in a set of polyethylenes. Relative to other polymers, considerably enhanced  $\eta_0$ ,  $E_a$  and elastic character seem to be a general feature of the materials examined. By comparing our results with the theoretical behaviour of polydisperse polymers of similar MWD we were able to conclude that the PEs contained LCB. It may be inferred from most published reports that the effects of polydispersity and LCB can be misleading. Notwithstanding, in the materials analysed here, the effects of LCB seem to be more marked than those predictable according to their polydispersity. The application of a simple molecular relaxation model developed for linear polydisperse polymers does not serve to explain the entire linear viscoelastic response when LCB is suspected. The following relaxation processes were observed: (i) a slower terminal relaxation behaviour than linear counterparts, and (ii) a faster additional branch relaxation at high frequencies. The latter is clearly distinguishable from polydispersity effects. Systematic variation of

viscoelastic functions as Newtonian viscosity and flow activation energy, and the zone in which the additional process appears in the relaxation time spectrum, all point towards the idea that these materials are blends of linear and branched species. The reduction noted in the steady-state compliance of the polymers suspected to be more highly branched, might be explained by a dilution effect caused by a substantial degree of long chain branching.

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