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Rheological behaviour of LDPE/EVA-c blends. I. On the effect of vinyl acetate comonomer in EVA copolymers

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Abstract

Low-density polyethylene (LDPE) has been the subject of several rheological studies trying to correlate rheological features with molecular parameters. As the ethylene vinyl acetate copolymer (EVA-c) and LDPE are obtained through the same polymerization process, it has been long assumed that both materials would exhibit a similar viscoelastic response. However, a recent work has put forward the question as to whether the presence of vinyl acetate (VAc) units could modify the expected viscoelastic behaviour. In order to further explore this effect, we have carried out a dynamic viscoelastic study in a series of seven EVA-c. At a first step, it will be shown that EVA-c presents a thermorheological complex behaviour. It will be shown that Newtonian viscosity (η_0) values are conspicuously higher than those reported for LDPE of similar molecular weight (M_w). Furthermore, a concurrent lower elastic character of the EVA-c samples is observed. The results are discussed in terms of molecular architecture and molecular weight distribution (MWD). However, a final explicit VAc content dependence of the viscoelastic properties up to 30% by weight of this comonomer is not observed. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Viscoelastic properties; Vinyl acetate; Ethylene

1. Introduction

Vinyl acetate/ethylene copolymers, often referred as EVA-c, are thermoplastic materials resulting from the co-polymerization of ethylene and vinyl acetate (VAc). As it is well known these copolymers are generally produced by a high pressure, high temperature, bulk polymerization process similar to that employed for conventional high pressure, free radical, low-density polyethylene (LDPE). The ability of the VAc monomer to co-polymerize over a wide range of composition with the ethylene monomer is a result of their similar reactivity ratios. Indeed, at higher temperature, where practical high-pressure reactions are performed, the reactivity ratio of the two monomers is close to 1 [1]. This condition produces statistically random copolymers with chemical compositions nearly identical to those of the comonomer feeds.

This kind of polymerization gives rise to branched products containing both long (LCB) and short chain branches (SCB) [2–5]. A great deal of studies has been devoted to show the relationship between molecular architecture and rheological properties. In particular, it is worth to mention here the works of Bersted [6] and Shroff and Mavridis [7] that tackled the important issue of how LCB affects processability. According to Bersted at a given M_w, the Newtonian viscosity, η_0, increases steeply with long chain branching up to a maximum value and then decreases monotonically reaching final values below the characteristic level of the linear polymer. Similarly, in a recent work, Shroff and Mavridis try to quantify the level of LCB for 'essentially linear' polymers, i.e. with very low LCB content, ca. less than 0.3/1000C. It has also been reported that the flow activation energy, E_a, increases with LCB being the former value controlled by the length, concentration and distribution of branches [8–10]. Finally, it has been observed that this type of structure produces an enhancement of melt elasticity and melt strength but in all cases strongly monitored by polydispersity and high-M_w tails [11].

Commercial LDPE has also been the scope of recent theoretical investigations. The basic explanation for the experimental facts observed in this type of materials is mainly the suppression of chain dynamics [12]. For instance, McLeish and Larson [13] have proposed a molecular constitutive equation for an idealized polymer architecture (pom–pom model) that like LDPE has multiple branched points per molecule. The aim of the model is to

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Table 1
Molecular parameters of the materials studied: VAc weight content, %VAc; melt flow index, MFI; weight average molecular weight, M_w; polydispersity index, M_w/M_n; short chain branching content, SCB; maximum value of long chain branching, LCB; intrinsic viscosity, $[\eta]$

Sample	%VAc	MFI[a]	M_w	M_w/M_n	Total CH_3/1000C[b]		$[\eta]$ (dl/g)
					SCB < 6C	Limit value of LCB	
EVA1	13.4	0.36	189,800	8.4	6.5	< 2.5	1.03
EVA2	27.0	6	91,100	3.9	5.5	< 0.5	0.73
EVA3	26.7	50	76,300	4.2	6.0	< 2.0	0.64
EVA4	28.4	150	48,500	3.3	14.0	< 2.0	0.45
EVA5	17.1	150	46,800	3.5	11.5	< 3.5	0.43
EVA6	27.1	400	40,200	2.9	11.5	< 2.5	0.39
EVA7	19.1	500	33,500	2.1	13.5	< 2.5	0.41

[a] ASTM D-1238.
[b] Aliphatic branching.

predict the rheological behaviour in both shear and extension deformation. At the end, the method provides a concise and functional way to characterize LCB in polymer melts [14].

At present, different EVA-based products are commonly found in patent literature, mostly due to their extensive use in several practical applications. Some of these patents deal with blend products containing LDPE that found common use in multilayer packaging films, sheets for automobile parts, self-adhesive protective plastic film, flame-retardant halogen-free polymer composition for electric cable insulation, biodegradable pollutant-free peelable films for information media such as postcards, etc. [15–17]. However, despite the increasing importance of these materials in polymer engineering, rheological studies of EVA-c are rare in the literature. The reason could be found in the traditional assumption that the rheological properties of EVA-c are similar to those of LDPE [10,18]. As we shall see later on, the viscoelastic properties of EVA-c substantially differ from that corresponding to LDPE. An essential point is the validity of the application of a unique Williams–Landel–Ferry (WLF) correlation to the time–temperature superposition (TTS) principle as it has been recently proposed by Arsac et al. [19]. The final aim of our work is to completely characterize the viscoelastic behaviour of a series of EVA-c that could have a potential use in blends with another polyolefins such as LDPE. Hence, we have first studied the viscoelastic properties of a series of EVA-c with different VAc content. These properties are correlated with molecular features such as M_w, MWD, branching and VAc content. In a second paper, we will present the results on the LDPE/EVA-c blends, emphasizing their possible applications as a consequence of the improvement of certain melt properties [20].

2. Experimental

2.1. Materials characterization

The EVA-c studied is a commercial set of free radical polymerized samples with different VAc content (between 13 and 28% by weight). All the EVA-c samples have been supplied by Repsol S.A. and they are listed in Table 1. The molecular parameters of the materials M_w, M_w/M_n, obtained by size exclusion gel permeation chromatography (SEC) using a 150 CV Waters GPC and the VAc content and chain branching level determined from the ^{13}C NMR spectra are also shown in Table 1. The ^{13}C NMR spectra were recorded at 100°C using a Brucker AC 300 spectrometer operating at 75 MHz. Sample solutions of 20% (v/v) were prepared using deuterated benzene and 1,2,5-trichlorobenzene (TCB) with trimethylsilane as an internal standard. For GPC evaluation, the universal calibration procedure was applied using a set of polystyrene standards dissolved in TCB at 145°C.

Melt flow rate (MFR) values have been measured at 125°C and at a constant weight of 2.16 kg using a Modular Flow Indexer CEAST 6542. MFI values have been derived from the following equation [10]:

$$\mathrm{MFI}_{(2.16\ \mathrm{kg},190°\mathrm{C})} = 8.621\mathrm{MFR}_{(2.16\ \mathrm{kg},125°\mathrm{C})} \tag{1}$$

The MFI values are given in Table 1. Intrinsic viscosity, $[\eta]$, has been calculated from the specific viscosity, η_{sp}, measured in 1,2,3-trichlorobenzene at 145°C and a nominal concentration, c, of 0.2 g/dl. The calculations have been performed using Martin's equation:

$$\log\left(\frac{\eta_{sp}}{c}\right) = \log[\eta] + K_m[\eta]c \tag{2}$$

where $K_m = 0.2138$ is the Martin's constant. The obtained $[\eta]$ values are also given in Table 1.

2.2. Oscillatory shear measurements

Disc specimens of 30 mm diameters and 0.5 mm of thickness were compression moulded in a Schwabenthan Polystat 200T for 2 min at 125°C and a nominal pressure of 150 bar. Rheological measurements were carried out in a dynamic thermal analyser Polymer Laboratories MKII (torsion system) using the parallel plates mode. Oscillatory viscoelastic measurements were carried out over the range of frequencies $0.0628 \leq \omega \leq 62.8$ rad/s within the linear viscoelastic region. The following viscoelastic functions were measured: storage modulus, $G'(\omega)$; loss modulus, $G''(\omega)$; dynamic viscosity, $\eta'(\omega)$; loss tangent, tan δ. The temperature range of measurements was from 130 to 190°C. Data from each sample were then shifted along the frequency and modulus axes in order to construct dynamic modulus master curves at a common reference temperature T_0 of 150°C. The frequency and modulus shifts, a_T and b_T, were expressed in term of a horizontal and vertical flow activation energies, E_{aH} and E_{aV} [10].

3. Results and discussion

3.1. Time–temperature superposition principle

The more commonly used equation to describe the viscosity–temperature behaviour of polymers is the WLF expression [9,21]. This expression is generally applicable in the temperature range between the glass transition temperature, T_g, and $T_g + 100$°C. At higher temperatures it predicts small and similar E_a values for all polymers [9,21]. However, it is experimentally found that at elevated temperature, E_a varies widely from polymer to polymer and its value depends mainly on chain flexibility, intermolecular interactions, concentration of polar groups and side-chain branches [9]. Generally, for semicrystalline EVA-c, the molten state is reached only at temperatures of around 100°C above its T_g, which is located in the vicinity of room temperature. At temperatures above 140°C where most of the polyolefin melts are processed, the WLF expression is commonly approximated by an Arrhenius-type equation [9,21]:

$$a_T = \exp\left[\frac{E_{aH}}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right)\right] \tag{3}$$

where R is the gas constant, T the experimental temperature, T_0 the reference temperature and E_{aH} is the 'horizontal activation energy'.

As it is known LDPE and EVA-c show a stress-dependent activation energy when data are shifted at constant stress, providing that the data are only horizontally shifted [9,11,21]. For this reason, a vertical shift involving a 'vertical activation energy' is also needed:

$$b_T = \exp\left[\frac{E_{aV}}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right)\right] \tag{4}$$

where R, T and T_0 have the same meaning as in Eq. (3) and E_{aV} is the vertical activation energy.

In a recent study [19], a WLF-type expression has been applied to commercial EVA-c with VAc content between 5 and 40% within the temperature range between 50 and 200°C. Apparently, the WLF fitting has been carried out using only a horizontal shift. The method seems to work nicely with complex viscosity, η^*, and storage modulus, G', functions. However, it is well known that the validity of the TTS principle lies on its applicability to all the viscoelastic functions [21]. Our results indicate that the approximation given by WLF does not hold for the loss tangent, $\tan\delta = G''/G'$, in any of the investigated samples. Consequently, the use of an Arrhenius-type equation applying both horizontal and vertical shifts seems to be more accurate. The existence of a vertical factor correction to the activation energy has been commonly associated with a thermorheological complex behaviour [8,10,22]. Graessley and co-workers [8,22] found indications of such a complex behaviour in various model branched polymers. Two explanations have been offered by these authors: a temperature dependence of the entanglement density and a difference in the paths of conformational relaxation of branched chains as compared to linear ones.

The E_a values of the copolymers studied are listed in Table 2. For most of the samples, the horizontal activation energy of flow lies around 13.0 kcal/mol, in between two extreme values of 15.5 kcal/mol (EVA2) and 10.4 kcal/mol (EVA6). These results could be most probably explained by differences in branching length and/or distribution of the branches. In fact, Raju et al. [8] found a nearly linear correlation between E_a (9–15 kcal/mol) and branch length, M_b (6000–45,000), in model star polybutadiene (PB). On the other hand, it can be seen that all the copolymers have vertical activation flow energies between 1.0 and

Table 2

Rheological parameters at 150°C of the materials studied: Newtonian viscosity, η_0; relaxation times, τ_0 and τ; pseudoplastic index, α; flow activation energy, E_a; steady-state recoverable compliance, J_e^0; cross-point modulus, G_x

Sample	η_0[a] (Pa s)	τ_0 (s)	α	E_{aH} (kcal/mol)	E_{aV} (kcal/mol)	η_0[b] (Pa s)	J_e^0 (Pa^{-1})	τ (s)	G_x (Pa)
EVA1	23,780	4.7	0.64	13.3	2.0	22,380	4.1×10^{-4}	9.2	20,500
EVA2	12,460	1.1	0.65	15.5	2.8	13,080	3.4×10^{-4}	4.4	43,500
EVA3	1225	6.2×10^{-2}	0.66	13.6	3.3	1250	2.9×10^{-4}	3.6×10^{-1}	58,000
EVA4	236	9.7×10^{-3}	0.65	12.9	2.3	240	1.7×10^{-4}	4.1×10^{-2}	> 60,000
EVA5	148	8.2×10^{-3}	0.69	12.2	2.5	144	1.8×10^{-4}	2.7×10^{-2}	> 60,000
EVA6	70	2.0×10^{-3}	0.65	10.4	0.0–1.0	64	8.0×10^{-5}	5.6×10^{-3}	–
EVA7	60	2.3×10^{-3}	0.65	13.2	3.6	59	1.3×10^{-4}	7.8×10^{-3}	> 60,000

[a] Estimated from Briedis and Faitelson fit.

[b] Estimated from Maxwell generalized model.

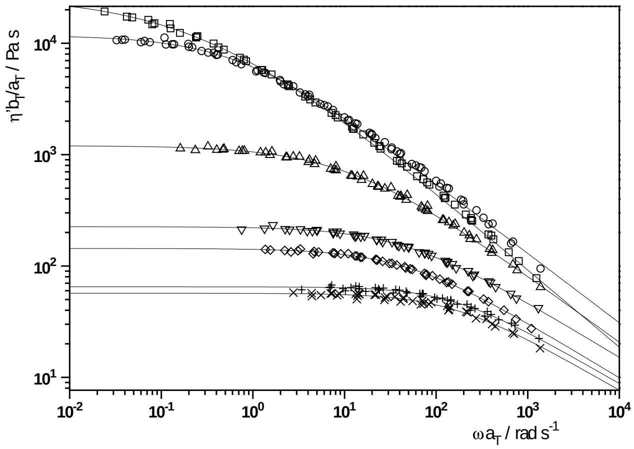

Fig. 1. Reduced dynamic viscosity versus reduced frequency at $T = 150°C$ for the copolymers studied: (□) EVA1; (○) EVA2; (△) EVA3; (▽) EVA4; (◇) EVA 5; (+) EVA 6; (×) EVA7. Solid lines represent the fit of experimental data to Eq. (5).

3.6 kcal/mol, far above the negligible values found in linear polymers [10].

3.2. Zero-shear viscosity

In Fig. 1, the reduced dynamic viscosity function versus reduced frequency is plotted using the TTS principle shift factors for all the investigated materials. Most of the materials show a characteristic Newtonian behaviour at relatively high frequencies. As an exception, the EVA1 copolymer does not reach the Newtonian plateau, which is concurrent with its higher pseudo-plastic character. As it can be seen in Table 1, this copolymer has the highest M_w and the broader MWD. Among the different available fitting equations [23], the Briedis and Faitelson fit has been proved to give the best results in our case. Thus, the following expression has been applied:

$$\eta' = \frac{\eta_0}{[1 + (\omega\tau_0)^{\alpha}]} \tag{5}$$

where η_0 is the Newtonian viscosity, defined in the general linear viscoelastic model [23] as de limiting value of η' at very low frequency, τ_0 a characteristic relaxation time that accounts for the onset of non-linear pseudo-plastic region and α an adjustable parameter. The different values obtained by using expression (5) are given in Table 2.

In Fig. 2, we have represented the values of η_0 obtained in the Briedis and Faitelson fit versus the intrinsic viscosity, $[\eta]$, for all the EVA-c studied. As a reference line, we have also included in the figure the data obtained by Shroff and Mavridis [7] on linear polyethylene. These later data have been corrected by the TTS principle in order to be comparable with our EVA-c results, that have been obtained at 150°C. The values for the shift coefficient have been calculated in our laboratory using a set of equivalent metallocene polyethylene samples that are presently under study [24]. This representation immediately shows that most of the EVA-c samples can be situated on a straight line with the same slope than linear polyethylene but with a higher pre-exponential factor. The mathematical expression is given by the power law:

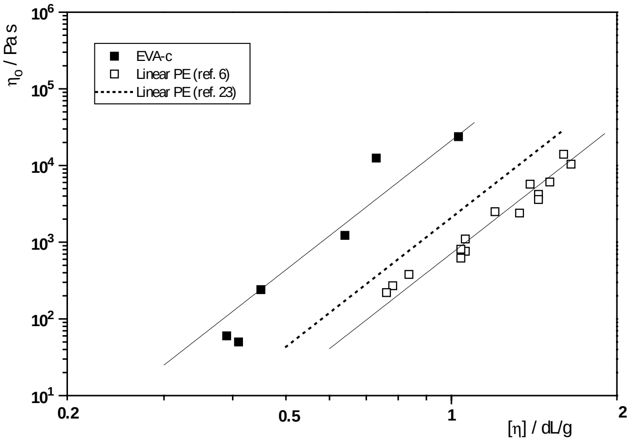

Fig. 2. Zero-shear melt viscosity versus intrinsic viscosity for EVA-c from Table 1 (■) at 150°C and for linear polyethylenes from Ref. [7] (□) at 190°C. The dotted line represents the results of linear metallocene polyethylenes at 150°C [24].

$$\eta_0 = 2.1 \times 10^3 [\eta]^{5.6} \tag{6}$$

The viscosities of EVA-c are considerably larger than those of the equivalent linear polyethylene. It is worthwhile to mention that the samples containing, respectively, the lowest and the highest content of VAc lie both on the same straight line. This result suggests that the VAc content is not itself the cause for the overall viscosity enhancement. Now, if one takes into account the ^{13}C NMR results concerning branches with length above six carbon atoms (see Table 1), it may be argued that the LCB present in this type of samples could be responsible of this viscosity enhancement.

In order to compare our EVA-c experimental data with LDPE data from the literature, it is convenient to plot η_0 against M_w. This is a suitable method since it is known that LDPE contains a larger number of LCB that affects seriously the factor g, defined as the ratio between the intrinsic viscosity of branched and linear molecules at the same molecular weight. As it is well known η_0 can be correlated with M_w by means of a power law equation, $\eta_0 \propto M_w^a$. There are in the literature a great number of values for the critical exponent, a, most of them lying between 3.3 and 3.9 for linear and branched polymers with the same degree of branching [9,12,25,26]. These values are only slightly higher than the predicted by the theory [27,28]. In addition, for polymers with different degree of branching, the scaling parameter, g, is often used [29]. Then higher values of the critical exponent ($a \approx 8$) are obtained. In general, the correlation between η_0 and M_w has been considered independent of polydispersity for conventional LDPE with the same branching content [12,26], for Phillips and

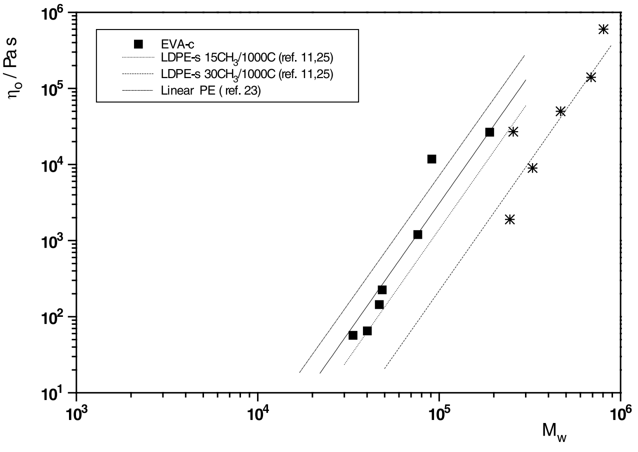

Fig. 3. Newtonian viscosity calculated from Eq. (5) versus weight average molecular weight at $T = 150°C$ for the copolymers studied. Solid line represents the fit to a power law function, $\eta_0 \propto M_w^a$ Eq. (7). Dashed lines and ($*$) are taken from literature data on LDPEs [11,26]. Dash-point line represents the behaviour of linear metallocene polyethylenes [24].

Ziegler-Natta high-density and low-density linear polyethylene (HDPE and LLDPE) [26], as well as for metallocene-catalysed polyethylene [25]. However, there are some literature data on HDPE that show polydispersity dependence on the Newtonian viscosity [30,31]. This behaviour has been generally attributed to the existence of high or lowmolecular weight tails that would give rise to different critical exponents in the power law correlation.

For most of the materials studied here, a clear power law exponent of 3.4 is obtained. This result is very different from that recently reported by Arsac et al. [19]. They found a much higher value, 5.6, attributed to peculiarities in the length and/or distribution of LCB and in the MWD. The correlation between η_0 and M_w that can be expressed by

$$\eta_0 = 3.1 \times 10^{-14}(M_w)^{3.4} \tag{7}$$

is plotted in Fig. 3. It is also clear in the figure that EVA2 copolymer deviates upward the linear correlation. On the other hand, the EVA6 sample shows a slightly lower value than that predicted by Eq. (7). These two apparently anomalous cases will be discussed later on in conjunction with other results. LDPE of different branching content taken from the literature are also included in the plot [26]. Finally, the correlation found for completely linear metallocene-catalysed polyethylene is plotted [24,31].

It is clearly observed that nearly the same critical exponent holds for the three sets of materials. For the EVA-c set, a slightly higher pre-exponential factor in the power law η_0–M_w than that observed for LDPEs ($K = 1.4 \times 10^{-14}$ and 2.2×10^{-15} at 150°C depending on branching content) has been found. On the other hand, for the same uncorrected for branching, molecular weight, all the branched polymers including our EVA-c exhibit lower Newtonian viscosity than the linear counterparts.

When the results are compared at the same value of molecular weight, branched polymers show a quite complex behaviour. Two effects affecting the entanglement density have been claimed [6]. In model star polymers (with one or two branches per molecule) and in polymers with low degrees of LCB, an increase in the viscosity and flow activation energy has been usually explained by the suppression of the reptation mechanism, more relevant as branch length increases [8,32,33]. Some early studies [34–36] have pointed out that melt viscosity in both branched polyvinyl acetate (PVA) and PB was higher than in the corresponding linear polymer, provided that the branch length, M_b, was above the characteristic molecular weight between entanglements, M_e. Entanglements containing LCB contribute to a more rapid increase in η_0 than in linear polymers or in polymers with shorter branches. Correspondingly, an increase in the scaling law exponent of the η_0–M_w correlation is found. On the other hand, Wang [37] established long ago that, for a given molecular weight, the viscosity of poly-α-olefins decreases exponentially with the length of side chains having its maximum effect at higher content of LCB. Similar conclusions were drawn by Bersted [6] on model branched polymers. In this case, the molecular size reduction effect dominates over viscosity. The result obtained for EVA-c reveals that an increase in the hydrodynamic volume, i.e. a lower content in LCB (see Table 1 for results), with respect to other branched polymers could be the cause of the higher values in the viscosity function. However, this increase in the hydrodynamic volume can also be affected by a reduction in the length of the branches. It is worth to note here the reduction of the flow activation energy observed in the EVA-c with respect to conventional LDPE (16–18 kcal/mol) as it has been highlighted in the preceding section. Unfortunately, the absolute content of LCB cannot be determined by ^{13}C NMR and only a maximum value given by the total number of branches exceeding six carbon atoms can be obtained [7]. Nonetheless, this limiting LCB value provides us with a good support to analyse the differences found in the behaviour of the different EVA-c.

In EVA2 and EVA6 copolymers, discrepancies in η_0 and E_a values appear when they are compared with the rest of EVA-c. We could attribute this deviation to differences among the samples in length, frequency and type of LCB and/or special features in the MWD.

The observed enhancement in η_0 for the EVA2 could be explained not only by an increase in the hydrodynamic volume of the macromolecules, i.e. a lower number of LCB per molecule as it has been proved for this copolymer by ^{13}C NMR data. Furthermore, the higher value of E_a may be an indication of longer LCB [8]. It is known that the viscosity increases exponentially with branch length, a universal feature of flexible chain molecules and presumably caused by a suppression of the reptation mechanism [38]. Thus, it seems reasonable that the exceptionally large value of η_0 would be accompanied by enhanced values of

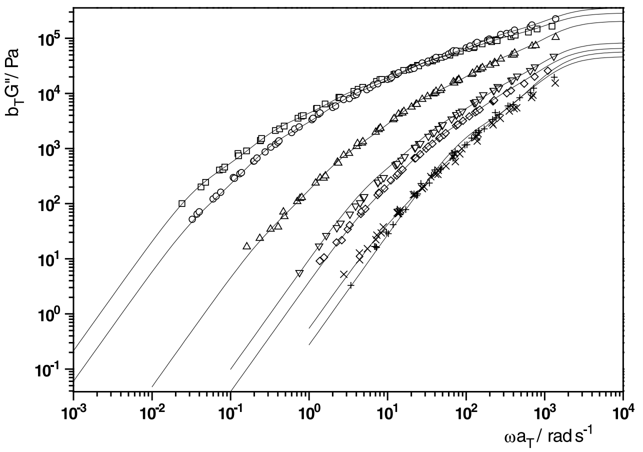

Fig. 4. Reduced storage modulus versus reduced frequency at $T_0 = 150°C$ for the copolymer studied. The symbols have the same meaning than in Fig. 1. The lines represent the fit of experimental data to the Maxwell function given by Eq. (10).

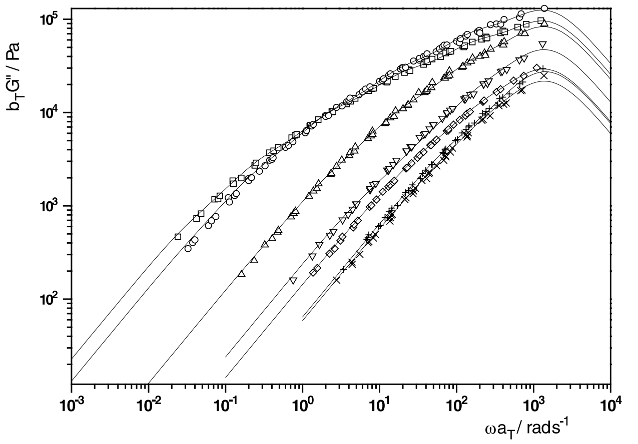

Fig. 5. Reduced loss modulus versus reduced frequency at $T_0 = 150°C$ for the copolymer studied. The symbols are the same as in Figs. 1 and 3. The lines represent the fit of experimental data to the Maxwell function given by Eq. (11).

E_a. Arsac et al. [19] have observed a similar behaviour in the viscosity function for a set of EVA-c copolymers. These authors attribute the higher viscosity of these copolymers to the presence of very long branches of polyethylene segments, reflected in DMTA measurements as a transition observed at 45°C, which they assigned to an absorption process of long branching points. However, this relaxation is actually near to the melting temperature that Brogly et al. [39] and Bistac et al. [40] have assigned to a highly disorganized crystalline structure of polyethylene segments containing VAc units.

On the contrary, sample EVA6 shows a slight decrease in η_0 and in E_a. Furthermore, a very low vertical activation energy value is obtained for this sample (see Table 2) [10]. It could be well possible that, in this particular case, the viscoelastic response is affected by the presence of a possible linear very low-M_w tail. In this context, it should be recalled that the use of small amounts of additives could cause several changes in the rheological behaviour of these materials [20].

To summarize this section, we may say that a group of EVA-c with different VAc content has been found to follow the power law between η_0 and $[\eta]$, and between η_0 and M_w with a critical exponents of 5.6 and 3.4, respectively. All of the samples show similar values of E_a. This result is an indication of a very similar molecular architecture as reflected by the ^{13}C-NMR data. However, the overall chain structure seems to differ notably from that of conventional LDPE. This difference could be attributed to a reduction in the number of LCB as a consequence of the introduction of the VAc comonomer during the polymerization process.

3.3. Elasticity

The fundamental viscoelastic function describing the elastic character of a molten polymer is the steady-state compliance J_e^0. As it is well known this function is the recoverable shear strain related to the shear stress in the steady state. We can obtain this function at sufficient low frequencies as [23]:

$$J_e^0 = \frac{1}{\eta_0} \lim_{\omega \to 0} \left(\frac{G'(\omega)}{\omega^2} \right) \tag{8}$$

In the same limit, the general linear viscoelastic model allows one to define the zero frequency viscosity [23]:

$$\eta_0 = \lim_{\omega \to 0} \left(\frac{G''(\omega)}{\omega} \right) \tag{9}$$

In order to obtain these functions, the dynamic modulus have been expressed in terms of the discrete Maxwell spectrum as [21]:

$$G'(\omega) = \sum_i G_i \frac{(\omega\lambda_i)^2}{1 + (\omega\lambda_i)^2} \tag{10}$$

$$G''(\omega) = \sum_i G_i \frac{\omega\lambda_i}{1 + (\omega\lambda_i)^2} \tag{11}$$

The experimental data and the fits to Maxwell functions of all of the EVA-c studied can be observed in Figs. 4 and 5.

The zero frequency viscosity calculated from the Maxwell spectra shows an excellent agreement with the values of η_0 calculated from Briedis and Faitelson fit (Eq. (5)) as it can be seen in Table 2. The steady-state recoverable shear compliance, J_e^0, calculated from Eq. (8) is also listed in Table 2. Let us now discuss the J_e^0 values as a function of polydispersity as they are represented in Fig. 6. It can be clearly seen that irrespective of the VAc content and M_w, J_e^0 increases as the polydispersity index increases up to values close to those characteristic of LDPE samples. This result is in agreement with previous experimental studies in polymer melt elasticity that indicate that J_e^0 is independent of M_w as long as the latter exceeds a critical value M_c' [21] and only depends on the molar mass distribution. If one compares EVA-c and LDPE in the same plot, the

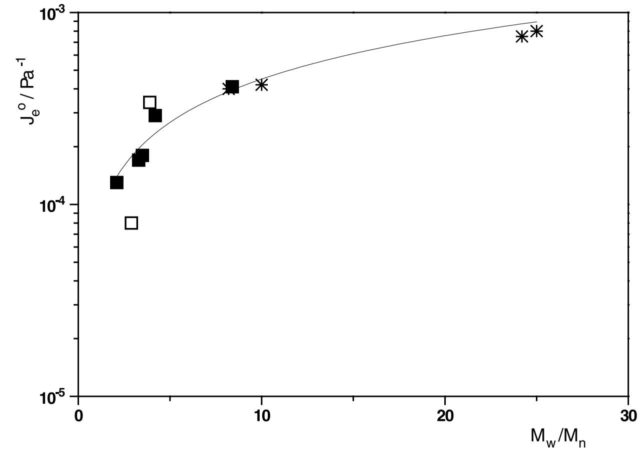

Fig. 6. Polydispersity index dependence of steady-state shear compliance for the copolymer studied at 150°C: (■) EVA-c that follow the power law in viscosity function (Eq. (7)); (□) EVA2 and EVA6 copolymers; (*) LDPE literature data [11]. The line is drawn only for the sake of clarity.

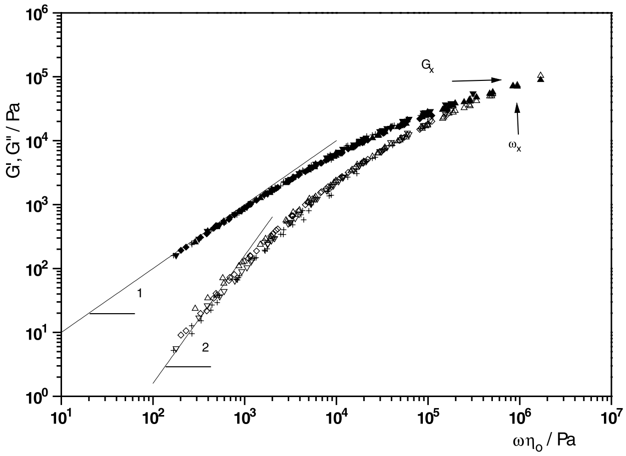

Fig. 7. Reduced curves of the storage (open symbols) and loss (filled symbols) moduli for the materials, which follow the power law between η_0 and M_w in Fig. 2 and present similar values in J_e^0 (1×10^{-4}–3×10^{-4} Pa^{-1}, see text). The symbols are the same as in Fig. 1.

EVA-c would represent a set of LDPE having the lowest elasticity and polydispersity values. Indeed the most polydisperse copolymer has a J_e^0 value close to the narrowest LDPE. Please note that again EVA2 and EVA6 slightly deviate from the overall trend.

Another measurement defining the elastic character of the material is the cross-point between the storage and the loss modulus, G_x [41,42]. This value defines the transition between the viscous ($G'' > G'$) and the elastic behaviour ($G' > G''$). The values of G_x have been calculated from Figs. 4 and 5 and given in Table 2. In the material with the lowest M_w, the cross-point cannot be experimentally reached. However, it can be obtained by extrapolation to higher frequencies in a reduced plot of the modulus versus $\eta_0\omega$ as it is shown in Fig. 7. This procedure yields an M_w-invariant asymptote $G''(\eta_0\omega) = \eta_0\omega$ for the loss modulus versus reduced angular frequency. For materials that follow the power law relation $\eta_0 \propto M_w^a$ and that present similar values in J_e^0, master curves on G' and G'' are observed. Consequently, a similar value in G_x is obtained. In these particular cases, a value over 6×10^4 Pa has been derived.

EVA2, in spite of its moderate MWD, shows an enhanced elastic character, that is, a higher value of J_e^0 and a lower value of G_x. Both variables are of the same order of magnitude than those exhibited by polydisperse EVA1. A compliance enhancement has been already observed in branched polymers [43]. According to Rouse–Ham theory, this viscoelastic function is also dependent on branching structure by means of the parameter g_2 [21]:

$$J_e^0 = \frac{2g_2M}{5\rho RT} \tag{12}$$

This parameter is analytically expressed for well-defined molecular model such as star polymers. In our case, it is very difficult to ascertain the molecular structure of the polymers due to the very complex mechanism of polymerization process. However, the different viscoelastic behaviour of sample EVA2 seems to indicate that a fundamental difference in chain structure may be causing the enhancement in all the viscoelastic functions studied, i.e. η_0, E_a and J_e^0. Finally, EVA6 copolymer is characterized by a low value of J_e^0. This feature could be an indication of the presence of very low molecular weight species, well below the critical molecular weight M_c', as it has been suggested in the preceding section.

3.4. Relaxation time

The general viscoelastic model allows one to define a relaxation time, which is approximately equal to the longest relaxation time of the generalized Maxwell model [21]:

$$\tau = \lim_{\omega\to0} \frac{G'}{\omega G''} = \eta_0 J_e^0 \tag{13}$$

The values of τ are listed in Table 2. It can be observed that there exists a clear relation between this longest relaxation time and that obtained from the fit of the dynamic viscosity through Eq. (5). This relation could be predicted if one recalls the experimental relation found for well-entangled polymer melts [43]:

$$\eta_0\omega_0J_e^0 = K \tag{14}$$

where ω_0 is the inverse of τ_0, the frequency for the onset of pseudo-plastic behaviour, and K a constant that, in this case, takes an average value of 4 (see the data listed in Table 2). Graessley [43] obtained a value of $K = 0.6 \pm 0.2$ for several families of polymers independently of the molecular structure, but this author defined $\dot{\gamma}_0$, instead of ω_0, as the shear rate in steady-state experiments at which the viscosity takes the values $0.8\eta_0$. For comparable molar mass distributions, J_e^0, is constant for $M_w > M'_c$. For this special case, the same dependence (power law exponent) of the relaxation time and the Newtonian viscosity with M_w is expected. For the materials studied here, different values of J_e^0, depending on polydispersity index, have been found, so the dependence of τ is more complex. Both molecular parameters, M_w and MWD affect this viscoelastic feature.

4. Conclusions

Seven commercial EVA-c, with VAc weight content between 13 and 28%, have been studied by rheological methods.

A slightly lower flow activation energy, E_a, than in conventional LDPE is found. Within the range of temperature used, all samples are proven to follow the Arrhenius approach with the introduction of a vertical shift to take into account the expected thermorheological complex behaviour.

When plotted against $[\eta]$ and M_w, η_0 follows two simple power laws, with critical exponents of 5.6 and 3.4, respectively, which are independent of VAc content in the range of composition studied. However, when the results are compared with linear polyethylene at a given value of $[\eta]$, one can observe an enhancement of the viscosity function. This enhancement can only be explained by the presence of equal amount of LCB that seems to be compatible with the maximum values of LCB estimated from ^{13}C NMR results. In fact, the sample containing the lowest amount of LCB deviates positively from the average behaviour showing an extra enhancement in the viscosity function. When EVA-c samples are compared with LDPE in an η_0–M_w log–log plot, it is found that the viscosity of EVA-c products lies well above the value of highly branched LDPE. This result is very striking since LDPE usually contains a very high number of LCB per molecule. A reasonable explanation can be offered by the Bersted's model if one assumes a reduction in LCB. This reduction could be due to a suppression mechanism of the growth of LCB points induced by the presence of VAc during the polymerization reaction of EVA-c.

On the other hand, it is confirmed that the strong elastic character of these materials is mainly monitored by polydispersity. In fact, similarly to what happens in conventional LDPE, a correlation between J_e^0 and polydispersity index is clearly visible.

The overall trend of E_a, η_0 and J_e^0 exhibited by the majority of the EVA-c samples is not followed by two of the copolymers studied that show limiting values for these magnitudes. In these two particular cases, one might argue that some molecular peculiarities such as differences in number or distribution and length of LCB with respect to the rest of the copolymers or even the presence of low-M_w tails could be playing an important role. Nonetheless, we would like to emphasize that most of the EVA-c samples follow the basic general rules of the viscoelastic functions and the deviations observed along this work can be understood in the framework of the complex structure underlying this important class of materials.

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