Rheological behaviour of LDPE/EVAc blends. II. Linear viscoelasticity and extrusion properties

J. Peón · J. F. Vega · M. Aroca · J. Martínez-Salazar

Abstract This study was designed to determine the linear viscoelastic and extrusion properties of a series of LDPE/EVAc blends. Newtonian viscosity was found to show strong positive deviation from the double reptation model, which assumes miscibility or, at least, cooperative relaxation between the mixed species. The blends also showed enhanced steady-state compliance and elastic indices compared to those of the pure components. These features, typical of emulsion-like polymer blends, seem to be attributable to additional relaxation processes at low frequencies associated with dispersed phase deformability. Good agreement with experimental dynamic results was shown by the Palierne model for emulsions of two viscoelastic liquids, for values of $\alpha/R = 3.5 \times 10^3$ Pa across the whole frequency range examined. The double reptation model, usually applied to miscible blends, showed good agreement with experimental data for frequencies higher than 10^{-2} rad s^{-1}. This could lead to erroneous conclusions on the miscibility of certain systems, for which a complete set of experimental data is lacking.

Introduction

Few publications have dealt with the rheological properties of ethylene vinyl acetate copolymers (EVAc) [1, 2] and

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their blends with polyethylene (PE) [3], yet there are many patents in the literature that describe blends of both these components, of widespread use in multilayer packaging films, sheets for car parts, self-adhesive protective plastic films, etc. [4–6]. Blending is a frequent industrial practice in the polyolefin area, its main aim being to obtain new materials with improved properties and/or reduced cost. It is known that blend properties are highly dependent on morphology, i.e., miscibility, composition and compounding conditions. In an immiscible blend, the size and shape of the dispersed phase, the character and size of the interphase domains, and the distribution of residual stresses, are all key factors [7, 8]. The miscibility of polyolefin blends has been the subject of basic research, and though one might expect interactions between repeat units to be similar, the liquid state phase shows separation [9]. Factors such as molecular weight, comonomer and degree of branching play an important role in these types of system. Blends of high-density polyethylene (HDPE) and linear low-density polyethylene (LLDPE) are miscible in the melt state and co-crystallise on cooling [10]. Blends of HDPE and low-density polyethylene (LDPE) show more complex behaviour, due to a certain degree of phase separation in the solid state [11] but seem to be miscible [12] or at least show co-operative molecular relaxation in the melt [13, 14]. Blends of Ziegler–Natta LLDPE and LDPE have been reported to exhibit phase separation both in the solid and melt state [13, 15]. In contrast, some studies have recently demonstrated that blends of metallocene LLDPE with HDPE and LDPE are miscible in the melt state at temperatures in the range 130–230 °C [16].

By applying molecular dynamics models, such as the double reptation model of Tsenoglou [17] and des Cloizeaux [18], it has been possible to explain the rheological behaviour of polymer blends in the melt state [13, 14].

These models are now being accepted as general blending laws for miscible blends. If there is any change between a miscible and a phase-separated state, it is generally accepted that there will be an asymmetric difference between a measured property and that calculated from the miscible blend relationship. In these cases, increased viscous and elastic properties compared to those of the base polymers are usually observed. Emulsion models [19] that account for the effects of interfacial tension have served to interpret the viscoelastic response of these phase-separated systems [20–23].

PE/EVAc blends have been long accepted as miscible systems [7], though one of the few reports in the literature [3] states that rheological functions in the melt state show complex behaviour. The present study describes an analysis performed on a series of LDPE and EVAc blends. Blend homogeneity was determined by complete rheological characterisation in the melt state. The viscoelastic response of the blends was then satisfactorily explained according to recently developed models for miscible and immiscible systems.

Experimental section

Materials and blend preparation

The mixed materials were obtained by conventional free radical polymerisation procedures. LDPE and EVAc were supplied by Repsol-YPF, Spain. The molecular variables of the materials, obtained by size exclusion gel permeation chromatography (SEC) and carbon nuclear magnetic resonance (^{13}C-NMR) are shown in Table 1. Melt flow rate (MFR) values were measured at 125 °C for the EVAc and at 190 °C for the LDPE at a constant weight of 2.16 kg. The MFI value at 190 °C for the EVAc was estimated from the following equation [2, 24]:

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

This relationship was obtained for a set of several samples of EVA copolymers taking into account the temperature dependence of viscoelastic properties of these materials [24]. Blending was carried out in an internal mixer Brabender Plasticorder fitted with a cam type rotor. Temperature was set at 160 °C and rotor speed at 60 r.p.m. Mixing was performed for about 5 min until the torque had stabilised. The mixed mass was then compression moulded for 2 min at 160 °C in an Schwabenthan Polystat 200T at a nominal pressure of 150 bar. Disk specimens 30 mm in diameter were stamped for dynamic torsion measurements and a portion of the mixed mass were pelletised for capillary extrusion rheometry measurements. The pure materials were treated in the same conditions. No differences in rheological properties were observed between the pure and treated samples.

Rheological testing

Dynamic measurements

Rheological measurements were performed in a dynamic thermal analyser Polymer Laboratories MKII (torsion system) and a Bohlin CVO rheometer in the parallel plates mode. Oscillatory viscoelastic measurements were made over the range of frequencies 6.3×10^{-3} to 6.3×10^2 rad s^{-1}, at a strain amplitude corresponding to the linear viscoelastic region, which was located by a previous strain sweep. The following viscoelastic functions were determined: storage modulus $G'(\omega)$; loss modulus $G''(\omega)$; and modulus of the complex viscosity $|\eta*(\omega)|$. The temperature range of measurements was 130–190 °C.

Extrusion

Extrusion measurements were performed using a piston-type capillary rheometer CEAST rheoscope 1000 at a temperature of 160 °C in the shear rate range from 6 to 2400 s^{-1}. The capillary is of circular cross section (diameter 1 mm) and has a length/diameter ratio (L/D) of 40,

Table 1 Characterisation of the materials studied: vinyl acetate content, melt flow index, weight average molecular weight, polydispersity index and branching content

Sample	% VAc[a]	MFI[b]	M_w (g mol^{-1})	M_w/M_n	SCB < 6 C[c]	LCB > 6 C[c]
LDPE	–	0.23	256800	7.6	n.d.	n.d.
EVAc	13.4	3.6	189800	8.4	6.5	< 2.5

[a]Weight % vinyl acetate comonomer

[b]ASTM D-1238

[c]Aliphatic branching

n.d. means not determined

which it is large enough to avoid Bagley corrections. The shear rate obtained was corrected using the conventional expressions of the Rabinowitsch method. The extrudates were cooled at room temperature and their diameters, d_j measured using a micrometer Mitutoyo Digimatic Indicator to determine the extrudate swell, $B = d_j/D$, where D is the diameter of the die.

Results and discussion

Time-temperature superposition principle (TTSP)

The time–temperature superposition principle (TTSP) is frequently applied either to determine the temperature dependence of rheological variables or to expand the time or frequency range at a reference temperature. In the case of polymer blends, the validity of the TTSP has been confirmed for several situations, but also the non-validity, independently of the miscibility or immiscibility of the blends. Thus, the TTSP cannot be considered a good test of miscibility [25]. In the materials studied here, what is needed above all is to distinguish between simple and complex thermorheological behaviour as has been recently pointed out by Mavridis and Shroff [24]. In our case, both blend components (EVAc and LDPE) show high flow activation energy E_a values and thermorheologically complex behaviour. This is a consequence of the presence of long chain branching (LCB), as discussed in a previous paper [2]. In a thermorheologically complex system, one has to define horizontal a_T and vertical b_T shift factors. Table 2 shows the horizontal E_{ah} and vertical E_{av} flow activation energies of our samples. It can be observed, that the E_{av} are slightly higher than those of the pure components but are in the range of other polymer systems (4.17–12.5 kJ mol^{-1}) [24]. A slight positive deviation from pure additivity was shown by the E_{ah} in the LDPE-rich compositions (high LDPE blend weight fraction, w) of the phase diagram. Similar slightly enhanced E_{ah} values have been reported for immiscible PETG/EVAc blends [22], which contrasts with the linear

dependence shown by blends of LLDPE and HDPE with LDPE [16, 26].

The viscosity function

Viscosity is a rheological function that is commonly used to describe coupling between the components of a blend in the melt state. In this section, we will describe the use of this function either to test the applicability of several blending models or to assess the degree of homogeneity of the blend components. Figure 1 shows the reduced modulus of the complex viscosity, $|\eta^*|b_T/a_T$, of the blends as a function of the reduced frequency ωa_T, at the reference temperature of 160 °C. To obtain a more complete picture of the rheological behaviour of the blends, we also prepared viscosity curves using data obtained by capillary extrusion rheometry at the same temperature (see Fig. 2). Also included in the figure, are values equivalent to those of the complex viscosity shown in Fig. 1 as derived by the Cox–Merz rule [27]

$$\eta(\dot{\gamma}) = |\eta^*(\omega)|]_{\dot{\gamma}=\omega} \tag{2}$$

It can be clearly observed, that this rule works nicely for the blends examined. The Cox–Merz rule has been always considered empirical, since it correlates linear and non-linear functions. However, this rule has been validated in a theoretical study assuming double reptation as the primary mechanism of stress relaxation [28]. Fulfilment of this rule is considered a prerequisite for assessing the homogeneity of blends [16]. However, as we will see later, it cannot be taken as proof of miscibility [8].

A first glance at Fig. 1 indicates that the viscosity of any blend composition falls roughly between the viscosities of the original components and is proportional to the content of each phase. However, peculiar phenomena appear in the low frequency range, c.a. typically lower than $\omega_c = 10^{-1}$ rad s^{-1}. The blends of high w show an inflexion in viscosity versus frequency curves below ω_c. Further, when passing to lower frequency, the viscosity of the blends tends towards values higher than that shown by the
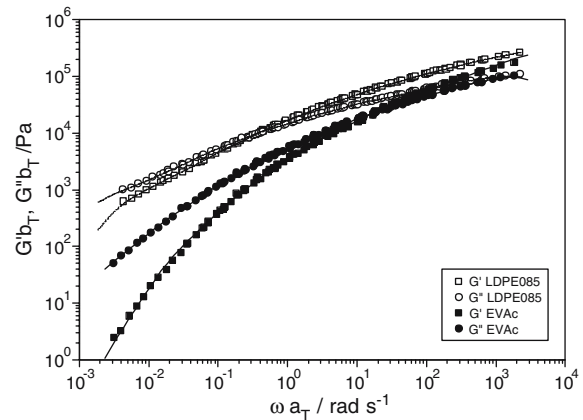
Table 2 Rheological variables of the materials at 160 °C

Flow activation energy, E_a, Newtonian viscosity, η_o, steady-state compliance, J_e^o, relaxation time, λ, and the elastic indices, E_R, and cross-point modulus, G_x

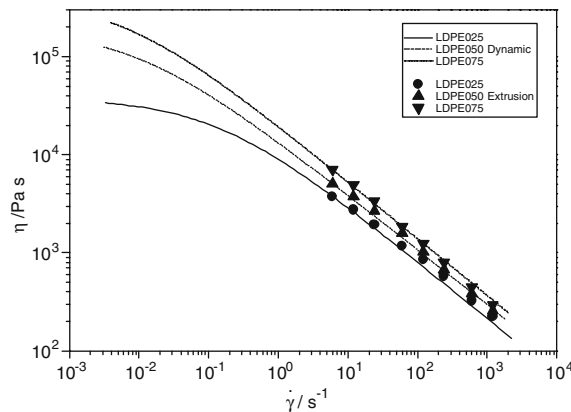| Sample	E_{aH} (kJ mol^{-1})	E_{aV} (kJ mol^{-1})	η_o (Pa s)	J_e^o (Pa^{-1})	λ (s)	E_R	G_x (Pa)
EVAc	55.4	6.3	16100	$3.5\ 10^{-4}$	5.64	0.57	20500
LDPE025	58.3	9.2	30800	$4.8\ 10^{-4}$	14.8	0.60	16900
LDPE050	59.2	8.3	105000	$4.2\ 10^{-4}$	44.1	0.96	12700
LDPE075	66.3	9.6	470000	$1.0\ 10^{-3}$	470	1.3	9400
LDPE085	65.8	9.6	540000	$1.0\ 10^{-3}$	540	1.4	8500
LDPE090	65.4	10.4	315000	$1.0\ 10^{-3}$	315	1.1	8900
LDPE	62.5	6.7	255000	$6.0\ 10^{-4}$	153	0.59	11300
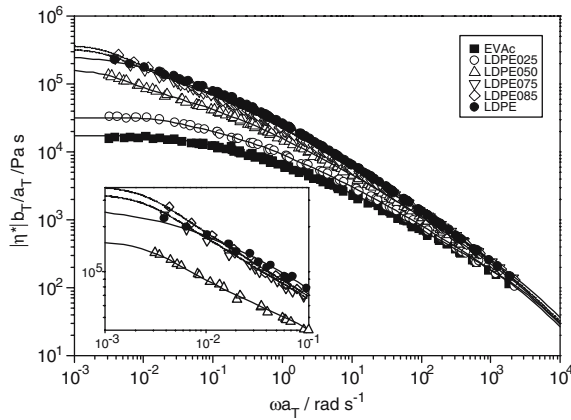
Fig. 1 Reduced modulus of the complex viscosity versus reduced angular frequency of the blends at 160 °C. (■) EVAc (○) LDPE025, (△) LDPE050, (▽) LDPE075, (◇) LDPE085 (●) LDPE. The lines correspond to the Maxwell fit

Fig. 2 Cox–Merz rule for some of the blends examined at 160 °C. Symbols as for Fig. 1. Lines: dynamic measurements; closed symbols: extrusion measurements

Fig. 3 Experimental storage and loss moduli G' (□, ■) and G'' (○, ●) at 160 °C for the LDPE085 blend (open symbols) and the pure EVAc (full symbols). Lines represent fitting curves of experimental data to the Maxwell model

$$J_e^o = \frac{1}{\eta_o^2} \lim_{\omega \to 0} \frac{G'}{\omega^2} \tag{4}$$

$$\lambda = \lim_{\omega \to 0} \frac{G'}{\omega G''} = \eta_o J_e^o \tag{5}$$

The values obtained for η_o, J_e^o and λ are shown in Table 2. As an example, the experimental data and fit to Maxwell functions are shown in Figs. 1 and 3 for some of the samples studied.

Applying blending laws and models

In Fig. 4, we plotted viscosity values taken at different levels of the modulus of the complex modulus $|G^*|$, or shear stress σ, against composition. Assuming the Cox–Merz rule holds, this is equivalent to working in the frequency range 10^{-1} to 10^3 rad s^{-1}. It may be observed, that the experimental values deviate slightly from the simple log-additivity rule. However, the tendency of the viscosity versus composition curve is very close to the behaviour shown by homogeneous systems [10, 12–14, 16]. At these levels of σ in steady-state capillary measurements, heterogeneous systems usually give rise to slippage phenomena between the phases and strong negative deviations from log-additivity [30]. The model most commonly used to characterise homogeneous polymer blends is the double reptation model, which is based on molecular reptation dynamics. Applying the double reptation model, the relaxation modulus of a homogeneous blend can be expressed as:

most viscous component (LDPE). Consequently, for certain compositions, limiting zero-shear viscosity η_o is higher than that of the pure components. This last result clearly suggests the presence of specific interactions between components, as reflected by viscoelastic properties.

To further evaluate the blend models available, characteristic terminal variables need to be determined. We thus established the values of η_o expressing dynamic storage G' and loss G'' moduli in terms of a discrete Maxwell spectrum [2]. A good fit of the results is obtained with a number of Maxwell modes between 6 and 8. Other variables such as steady-state compliance J_e^o and longest relaxation time λ were also determined using the expressions [29]:

$$\eta_o = \lim_{\omega \to 0} \frac{G''}{\omega} \tag{3}$$

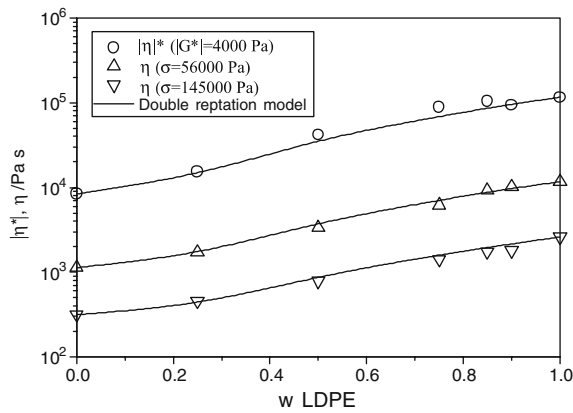**Fig. 4** Compositional dependence of viscosity at 160 °C: (○) $|\eta^*|$ ($|G^*| = 4000$ Pa), (△) η ($\sigma = 56000$ Pa) (▽) η ($\sigma = 150000$ Pa). Lines correspond to the double reptation model fit given by Eq. 7

$$G(t) = \left[\sum_i w_i G_i^{1/2}(t) \right]^2 \qquad (6)$$

where w_i are the weight fraction of each blend component and $G_i(t)$ the respective relaxation modulus. This model, formerly introduced by Tsenoglou [17], assumes that coupling between two macromolecular species along a single chain in the blend is random and occurs in a proportional manner to the fractional participation of the blend components. A blend's viscoelastic functions can thus be expressed in terms of the properties of the pure components. For example, the Newtonian viscosity function can be expressed using [13]:

$$\eta_o \cong 2 \sum_{i=1}^{n} \sum_{j=1}^{n} w_i w_j \left(\frac{1}{\eta_{oi}} + \frac{1}{\eta_{oj}} \right)^{-1} \qquad (7)$$

We systematically applied Eq. 7 to fit the compositional dependence of the viscosities represented in Fig. 4. From these fits, shown in Fig. 4 as dashed lines, it can be concluded that the double reptation model is valid when operating at moderate to high values of $|G^*|$ and σ (moderate to high frequency ω and shear rate $\dot{\gamma}$). This finding is consistent with those reported by others for blends of olefinic polymers [10, 12–14, 16].

To better illustrate the lowest frequency limit ω_c for application of the double reptation model, it is convenient to use the viscoelastic storage G' and loss G'' moduli. Assuming that both polymers have the same entanglement modulus G_N^o, same melt density ρ, and that measured dynamic moduli in the terminal region are much smaller than G_N^o over the range of frequency examined, the equations for G' and G'' can be expressed as a function of the pure components' properties as [13]:

$$G'(\omega) \cong \sum_{i=1}^{n} \sum_{j=1}^{n} w_i w_j \left[\frac{1}{4} \left(G_i'(\omega)^{-1/2} + G_j'(\omega)^{-1/2} \right)^2 \right]^{-1} \qquad (8)$$

$$G''(\omega) \cong 2 \sum_{i=1}^{n} \sum_{j=1}^{n} w_i w_j \left(\frac{1}{G_i''(\omega)} + \frac{1}{G_j''(\omega)} \right)^{-1} \qquad (9)$$

The experimental values of G' and G'' and the predictions of the double reptation model given by Eqs. 8 and 9 are plotted in Fig. 5 for two of the blends studied (LDPE025 and LDPE085). It is of interest that the predictions of the model coincide very well with the experimental data over a broad frequency range (from 10^{-1} to 10^3 rad s^{-1}). However, on passing to lower frequencies, the picture is quite different. One then finds that G' shows strong positive deviation from the double reptation model for the LDPE085 blend. This behaviour has been observed in heterogeneous emulsion-like polymer blends [20–23]. The deviation corresponding to the LDPE025 blend is less pronounced. This observation will be discussed later.

From the above analysis, it can be concluded that while operating at moderate to high frequency and shear rate, our blend systems behave as homogeneous blends and show no enhancement in viscoelastic functions at low frequencies, nor slippage between the phases in steady-state capillary measurements. We would like to emphasise that this type of analysis would lead to an incorrect idea of the miscibility of these polymer blends.

To consider the effect obtained at frequencies below ω_c, models that contemplate blend heterogeneity need to be applied. The one proposed by Oldroyd for dilute emulsions is perhaps the most used [31]. In this model, the viscosity
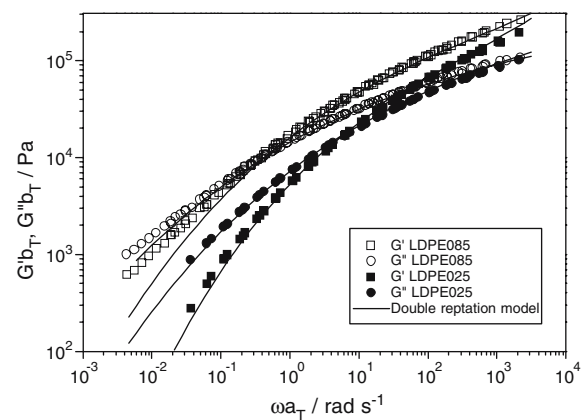
Fig. 5 Predictions of the double reptation model (Eqs. 8 and 9) for G' (□, ■) and G'' (○, ●) in blends LDPE085 (open symbols) and LDPE025 (full symbols) at $T = 160$ °C

of a dilute emulsion of two incompressible and immiscible Newtonian fluids in the linear viscoelastic range is given by

$$\eta_o = \eta_{o,m} \left[1 + \phi \frac{5K+2}{2(K+1)} + \phi^2 \frac{(5K+2)^2}{10(K+1)^2} \right] \quad (10)$$

where ϕ is the volume fraction of the dispersed phase, $\eta_{o,m}$ is the viscosity of the matrix liquid and $K = \eta_{o,d}/\eta_{o,m}$, $\eta_{o,d}$ being the viscosity of the dispersed droplets.

In Fig. 6 the model has been applied to the compositional dependence of η_o (see Table 2) and viscosity values shown in Fig. 4, assuming that the weight w and volume ϕ fractions to be equal, i.e., both components were taken to have the same melt density ρ. In our case, $K = 0.063$ for high values of w and $K = 14$ for low values of w. For low values of w, the Oldroyd's model provides similar results than the double reptation model applied in Fig. 4. Additionally, at high w, the model is unable to describe the maximum viscosity observed. At this point, again one has to go one step further and invoke more complicated models such as that formerly described by Utracki [32]. Considering that both positive deviation at low values of shear stress and negative deviation at high values of shear stress have been observed of immiscible blends, this author developed a general model given by the expression:

$$\log \eta = -\log \left[1 + \beta(\phi_1\phi_2)^{1/2} \right] - \log \left(\frac{\phi_1}{\eta_1} + \frac{\phi_2}{\eta_2} \right) \\ + \eta_{max} \left\{ 1 - \left[\frac{(\phi_1 - (1 - \phi_{2d}))^2}{\phi_1\phi_{2d}^2 + \phi_2(1 - \phi_{2d})^2} \right] \right\} \quad (11)$$

In this equation β is the interlayer slip factor that accounts for negative deviating behavior from log-additivity.
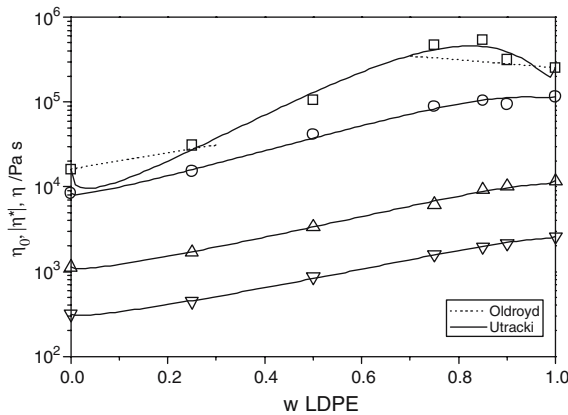
Fig. 6 Predictions of the Oldroyd's model for the compositional dependence of Newtonian viscosity η_o (Eq. 10, dashed lines) at 160 °C and predictions of the model of Utracki (Eq. 13, solid lines) for the compositional dependence of: ($\square$) η_o, ($\bigcirc$) $|\eta^*|$ ($|G^*| = 4000$ Pa), ($\triangle$) η ($\sigma = 56000$ Pa) (∇) η ($\sigma = 150000$ Pa) at 160 °C

The variable η_{max} determines positive deviating behavior. The phase inversion concentration ϕ_{2d} is usually known from K as [32, 33]:

$$K = \left[\frac{(\phi_m - \phi_{2d})}{\phi_m - (1 - \phi_{2d})} \right]^{-[\eta]\varphi_m} \quad (12)$$

where $[\eta] = 1.9$ and $\phi_m = 0.84$ [32]. A value $\phi_{2d} = 0.75$ for $K = 0.063$ is obtained, very close to the experimental value, $\phi_{2d} = 0.80$. Then expression 11 contains only two adjustable variables, β and η_{max}. We applied the model to our viscosity results shown in Fig. 6. The β and η_{max} values obtained, listed in Table 3. Diminishing β and η_{max} values were observed with increasing $|G^*|$ and σ, as shown in Table 3. Moreover, a pronounced relative decrease in the β/η_{max} ratio was observed. This suggests that the effect of interlayer slip, given by β, is offset by the positive deviating effect modulated by η_{max}, which happens to be the predominant term in expression 11. Hence, it may be postulated that well-stabilised emulsion-like behaviour prevails over the entire range of $|G^*|$ and σ examined. In this case, the phases have a degree of miscibility due, for example, to the similar chemical structure of the polymers or to macromolecular chains interacting and interlinking in a three-dimensional zone (interphase). This assumes a low value of interfacial tension α and increased viscosity in the interfacial zone. In this case, negative deviating behaviour is not observed at high shear stress levels, as occurs in our blends.

The discussion so far represents the maximum amount of information that can be obtained or deduced through application of the different models available. However, we would like to go one stage further and try to better characterise the interphase between the blends' two main components.

Palierne [19, 20] developed a general expression for the complex shear modulus of an emulsion of undiluted viscoelastic fluids, in terms of the ratio between interfacial tension and the dispersed phase radius α/R:

$$G*(\omega) = G_m^*(\omega) \frac{1 + 3\sum_i \phi_i H_i(\omega)}{1 - 2\sum_i \phi_i H_i(\omega)} \quad (13)$$

Table 3 Variables of Eq. 11 used to compute the concentration dependent viscosities in Fig. 6

| $|G^*|$ or σ (Pa)	β	η_{max}	β/η_{max}	ϕ_d
0	6.58	1.48	4.34	0.75
4000	1.5	0.72	2.08	0.75
56000	0.78	0.41	1.92	0.75
150000	0.24	0.34	0.71	0.75

with $H_i(\omega)$ given by

$$H_i(\omega) = \frac{4\left(\frac{\alpha}{R_i}\right)\left[2G_m^* + 5G_d^*\right] + \left[G_d^* - G_m^*\right]\left[16G_m^* + 19G_d^*\right]}{40\left(\frac{\alpha}{R_i}\right)\left[G_m^* + G_d^*\right] + \left[2G_d^* + 3G_m^*\right]\left[16G_m^* + 19G_d^*\right]}$$

(14)

The storage and loss moduli at 160 °C of the LDPE085 and LDPE025 blends are presented in Fig. 7

The predictions of the Palierne model over a wide range of frequencies (six decades) are given in the same figure, showing the best fit for a value of the ratio $\alpha/R = 3.5 \times 10^3$ Pa. In these semi-crystalline systems, it is very difficult to obtain experimental evidence of the morphological melt state due to the lack of contrast between the two phases. However, in the solid state, a clear domain separation between the paths of the most and least crystallisable phases can be observed using microscopy techniques. One can then assume that domain size in the melt is of the same order as that observed in the solid state at a temperature at which the phase with the lower crystalline content (EVAc) melts. In our blends, one can postulate an average droplet radius of 2.5 μm. This leads to an interfacial tension value between the phases of $\alpha = 7.0$ mN m^{-1}. This is certainly a low value of α, which may reach values in the vicinity of 20 mN m^{-1} in polymer systems [13, 22, 23].

The presence of a dispersed phase and an interphase in heterogeneous systems usually determines the enhancement in viscosity and elasticity observed in our blends. These experimental features have been attributed to additional long-time relaxation processes that correspond to the deformability of the dispersed phase. Evidence for these relaxation mechanisms in our systems can be found in
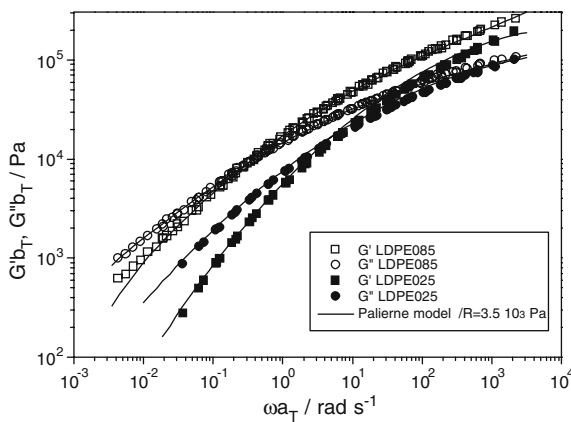
Table 2 in the relaxation times, λ. It can be clearly observed that the blends with high w values, those formed by a continuous matrix of LDPE and a dispersed deformable (less viscous) EVAc phase, show the highest values of λ. For low values of w, the enhanced character in viscoelastic functions can hardly be seen. In this case, the additional relaxation process due to the deformability of the hard LDPE dispersed phase is not clearly observed.
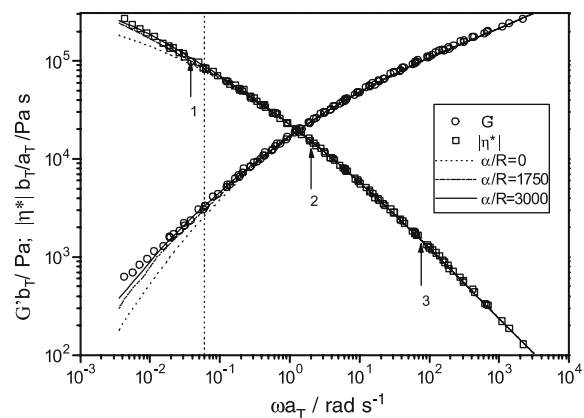
Figure 8 can be used to clarify an experimental consideration. In this figure, we represent the Palierne model applied to the storage modulus and to the complex viscosity for the LDPE085 blend using α/R as a variable. It can be clearly seen that, at frequencies higher than ω_c, the model is insensitive to α/R and coincides with the double reptation model. This indicates that using certain rheometers, care should be taken when making assessments above the miscibility of polymer systems.

Elasticity: implications in polymer processing

The blends of high LDPE content showing viscoelastic function maxima deserve special attention. These blend compositions are of interest in polymer processing. Shroff and Mavridis [34] described several indices to quantify the elasticity of polymeric materials. These indices were found to define the rheological polydispersity of molten polymers, mainly affected by molecular weight distribution (MWD) and LCB. The first index we calculated is denoted E_R:

$$E_R = C \cdot G'|_{G''=500\,\text{Pa}}$$

(15)

where C is an arbitrary constant chosen so that E_R falls between 0.1 and 10. E_R is actually a measure related to the steady state shear compliance, J_e^o:


Fig. 7 Predictions of the Palierne model (Eqs. 13 and 14) with $\alpha/R = 3.5\ 10^3$ Pa for G' ($\square$, $\blacksquare$) and G'' ($\bigcirc$, $\bullet$) in blends LDPE085 (open symbols) and LDPE025 (full symbols) at $T = 160$ °C

Fig. 8 Predictions of the Palierne model (Eqs. 13 and 14 for variable α/R) for G' ($\bigcirc$) and $|\eta^*|$ ($\square$) in the blend LDPE085 at $T = 160$ °C. Arrows indicate the viscosity values from Fig. 4 for LDPE085

$$G'(\omega) = J_e^o [G''(\omega)]^2 \quad \text{when} \quad \omega \to 0 \qquad (16)$$

which accounts for the effect of the MWD (mainly the high molecular weight tails) and/or LCB. The cross-modulus between G' and G'', G_x, was also determined. MWD has been reported to affect this parameter [34], and consequently it can be also considered a measure of the rheological polydispersity of polymers and blends. Both these elastic indices calculated for all the samples are shown in Table 2. The rheological polydispersity indices E_R and G_x were plotted in Fig. 9.

Maximum E_R index values were noted, accompanied by a slight local minimum G_x for high values of w. The values of J_e^o provided in Table 3 follow the same pattern: maximum values of J_e^o corresponding to high values of w. The double reptation model was then applied to E_R and G_x. In the case of G_x, calculated values showed similar behaviour to experimental values since the cross-point usually appears in the short-term regime, in which relaxation of the dispersed phase has not had time to occur. Differences between experimental values and those predicted by the model are of the order of 10%. In contrast, pronounced positive deviation from predicted values was shown by the E_R index. This index is a measure of elasticity in the low frequency zone and it accounts for the effects of long-term relaxation structures, such as high-M_w tails, LCB or deformation of the dispersed phase.

A direct extrusion rheological property that quantifies melt elasticity is the die swell $B = d_j/D$ [35], where d_j is the extrudate diameter and D is the diameter of the die. Figure 10 shows the compositional variation of the die swell for the samples studied. A conspicuous increase in die swell at high values of w with respect to the base polymers may be clearly observed. This result parallels that noted for the E_R index by means of dynamic measurements. The morphology of the flowing blend is not expected to remain
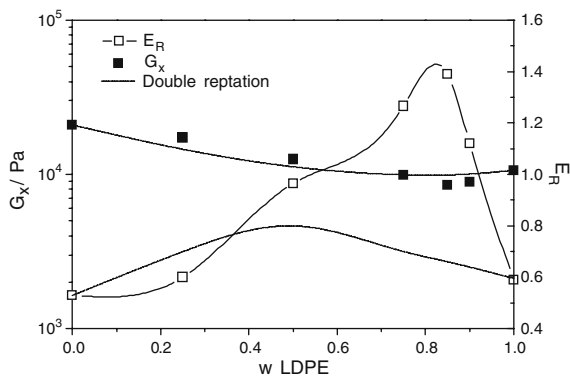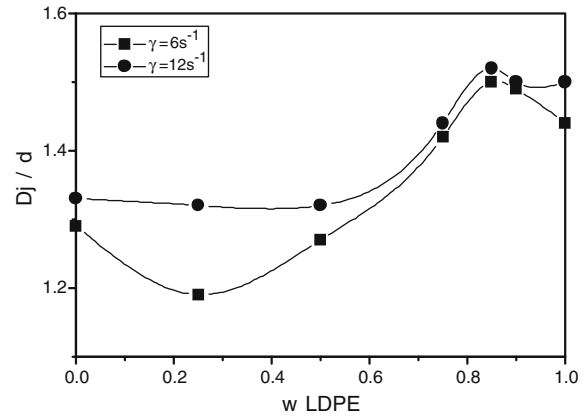
Fig. 10 Die swell d_j/D versus blends' composition at $T = 160$ °C. Results were obtained at the shear strain rates (■) 6 s^{-1} and (●) 12 s^{-1}

stable during flow at high stresses. A large deformation of the dispersed phase droplets with the corresponding additional elastic energy storage could mean that, at the die exit, part of the extra elastic energy is recovered in the form of a large extrudate swell. This may be highly relevant in industrial applications such as blow moulding, which require good bubble stability, generally associated with high resistance and elasticity of the melt.

Finally, there is a chance that thermal/shear induced degradation will affect blending or experimental procedures. In these types of polymer, degradation usually leads to LCB-type complex structures, and thus, to an enhanced viscosity and elastic character of the blends relative to the pure polymers. However, in a detailed study of the blends by IR spectroscopy, we observed no significant changes in the most characteristic reactive chemical groups (carbonyl and vinyl) in the blended materials [36]. Moreover, we found that rheological measurements were repeatable at low frequencies in successive frequency sweeps, indicating no morphological nor structural modifications in these samples.

Conclusions

In spite of their highly complex thermorheological behaviour, LDPE/EVAc blends comply with the time–temperature superposition principle. A slight increase in flow activation energy values with LDPE content was noted, as in the case of some heterogeneous binary systems. These blends also showed a positive deviation in Newtonian viscosity and good agreement between dynamic and steady state viscosity data at medium to high frequency/shear rates. Maximum viscosity was reached for compositions in the range $w = 0.7$–0.8, as for other heterogeneous poly-

Fig. 9 Rheological polydispersity indices versus blends' composition at $T = 160$ °C. (□) E_R ($C = 5 \times 10^{-3}$) and (■) G_x. Dashed lines correspond to values predicted by the double reptation model (Eqs. 8 and 9)

olefin blends of comparable component viscosity ratio. The Palierne model for emulsion-like polymer blends was able to satisfactory explain the viscoelastic behaviour of the blends, despite the pure polymers being of high structural complexity, i.e., broad molecular weight distribution and the presence of long side branches. The double reptation model, usually applied to miscible blends, showed good agreement with experimental data for frequencies higher than 10^{-1} rad s^{-1}. This may lead to wrong conclusions concerning the miscibility of certain systems, for which the experimental picture is incomplete. A conspicuous increase in elastic character was detected in blends of high LDPE content. Along with higher Newtonian viscosity, this observation suggests the existence of a deformation relaxation mechanism of dispersed droplets, in accordance with the Palierne model. The blends' heterogeneous morphology leads to the possibility of extra-storage of elastic energy mechanisms due to interfacial phenomena during shear. As a final remark, the addition of small amounts of EVAc to LDPE (10–25%) could lead to improved melt properties. This is of great interest in industrial applications such as blow moulding.

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