JOURNAL OF MATERIALS SCIENCE **38** (2003) 4757 – 4764

Viscoelastic behaviour of metallocene-catalysed polyethylene and low density polyethylene blends: Use of the double reptation and Palierne viscoelastic models

J. PEÓN, C. DOMÍNGUEZ, J. F. VEGA
GIDEM, Instituto de Estructura de la Materia, CSIC, Serrano 113-123, 28006 Madrid, Spain
M. AROCA
Repsol I+D, Embajadores 183, 28006 Madrid, Spain
J. MARTÍNEZ-SALAZAR*
GIDEM, Instituto de Estructura de la Materia, CSIC, Serrano 113-123, 28006 Madrid, Spain
E-mail: jmsalazar@iem.cfmac.csic.es

The linear viscoelastic behaviour of a series of mPE/LDPE blends was evaluated. Newtonian viscosity showed slight positive deviation from the double reptation model, which assumes miscibility or, at least, cooperative relaxation between the mixed species. This feature is typical of emulsion-like polymer blends and is attributable to additional relaxation processes that occur at low frequencies associated with deformability of the dispersed phase. Close agreement between data obtained by applying the Palierne model for emulsions of two viscoelastic liquids and experimental data was only shown for the blend of lowest LDPE content. Good predictions were derived for the higher LDPE contents, when partial miscibility of the components was assumed. In these cases, the viscoelastic response can be modelled through a hybrid model that takes into account the double reptation approach in the miscible phase models. Contrary to other heterogeneous blends, the blends examined here do not show an enhanced elastic character. This behaviour is probably due both to the extremely different relaxation times of the phases in the blends rich in mPE, and to the partial miscibility of the components in the blends of high LDPE content.

---

1. Introduction

Polyolefin blends have been widely investigated in terms of their rheological properties, though recently this topic has generated renewed interest [1–4]. In general descriptions of rheological behaviour, the miscibility of a blend's components is the limiting factor. The literature is full of interesting results related to the rheology and morphology of polyolefin blends. Acierno *et al.* [5–7] and Utracki and Schlund [8–12] extensively explored the rheological behaviour of high density and linear low density polyethylene (HDPE/LLDPE) as well as HDPE/low density PE (LDPE) and LLDPE/LDPE blends. More recently, Cho and co-workers [13–17] performed a series of studies on the rheology and mechanical properties of polyolefin blends. These works established that polyolefin blends can be miscible, partially-miscible or immiscible. However, some authors infer single phase behaviour for blends HDPE/LLDPE and LLDPE/LDPE in the melt also from rheological measurements [3, 11, 12, 14], while Alamo *et al.* [18] consider phase segregation in blends of model polyethylene of hydrogenated polybudadiene (HPB/HPB1-butene). Martínez-Salazar and co-workers [19] published experimental findings that indicate phase separation at 160°C in blends of HDPE and short branched PE (BPE) for branching content values above 10 branches per thousand carbon atoms. Donnatelli [20], and more recently Xanthos and Ponnusamy [21], discovered that HDPE/LDPE blends were immiscible over the temperature range 170–210°C. Further, according to Utracki and Schlund [11, 12], LLDPE/LDPE blends are thermodynamically immiscible. In these blends, the possibility of a compatible mixture of emulsion type morphology in the temperature range 150–230°C is suggested. Lee and Denn [3] and Hussein and Williams [4] reached similar conclusions for LLDPE/LDPE blends. These latter authors proposed molecular order and mismatch of the molecular conformations of different polyolefin structures to account for immiscibility in polyethylenes. In

---

[*] Author to whom all correspondence should be addressed.

contrast, Yamaguchi and Abe [2] observed miscibility in LLDPE/LDPE blends. Cho *et al.* [14] found that HDPE/LDPE and LLDPE/LDPE blends were miscible in the melt state in the temperature range 130–230°C. The findings of Groves *et al.* [22] also point to miscibility or, at least, cooperative relaxation between linear and branched species in HDPE/LDPE blends at temperatures of around 160 and 190°C.

Of particular recent interest, is the miscibility and processability of polyolefins generated by a single-site (metallocene) catalyst (mPEs) compared to conventional polyolefins such as LLDPE and HDPE, made by the Ziegler-Natta catalyst [13, 24]. Available results indicate that the degree of miscibility between mPEs (1-octene comonomer) and LLDPE in the melt state depends on the relative molecular weight (or the melt flow index), the density and the comonomer content. In a thermodynamic study of polyolefin blends, Mehta showed that the melt miscibility of LLDPE depends on the factors molecular weight and density [25]. These findings confirmed earlier conclusions [26–28].

Collectively, the findings of these studies clearly indicate that the rheology and other physical properties of a blend strongly depend on morphology [29]. The state of dispersion, which corresponds to the final morphology but is not necessarily an equilibrium state, is directly linked to the conditions of blend preparation. This means that the mixing method or mixing conditions can affect the characteristics of a blend [29, 30]. In most rheological studies, melt blending is achieved in twin-screw continuous extruders, batch discontinuous or two-roll mill mixers, which, depending on the conditions, give rise to very different morphologies and thermo-mechanical histories.

The behaviour patterns of rheological properties are related to the morphological state in the melt, and, in turn, depend on the viscosity ratio of the components, temperature, phase interactions, interfacial tension and hydrodynamic effects [29, 31]. Unfortunately, it is very difficult to ascertain molten state morphology in polyolefin blends, due to the lack of contrast between pure materials. Moreover, this morphology may be very different to that shown in the solid state. For example, HDPE/LLDPE blends co-crystallise [3, 32, 33], yet blends of HDPE/LLDPE/LDPE usually form crystals separate from each other [3, 13].

The development of theoretical and phenomenological models for miscible and immiscible blends is another subject of current interest. The double reptation model [34, 35] for miscible blends and the Palierne emulsion model [36] for immiscible blends are both frequently applied to explain the viscoelastic behaviour of polyolefin melts [3, 4, 22]. Indeed, rheology has become a potent tool for inferring morphological state in this type of blends.

This study was designed to explore relationships between the rheological properties and the possible morphology of mPE/LDPE blends. The rheological properties of these blends were then compared with data obtained for blends of HDPE and a slightly short branched PE (BPE) in our laboratory. We must stress that all the blends were prepared in the same conditions. In both cases, the pure materials were supplied as powders, to allow better initial contact between the polymers in blend preparation.

2. Experimental

2.1. Materials and blend preparation

We prepared blends of a metallocene catalysed ethylene homopolymer (mPE) and a conventional low density polyethylene (LDPE). For comparative purposes, we also examined data corresponding to blends of conventional high density polyethylene of low molar mass (HDPE) and low density or branched polyethylene (BPE) of high molar mass [37]. All the materials used were supplied by Repsol-YPF, in the form of a powder. Blending was performed with small amounts of Irganox 1010 as an oxidation inhibitor in a batch Haake mixer at a temperature of 160°C, increasing the rotor speed until a constant value of the torque of 15 mN. Blending time was 5 min in all the cases. The blends were denoted LDPEw and BPEw; where w represents the weight fraction of LDPE and BPE in the mPE and HDPE blends respectively. The samples were pressed in a laboratory Schwabenthan Polystat 200T hot press at a temperature of 160°C and a nominal pressure of 150 bar, and then quenched at room temperature. Disk specimens 25 mm in diameter were stamped for dynamic torsion measurements. The thickness of the compression-moulded samples was adjusted for the rheological measurements. The molecular variables of all the materials examined as obtained from GPC and ^{13}C NMR are listed in Table I.

2.2. Measurements

Linear viscoelastic properties in the molten state were measured using a Bohlin CVO rheometer with the parallel plates geometry in the oscillatory shear mode. It is well documented in the literature that linear viscoelastic measurements in the melt can be performed from this kind of experiments. Determinations were made within the linear viscoelastic range at 15% strain. This value was identified with the aid of previous strain sweeps carried out for all the samples. The angular frequency dependence of viscoelastic functions, storage modulus G', loss modulus G'' and complex viscosity η^*, at a temperature range of 130–190°C were measured in the frequency range 10^{-3}–10^{2} rad s^{-1}. Measurements were repeated several times on the same sample and on fresh samples to avoid blending shear history and

TABLE I Characterization of the materials studied: weight-average molecular weight (M_w), polydispersity index (M_w/M_n) and branching content; short chain branching (SCB) and long chain branching (LCB)

Sample	M_w (gmol^{-1})	M_w/M_n	SCB (CH3/1000C)	LCB (CH3/1000C)
mPE	180000	2.0	0	0
LDPE	223000	7.7	14.9	2.7
BPE	403000	3.3	3.5	0
HDPE	44400	4.6	0	0

TABLE II Rheological parameters of the materials and blends examined here determined at 160°C. Newtonian viscosity η_o, steady-state compliance J_e^o, relaxation time λ, lastic index E_R, cross-point modulus G_x, and flow activation energies E_{ah} and E_{av}

Sample	η_o/kPa s	J_e^o/kPa^{-1}	λ/s	E_R	G_x/kPa	E_{ah}/kJ mol^{-1}	E_{av}/kJ mol^{-1}
mPE	34	0.64	22	0.25	251	22.5	1.66
LDPE010	43	0.54	23	0.55	199	26.3	4.17
LDPE020	55	0.49	27	0.60	166	26.3	6.25
LDPE030	68	0.47	32	0.69	142	30.0	7.50
LDPE040	80	0.53	42	0.71	121	41.7	5.83
LDPE050	90	0.64	58	0.80	85	31.7	10.0
LDPE060	105	0.61	64	0.77	65	40.0	10.8
LDPE070	120	0.69	83	0.79	43	49.2	8.33
LDPE080	130	0.89	116	0.75	27	44.6	14.2
LDPE090	120	0.85	102	0.78	14	60.4	11.7
LDPE	110	0.86	95	0.78	8	66.7	12.5

degradation effects. The time-temperature superposition was applied to frequency dependence and modulus dependence at the different temperatures. A good review about this procedure can be found elsewhere [38]. At temperatures above melting temperature, T_m, where most of the polyolefin melts are processed, the temperature dependence of relaxation times follows an Arrhenius-type equation:

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

where a_T is the horizontal relaxation time (frequency) shift factor, R is the gas constant, T is the experimental temperature, T_o is the reference temperature and E_{aH} is called "horizontal activation energy."

As it is known some polymers, mainly those containing long chain branches as LDPE and ethylene/vinyl acetate copolymers (EVA), show a stress-dependent activation energy when data are shifted at constant stress, providing that the data are only horizontally shifted. For this reason a vertical shift involving a "vertical activation energy" is also needed:

$$b_T = \exp\left[\frac{E_{aV}}{R}\left(\frac{1}{T} - \frac{1}{T_o}\right)\right] \tag{2}$$

where b_T is the vertical stress (modulus) shift factor, and R, T, and T_o have the same meaning than in Equation 1. E_{aV} is the "vertical activation energy." Materials showing high E_{av} values are frequently called thermorheological complex systems [38].

The E_{ah} values recorded were 22.5 kJ mol^{-1} for mPE, and 66.7 kJ mol^{-1} for LDPE, in good agreement with results quoted in the literature [38]. For the LDPE, it was necessary to apply a vertical shift to yield an $E_{av} =$ 12.5 kJ mol^{-1}, which corresponds to branched, thermorheologically complex ethylene based polymers. The blends also fulfilled the time-temperature superposition principle. E_{ah} and E_{av} varied linearly with composition (see Table II). The HDPE/BPE samples also followed the time-temperature superposition. No thermorheological complexity was observed in this case, as expected for linear polyolefins. E_{ah} varied slightly between 20.8 and 27.1 kJ mol^{-1}. The results of superposition are omitted here for the sake of brevity and because they provide no additional information on the possible miscibility or immiscibility of the blends [39]. Hereafter, only the results obtained at 160°C for the LDPEw series and at 190°C for the BPEw series are presented.

3. Results and discussion

Fig. 1 provides $|\eta^*(\omega)|$ data on the mPE/LDPE blends determined at 160°C. It is clear that in the LDPE-rich compositions or the blends with high w values, η^* exceeded the viscosity of the most viscous component (LDPE). The values of G' were also enhanced at these high w values, as can be observed in Fig. 2. These

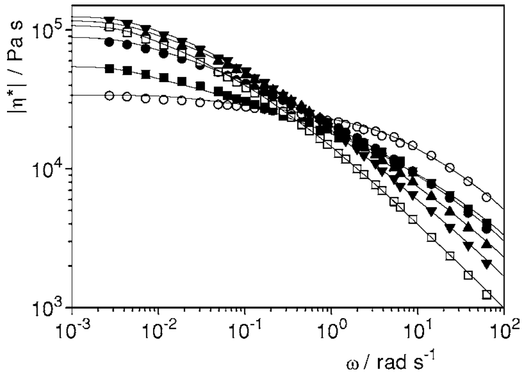


Figure 1 Modulus of complex viscosity vs. angular frequency of the blends examined at 160°C. (○) mPE, (■) LDPE020, (●) LDPE040, (▲) LDPE060, (▼) LDPE080, (□) LDPE. The lines correspond to the Maxwell fit of experimental data.

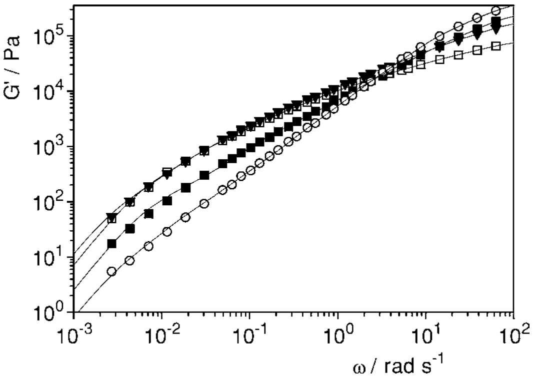


Figure 2 Experimental storage modulus at 160°C for the pure materials (open symbols) and two of the blends (full symbols). Symbols as for Fig. 1. Lines represent fitting the experimental data to the Maxwell model.

results suggest heterogeneity in the blends and indicate emulsion-like rheology. For these blends, Groves *et al.* [22] found agreement between measurements and predictions derived from the double reptation theory, by empirically varying the exponent blending law C of the generalised form of the double reptation blending law [34, 35]:

$$G(t) = \left[\sum_{\mathrm{i}} \phi_{\mathrm{i}} G_{\mathrm{i}}^{1/\mathrm{C}}(t)\right]^{\mathrm{C}} \tag{3}$$

In the case of HDPE/LDPE blends, C depends on the viscosity ratio of blend components as follows:

$$C = 1.08\left(\frac{\eta_{\mathrm{oB}}}{\eta_{\mathrm{oL}}}\right)^{\frac{1}{3.6}} + 0.82 \tag{4}$$

where η_{oB} and η_{oL} is the Newtonian viscosity of the linear and branched polymers, respectively. This model has been found to describe the linear rheology of blends of linear and branched PEs for a range of C values between 1.25 and 4 [22]. Variability was explained in terms of the different degrees to which branched and linear species co-operatively relax in the molten state. In the case of the mPE/LDPE blends studied here, the value of C is 2.3, very close to the double reptation case ($C = 2$). The value of $C = 2.3$ can be extracted from the Newtonian viscosity ratio ($\eta_{\mathrm{oB}}/\eta_{\mathrm{oL}} = 3.2$) applying Equation 2 (see Table II). In Fig. 3, we represent the result of the model given by Equation 1 applied to the LDPE050 blend at 160°C. The modified double reptation model of Groves *et al.* [22], which assumes miscibility, does not fit the experimental results. Higher values of G' and G'' than those predicted by the model at low frequencies are obtained. We computed the relaxation modulus $G(t)$ of the individual components and the blend by Fourier transforming the measured dynamic moduli. The computed curve for the blend is shown in the inset to Fig. 3. The line represents the modified double reptation model with $C = 2.3$. The shift of the experimental viscoelastic response towards higher times would be directly linked to a heterogeneous morphology. This response is characteristic of emulsion-like systems of viscoelastic materials. An additional slow relaxation mechanism is observed at longer times (low frequencies) that can be interpreted as disperse phase droplets deformation-relaxation process. Lower values of C ($\mathrm{C} \sim 1$) would be needed to describe the experimental behaviour reproducing the relaxation modulus curve. This value of C corresponds to a viscosity ratio of $\eta_{\mathrm{oB}}/\eta_{\mathrm{oL}} \sim 10^{-3}$ in Equation 4, far from the experimentally observed viscosity ratio.

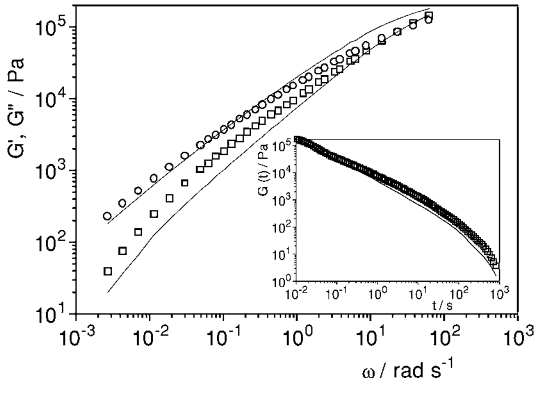


Figure 3 Predictions of the reptation model with $C = 2.3$ [22] (solid line) and experimental results of for G' (□) and G'' (○) in blend LDPE050 at 160°C. The figure inset shows the prediction of the computed relaxation modulus $G(t)$ for the same blend.

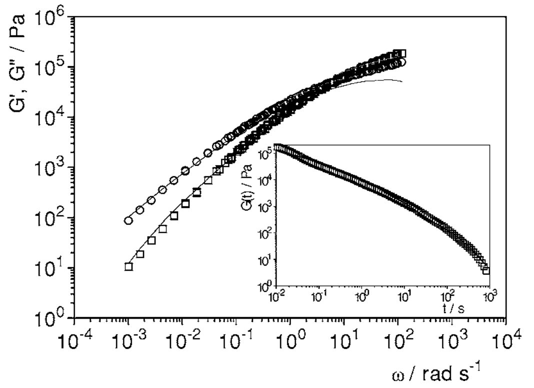


Figure 4 Predictions of the reptation model with $C = 2.7$ [22] (solid line) and experimental results of for G' (□) and G'' (○) in blend BPE050 at 160°C. The figure inset shows the prediction of the computed relaxation modulus $G(t)$ for the same blend.

Fig. 4 shows the viscoelastic response at 190°C for the BPE050 blend. We selected this blend and temperature of 190°C since the viscoelastic fingerprint, blend preparation conditions and initial morphology of the materials are very similar to those corresponding to the LDPE050 blend in Fig. 3. The optimum value of C in this case is $C = 2.7$. As can be seen in Fig. 4, there is very good agreement between the computed curves for the double reptation theory and the experimental results in the terminal region. This is consistent with the notion that the polymers are miscible in the melt. The result is virtually identical to that obtained by Groves *et al.* [22] for linear/linear polymer blends. These authors found that values of C between 2-3 explained the viscoelastic response in this type of blend. It was found that the blends of linear/linear species (HDPE/HDPE and HDPE/BPE) did not confirm the C index prediction given by Equation 2. In these cases, the blends always closely, though not precisely, followed the original Tsenoglou rule with $C = 2$. Recently, Lee and Denn [3] also obtained accurate predictions with values of $C = 2$ for this type of system. Thus, in these blends, unlike the case for linear/branched blends, it seems that the value of C is independent of the viscosity ratio. In our case, $\eta_{\mathrm{o1}}/\eta_{\mathrm{o2}}$ is of the order of 10^4 (see Table III). Lee and Denn [3] and Groves *et al.* [22] worked with viscosity ratios in the range 2.2 to 84.

From the dynamic results at low frequencies, we can extract data to infer the compositional dependence of the characteristic terminal parameters shown in Table II for the mPE/LDPE blends. Values of Newtonian viscosity η_{o}, steady-state compliance $J_{\mathrm{e}}^{\mathrm{o}}$, and relaxation time λ, were obtained by applying the Maxwell generalised model, as shown elsewhere [40]. As can be seen in Fig. 5, a positive deviation of η_{o} from that expected according to the modified double reptation model with

TABLE III Newtonian viscosity η_o, of the materials and blends examined here determined at 190°C

Sample	η_o/Pa s
HDPE	140
BPE030	18000
BPE040	46250
BPE045	80000
BPE050	95000
BPE055	130000
BPE060	170000
BPE070	250000
BPE	820000

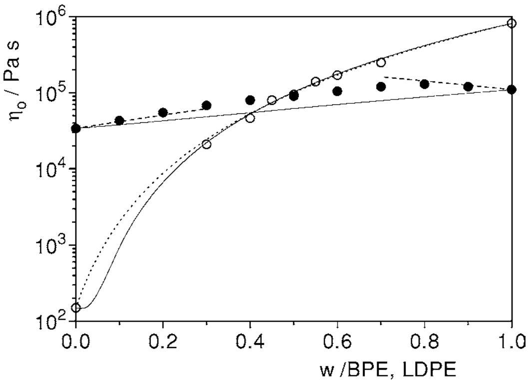


Figure 5 Compositional dependence of Newtonian viscosity η_o at 160°C for (●) mPE/LDPE blends, and at 190°C for (○) HDPE/BPE. The solid lines represent the predictions of the reptation model for values of $C = 2.3$ (see text). The dotted line represents the predictions given by Equation 7 for miscible blends applied to HDPE/BPE blends. The dashed line represents the predictions of the Oldroyd model for immiscible blends (Equation 8) applied to mPE/LDPE blends.

$C = 2.3$ (shown as a dotted line) is obtained for the mPE/LDPE blends examined. A maximum value of η_o, above that corresponding to the most viscous component (LDPE), for the $w = 0.70$ LDPE composition can also be observed. Conversely, for the HDPE/BPE blends, the model with values close to $C \sim 3$ fit the experimental η_o results very well in the composition range studied. This value is in close agreement with that obtained from the fit of $G(t)$ ($C = 2.7$) to the model over the whole time interval analysed (see Fig. 4). There are several available blending laws for η_o, for which the starting point is defined in terms of an additivity in the weight-average molecular weight, M_w [41–44]:

$$M_{\text{wblend}} = \sum_{i} w_i M_{wi} \tag{5}$$

According to the well-known dependence of η_o on M_w of linear polymers:

$$\eta_o = K M_w^{3.4} \tag{6}$$

it is easy to obtain the following expression for the compositional dependence of η_o as a function of the characteristic values of η_o of the components:

$$\eta_{o,\text{blend}} = \left[\sum_{i} w_i (\eta_{oi})^{1/3.4}\right]^{3.4} \tag{7}$$

This expression was applied to the HDPE/BPE blends examined (Fig. 5). In general, the modified reptation model and the blending law given by Equation 7 show agreement for weight fractions higher than $w = 0.30$ of the most viscous component (BPE).

The positive deviation observed in the compositional dependence of η_o for mPE/LDPE blends identifies a heterogeneous morphology. This behaviour is commonly explored by applying simple emulsion models. Among the various existing emulsion models, the one proposed by Oldroyd is perhaps the most used [45]. Here, the viscosity of a dilute emulsion of two incompressible and totally immiscible Newtonian fluids in the linear viscoelastic range is given by:

$$\eta_o = \eta_{o,m}\left[1 + \phi\frac{5K+2}{2(K+1)} + \phi^2\frac{(5K+2)^2}{10(K+1)^2}\right] \tag{8}$$

where ϕ is the volume fraction of the dispersed phase and $K = \frac{\eta_{o,d}}{\eta_{o,m}}$, where $\eta_{o,m}$ and $\eta_{o,d}$, are the viscosity of the matrix liquid and the dispersed droplets, respectively. This dilute emulsion model is commonly used to predict the viscosity on both sides of the phase diagram. We considered the weight, w, and volume, ϕ, fractions to be equal, i.e., both components were taken to have the same melt density ρ. It seems that the model works well for compositions below $w = 0.10$ and higher than $w = 0.90$ (dashed lines in Fig. 5).

In Fig. 6, we present the variation in experimental viscosity relative to that expected according to the reptation miscible model for all the blends. It can be seen that the HDPE/BPE blends scarcely deviate from the behaviour expected by the miscible reptation approach (differences are always less than 10%). The mPE/LDPE blends, however, show a strong positive deviation at intermediate compositions. The enhanced η_o for the mPE/LDPE blends is not as abrupt as that observed in immiscible systems such as polyethylene-terephthalate-glycol)/EVA, polypropylene/EVA or EVA/PE blends [46–48]. In all these cases, it has always been assumed that enhanced viscoelastic functions may be attributed to a very long relaxation time associated with deformation of the dispersed phase. The model recently developed

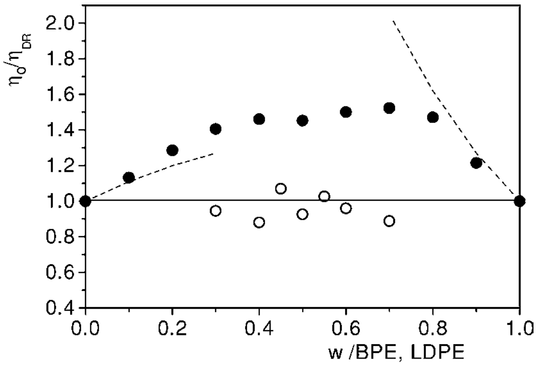


Figure 6 Relative deviation of experimental Newtonian viscosity η_o of the blends from values predicted by the miscible reptation model. Symbols are the same as for Fig. 5. The horizontal solid line represents the expected behaviour of miscible blends. The dashed lines indicate the normalised Oldroyd model predictions.

by Palierne [36], describes the linear viscoelastic response in this type of system in terms of the viscoelastic behaviour of each phase, the matrix (m) and the dispersed phase (d) by means of the general expression:

$$G^*(\omega) = G^*_{\mathrm{m}}(\omega)\frac{1+3\sum_{\mathrm{i}}\phi_{\mathrm{i}}H_{\mathrm{i}}(\omega)}{1-2\sum_{\mathrm{i}}\phi_{\mathrm{i}}H_{\mathrm{i}}(\omega)} \tag{9}$$

with $H_{\mathrm{i}}(\omega)$ given by:

$$H_{\mathrm{i}}(\omega) = \frac{4\left(\frac{\alpha}{R_{\mathrm{i}}}\right)[2G^*_{\mathrm{m}}+5G^*_{\mathrm{d}}]+[G^*_{\mathrm{d}}-G^*_{\mathrm{m}}][16G^*_{\mathrm{m}}+19G^*_{\mathrm{d}}]}{40\left(\frac{\alpha}{R_{\mathrm{i}}}\right)[G^*_{\mathrm{m}}+G^*_{\mathrm{d}}]+[2G^*_{\mathrm{d}}+3G^*_{\mathrm{m}}][16G^*_{\mathrm{m}}+19G^*_{\mathrm{d}}]} \tag{10}$$

In our particular case $i = 1$ since we consider a single-sized droplet distribution of radius R. This model predicts that enhancement of viscoelastic functions due to the presence of a dispersed phase greatly depends on the relaxation time ratio χ and the viscosity ratio K of the phases, the interfacial tension between the phases α, the particle radius R, and the volume fraction of dispersed phase ϕ [49]. For given values of α, R and ϕ, the enhancement in G' is usually seen as a secondary plateau, G_{P}, at low frequencies. For values of $K = \frac{\eta_{\mathrm{od}}}{\eta_{\mathrm{om}}} < 1$, G_{P} is almost constant and shows values of around 10^3 Pa [48, 49]. However, G_{P} becomes ill defined when the relaxation time of the matrix is high relative to that corresponding to the dispersed phase. In the blends examined here, the LDPE displays a higher relaxation time than the mPE, which is normal for a polymer of broad molecular weight distribution and long chain branching. As a first approximation, the Cross fit (not shown here) of pure polymers to $|\eta^*|$ data leads to a relaxation time ratio of $\chi = (\tau_{\mathrm{od}}/\tau_{\mathrm{om}}) > 100$. This might explain why dispersed phase deformation phenomena could hardly be observed in the blends examined, compared to other blends with similar values of K and a χ ratio of 1 [49].

Fig. 7 shows the effect of the relaxation time of the matrix in the viscoelastic response of the LDPE080 blend compared to an EVA/mPE blend with a mPE weight fraction of $w = 0.80$ [48]. In both cases, the dispersed phase has a relaxation time of the order of 0.1. The relaxationtime of LDPE is, however, two orders of magnitude higher than that corresponding to mPE. In the LDPE080 blend, although the relaxation mechanism is not easily observable in G', the increased values of this function with respect to the more viscous and elastic blend component (LDPE) is appreciable. Very similar behaviour has been recently observed in LLDPE/LDPE blends [3, 4]. The difference between these two reports is that, in the former, the Palierne model itself was not able to predict the rheological response of the blends, and thus the possibility of partial miscibility had to be accounted for.

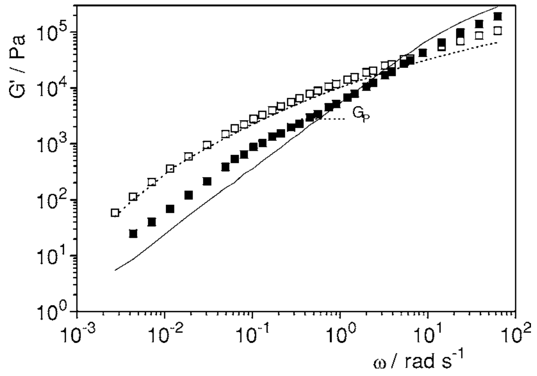
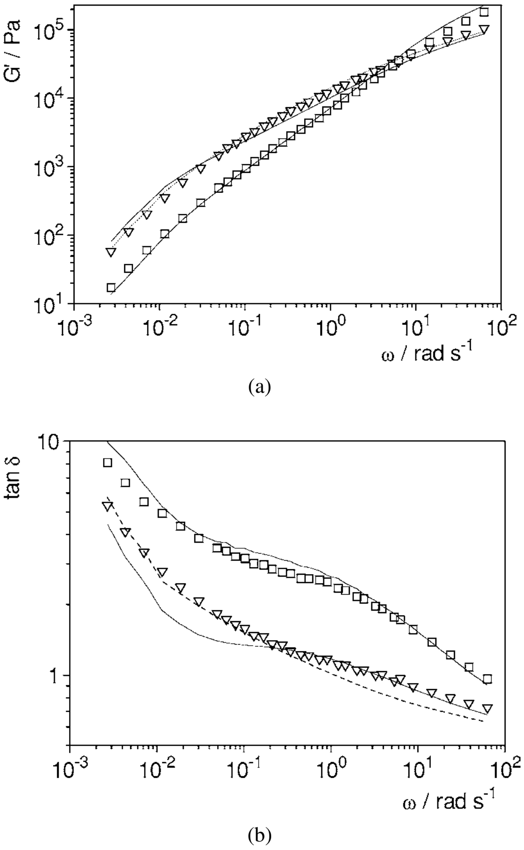


Figure 7 Storage modulus G' of the LDPE080 (□) blend at 160°C. Results were compared with those obtained for an EVA/mPE blend of the same composition (mPE080) (■) and with those of the pure components mPE (solid line) and LDPE (dotted line).

In Fig. 8a and b, we show predictions of G' and tan δ at both ends of the phase diagram (LDPE080 and LDPE020) over a wide range of frequencies (5 decades). Exceptional agreement was shown between the experimental and predicted value of $\alpha/R = 2.0 \times 10^3$ Pa for LDPE020. The model reproduces very well the curve of loss tangent against frequency. Similar results were obtained for mPE010 and mPE030 blends (data not shown). The value of α/R is in good agreement with those reported for LLDPE/LDPE and EVA/PE blends [3, 4, 48, 49].

For the LDPE080 blend, the value of $\alpha/R = 2.0 \times 10^3$ Pa does not reproduce the experimental results well. A clear inflexion between 0.1–1 rad s^{-1} is predicted yet not experimentally observed. The predicted values for tan δ are also lower than those experimentally observed at low frequencies. An increase in α/R of two orders of



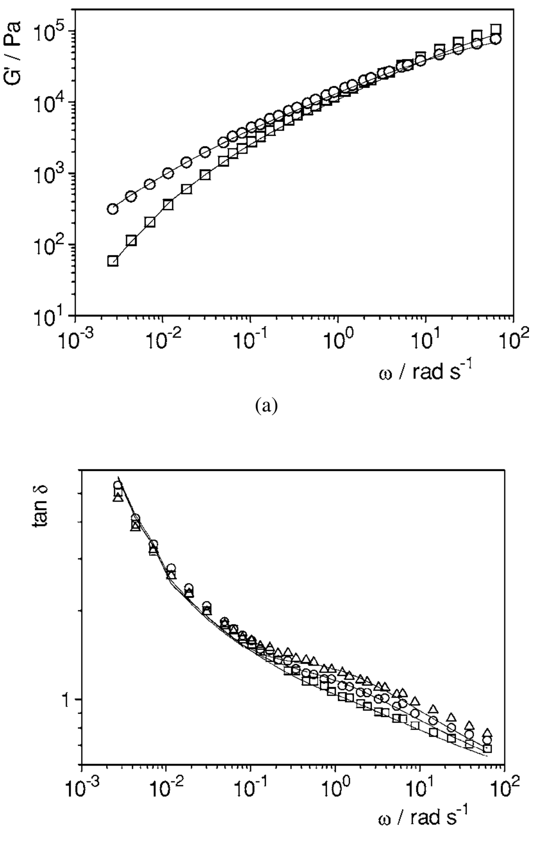
(a)

(b)

Figure 8 Experimental values of (a) G' and (b) tan δ of LDPE020 (□) and LDPE080 (▽) at 160°C. The lines represent the predictions of the Palierne model (Equations 9 and 10). Solid lines: $\alpha/R = 2 \times 10^3$ Pa for both LDPE20 and LDPE80 blends. Dashed line: $\alpha/R = 2 \times 10^5$ Pa only for LDPE80 blend. Please note that for the blend LDPE020 the two lines coincide.

magnitude ($\alpha/R = 2.0 \times 10^5$ Pa) would fit the experimental G' values well, but fails to describe the tan δ curve at high frequencies. A high degree of variation in α is not plausible since this variable depends mainly on the chemical nature of the polymers in contact. Different preparation conditions of the blends might lead to a decrease in particle radius of two orders of magnitude and changes in mixing shear rate or torque would give rise to morphological alterations in the blends, i.e., different particle radius depending on composition. However, the mixing velocity and torque were set at 15 Nm and 15 r.p.m. for all the mPE/LDPE blends. A possible explanation for the differences noted could be partial miscibility.

Lee and Denn [3] extended the emulsion model to partially miscible systems, assuming a fraction X of the minor component is miscible with the major component. The matrix properties are then determined from the double reptation theory (with $C = 2.3$), and the properties of the blend are defined by the emulsion model with a dispersed phase consisting of $1 - X$ of the minor component. There are two parameters in this hybrid approach, X and α/R. We followed the same procedure as Lee and Denn [3]. α/R was fixed in ascending power of ten and a suitable value of X was found. In this case, a good fit of the experimental data was obtained at a value of $\alpha/R = 1.0\ 10^4$ Pa and a value of $X = 0.40$ (see Fig. 9a). Identical values were found for the LDPE070 and LDPE090 compositions. Fig. 9b shows the result of this "hybrid" model applied to loss tangent for LDPE-rich compositions. The values show very close agreement with those obtained by Lee and Denn for LLDPE/LDPE blends.



(a)

(b)

Figure 9 Predictions of the Lee and Denn hybrid model (solid lines with $C = 2.3$, $\alpha/R = 1.0 \times 10^4$ Pa and $X = 0.4$) [3]: (a) G' (□) and G'' (○) in the LDPE080 blend and (b) tan δ for the LDPE070 (△), LDPE080 (○) and LDPE090 (□) blends at 160°C.

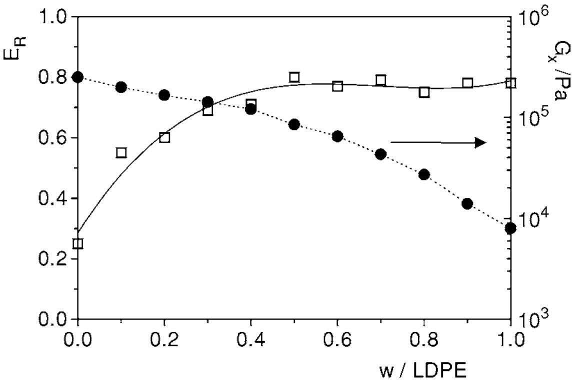


Figure 10 Cross-point modulus ,G_x, and rheological polydispersity index E_R vs. composition at 160°C. (●) G_x, (□) E_R ($C_1 = 5 \times 10^{-3}$). The lines are drawn to guide the eye.

Shroff and Mavridis [50] described several indices to quantify the elasticity of polymeric materials in the melt. These indices were found to define the rheological polydispersity of molten polymers. The first index we calculated is denoted E_R:

$$E_R = C_1 \cdot G'|_{G''=500\text{Pa}} \tag{11}$$

where an arbitrary constant, $C_1 = 5 \times 10^{-3}$, is 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:

$$G'(\omega) = J_e^o[G''(\omega)]^2 \quad \text{when } \omega \to 0 \tag{12}$$

The cross-point modulus (tan $\delta = 1$), G_x, is also considered to be a measure of rheological polydispersity of polymers and blends [50]. Table II shows the steady-state compliance J_e^o and the elastic indices, E_R and G_x, for the mPE/LDPE blends analysed. It may be observed, that the elastic indices systematically increase with w. In Fig. 10, we plotted the compositional variation of J_e^o and E_R. The characteristic maxima of heterogeneous systems at the intermediate compositions cannot be appreciated [48, 50]. For low values of w, although the Palierne model for immiscible systems predicts the viscoelastic behaviour of the blends, the relaxation process of the hard (long relaxation time) dispersed phase is not observed. For high values of w, the possible partial miscibility of the materials (higher α/R ratio and a certain miscible fraction, X) does not allow the less viscous and more deformable particles of mPE to store an additional form of recoverable energy.

4. Conclusions

The mPE/LDPE blends showed positive deviation of Newtonian viscosity from the double reptation model that assumes miscibility. Results were compared with those obtained for HDPE/BPE blends prepared in similar conditions. These latter blends show very close agreement with the model. The Palierne model for emulsion-like heterogeneous polymer blends applied to mPE/LDPE blends was found to only satisfactorily explain the viscoelastic behaviour of the blends of low LDPE contents. The values of the α/R ratio are very similar to those reported for heterogeneous EVA/LDPE and EVA/mPE blends. This is not the case for blends rich in LDPE, for which it was necessary to assume partial miscibility of the components. A hybrid model that includes the double reptation approach for the miscible phase (the matrix) and the linear Palierne approach for the whole system, was able to successfully explain the viscoelastic response of these blends. The values of the α/R ratio, and the miscible fraction of the minor component X, were one order of magnitude lower than that of mPE-rich blends and 0.40 respectively. These results are consistent with those cited for conventional linear/branched PE blends in the literature. Contrary to heterogeneous blends, the blends analysed here do not show enhanced elastic character. A systematic but slight increase in steady-state compliance and elastic indices was noted as the LDPE content of the blend increased. This behaviour is probably due to the extremely different relaxation times of the phases in the blends of lower LDPE content on the one hand, and to the partial miscibility of the components in the blends rich in LDPE, on the other.

Acknowledgements

Thanks are due to the MCYT (Grant MAT2002-01242) for financial support. The authors also acknowledge Repsol-YPF, Spain for their permission to publish these data.

References

1. K. E. ABRAHAM, E. GEORGE and D. J. FRANCIS, *J. Appl. Polym. Sci.* **67** (1998) 789.
2. M. YAMAGUCHI and S. ABE, *ibid.* **74** (1999) 3153.
3. H. S. LEE and M. M. DENN, *Polym. Eng. Sci.* **40** (2000) 1132.
4. I. A. HUSSEIN and M. C. WILLIAMS, *ibid.* **41** (2001) 696.
5. D. ACIERNO, F. P. LA MANTIA and D. CURTO, *Polym. Bull.* **11** (1984) 223.
6. F. P. LA MANTIA and D. ACIERNO, *Plats. Rubber Proc. Appl.* **5** (1985) 183.
7. D. ACIERNO, F. P. LA MANTIA and A. VALENZA, *Polym. Eng. Sci.* **26** (1986) 28.
8. B. SCHLUND and L. A. UTRACKI, *ibid.* **27** (1987) 359.
9. L. A. UTRACKI and B. SCHLUND, *ibid.* **27** (1987) 367.
10. B. SCHLUND and L. A. UTRACKI, *ibid.* **27** (1987) 380.
11. L. A. UTRACKI and B. SCHLUND, *ibid.* **27** (1987) 1513.
12. B. SCHLUND and L. A. UTRACKI, *ibid.* **27** (1987) 1523.
13. H. LEE, K. CHO, T. K. AHN, S. CHOE, I. J. KIM, I. PARK and B. H. LEE, *J. Polym. Sci.: Polym. Phys. Ed.* **35** (1997) 1663.
14. K. CHO, T. K. AHN, I. PARK, B. H. LEE and S. CHOE, *J. Ind. Eng. Chem.* **3** (1997) 147.
15. K. CHO, T. K. AHN, B. H. LEE and S. CHOE, *J. Appl. Polym. Sci.* **63** (1997) 1265.
16. K. CHO, H. LEE, B. H. LEE and S. CHOE, *Polym. Eng. Sci.* **38** (1998) 1969.
17. D. RANA, C. H. LEE, K. CHO, B. H. LEE and S. CHOE, *J. Appl. Polym. Sci.* **69** (1998) 2441.
18. R. G. ALAMO, W. W. GRAESSLEY, R. KRISHNAMOORTI, D. J. LOHSE, J. D. LONDOMO, L. MANDELKERN, F. C. STEHLING and G. D. WIGNALL, *Macromol.* **30** (1997) 561.
19. J. MARTINEZ-SALAZAR, M. SANCHEZ CUESTA and J. PLANS, *Polymer* **32** (1991) 2984.
20. A. A. DONATELLI, *J. Appl. Polym. Sci.* **23** (1979) 3071.
21. M. XANTHOS, V. TAN and A. PONNUSAMY, *Polym. Eng. Sci.* **37** (1997) 1102.
22. D. J. GROVES, T. C. B. MCLEISH, R. K. CHOHAM and P. D. COATES, *Rheol. Acta* **35** (1996) 481.
23. H. KWAG, D. RANA, K. CHO, J. RHEE, T. WOO, B. H. LEE and S. CHOE, *Polym. Eng. Sci.* **40** (2000) 1672.
24. D. RANA, H. L. KIM, H. KWAG, J. RHEE, K. CHO, T. WOO, B. H. LEE and S. CHOE, *J. Appl. Polym. Sci.* **76** (2000) 1950.
25. I. B. KAZATCHKOV, N. BOHNET, S. K. GOYAL and S. G. HATZIKIRIAKOS, *Polym. Eng. Sci.* **39** (1999) 804.
26. D. R. PAUL and S. NEWMAN, in "Polymer Blends" (Academic Press, San Diego, California, 1978).
27. G. D. WIGNALL, R. G. ALAMO, J. D. LONDOMO, L. MANDELKERN and F. C. STEHLING, *Macromol.* **29** (1996) 5332.
28. P. MICIC, S. N. BAHTTACHARYA and G. FIELD, *Intern. Polym. Procc.* XI **1** (1996) 14.
29. L. A. UTRACKI, in "Polymer Alloys and Blends: Thermodynamic and Rheology" (Hanser Publishers, München, 1989).
30. N. NUGAY and C. TINCER, *Eur. Polym. J.* **30** (1994) 473.
31. C. D. HAN, in "Multiphase Flow in Polymer Processing" (Academic Press, New York, 1981).
32. A. K. GUPTA, S. K. RANA and B. L. DEOPURA, *J. Appl. Polym. Sci.* **44** (1992) 719.
33. *Idem.*, *ibid.* **49** (1993) 447.
34. J. DES CLOISEAUX, *J. Polym. Sci. Phys. Ed.* **5** (1988) 437.
35. C. TSENOGLOU, *Macromol.* **24** (1991) 1761.
36. J. F. PALIERNE, *Rheol. Acta* **29** (1990) 204.
37. J. F. VEGA and J. MARTÍNEZ-SALAZAR, unpublished results (2003).
38. H. MAVRIDIS and R. N. SHROFF, *Polym. Eng. Sci.* **32** (1992) 1778.
39. M. VAN GURP and J. PALMEN, *Rheol. Bull.* **67** (1998) 5.
40. J. D. FERRY, in "Viscoelastic Properties in Polymers" 3rd. ed. (Wiley, New York, 1980).
41. E. M. FRIEDMAN and R. S. PORTER, *Trans. Soc. Rheol.* **19** (1975) 493.
42. J. P. MONTFORT, G. MARIN, J. ARMAN and P. MONGE, *Polymer* **19** (1978) 277.
43. B. H. BERSTED, *J. Appl. Polym. Sci.* **31** (1986) 2061.
44. Y. H. ZANG, R. MULLER and D. FROELICH, *Polymer* **28** (1987) 1577.
45. J. G. OLDROYD, *Proc. Roy. Soc.* (London) Ser. A **218** (1953) 122.
46. C. LACROIX, M. BOUSMINA, P. J. CARREAU, B. D. FAVIS and A. MICHEL *Polymer* **37** (1996) 2939.
47. C. LACROIX, M. ARESSY and P. J. CARREAU, *Rheol. Acta* **36** (1997) 416.
48. J. PEÓN, PhD Dissertation, University Complutense of Madrid (Spain) 2002.
49. D. GRAEBLING, R. MULLER and J. F. PALIERNE, *Macromol.* **26** (1993) 320.
50. R. N. SHROFF and H. MAVRIDIS, *J. Appl. Polym. Sci.* **57** (1995) 1605.

Received 28 August 2002
and accepted 7 August 2003