The Role of the Interface in Melt Linear Viscoelastic Properties of LLDPE/LDPE Blends: Effect of the Molecular Architecture of the Matrix

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ABSTRACT: The rheological properties of blends consisting of a long chain branched low-density polyethylene (LDPE) and two linear low-density polyethylenes (LLDPE) are studied in detail. The weight fractions of the LDPE used in the blends are 5 and 15%. The linear viscoelastic characterization is performed at different temperatures for all the blends to check thermorheological behavior and miscibility in the melt state. Blends containing metallocene LLDPE as the matrix display thermorheologically complex behavior and show evidences of immiscibility in the melt state. The linear viscoelastic response exhibits the typical additional relaxation ascribed to the form deformation mechanism of dispersed phase droplets (LDPE). The Palierne model satisfactorily describes the behavior of these blends in the whole frequency range explored. However, those blends with Ziegler-Natta LLDPE as the matrix ful-fill the time-temperature superposition, but exhibit a broad linear viscoelastic response, further than the expected for an immiscible system with a sharp interface. The rheological analysis reveals that, in addition to the droplets form relaxation, another mechanism at lower frequencies exists. The broad linear response of the blends with the Ziegler-Natta LLDPE can be explained by hypothesizing a strong interaction between the high molecular weight linear fraction of the LLDPE and the low molecular weight (almost linear) chains of the LDPE phase, forming a thick interface with its own viscoelastic properties. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 114: 420–429, 2009

Key words: polyolefins; blends; interface; viscoelastic properties

INTRODUCTION

Blending two or more polyolefins is a widely used practice to develop new materials with a suitable balance between desirable physical properties and ease of processing. The experimental observation of improved processability, optical and other solid state properties by the addition of low-density polyethylene (LDPE) to linear low-density polyethylenes (LLDPE) has always generated a strong interest. Utracki and Schlünd extensively explored in the 1980's the rheological behavior of LLDPE/LDPE.[1,2] Notwithstanding, the study of rheological properties of polyolefin blends has been the subject of an important number of investigations along the last decade.[3–25] A detailed examination of all these works is essential to understand the intriguing features of this type of blends, such as miscibility and crystallization, optical and mechanical properties, and processability. Utracki and Schlünd determined that LLDPE/LDPE blends are thermodynamically immiscible.[1,2] 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 reached similar conclusions.[6] Cho et al.[4] and Yamaguchi and Abe[5] found that LLDPE/LDPE blends were miscible in the melt state in the temperature range 130–230°C. More recently, Hussein et al. have extensively studied LLDPE/LDPE blends, considering the effect of the molecular architecture of the different types of LLDPE available in the market (Ziegler-Natta and metallocene).[1,8,12,16,17] All these studies found that these blends are almost miscible in LLDPE-rich compositions, irrespective of the LLDPE type (metallocene or Ziegler-Natta). In the case of Ziegler-Natta LLDPE/LDPE blends, Wagner et al. have recently reported a singular behavior understood by assuming a two phase system; one phase formed by the branched shorter chains of both components and a second phase composed of the longer chains (mostly linear) of both components.[20] In more recent works, Fang et al.,[21] Zhao and Choi[24] and Delgadillo-Velázquez et al.[25] have reported that these blends are immiscible in the melt state, with both short and long chain branching being important factors contributing to the rheological response. All these studies clearly indicate that the physical properties of the blends are mainly

TABLE I
Description of the Materials Employed in this Study: M_w Is the Weight Average Molecular Weight M_w/M_n Is the Polydispersity Index, σ is the Standard Deviation of the Comonomer Distribution, T_1 and T_2 are the Temperature Peaks of the Comonomer Distribution and η_0 is the Newtonian Viscosity

Resin type	Process	Comonomer	Catalyst	M_w (kg·mol^{-1})	M_w/M_n	σ (°C)	T_1 (°C)	T_2 (°C)	Melt index[a] (g/10 min)	Density (g·cm^{-3})	η_0 (kPa·s)
LLDPE1	Gas phase	1-hexene	Metallocene	108.2	2.53	9.7	67.9	79.6	1.0	0.918	6.3
LLDPE2	Solution	1-octene	Ziegler-Natta	112.4	3.96	13.4	67.9	82.9	1.1	0.919	8.7
LDPE	Tubular			89.4	4.91	–	–	–	0.8	–	12.2

M_w and M_w/M_n from high temperature gel permeation chromatography with refraction index detector.
σ, T_1 and T_2 from Crystaf analysis with crystallization rate 0.2 °C/min.
[a] Melt Index: 190°C, 2.16 Kg.

determined by the morphological aspects of the state of dispersion, which eventually depends on the mixing method and conditions and also on specific molecular features of the polymers.[14,15,18,19,26]

It is not an easy task to establish the molten state morphology in this kind of blends. In this context, the development of theoretical and phenomenological models for miscible and immiscible blends is a subject of current interest. The reptation model[27] for miscible blends and the Palierne emulsion model[28] for immiscible blends are both frequently applied to explain the viscoelastic behavior of polyolefin melts. Indeed, rheology has become a potent tool for inferring morphological state. For example, the determination of the relaxation spectra from the linear response and the evaluation of the basic rheological parameters (Newtonian viscosity, relaxation time, or steady-state compliance) are used methodologies to deduce the morphology of a blend due to additional relaxation mechanisms associated with the existence of an interface, or even to detect co-continuous morphologies.[3,6–8,14–17,21,23]

In this article, we have studied the thermorheological properties of blends consisting of two LLDPE (metallocene and Ziegler-Nata LLDPEs) and a branched LDPE. The miscibility of the various blends is studied by means of the application of theoretical models developed for miscible and immiscible blends to the linear viscoelastic results. The main objective is to compare the behavior of the blends with respect to the matrix (LLDPE type) present in the system. As it is known both LLDPE samples have a very different molecular architecture. Consequently, the interaction with other macromolecular system (in our case a LDPE sample) may be different depending on the LLDPE type, giving rise to particular rheological properties.

EXPERIMENTAL SECTION

The two LLDPE samples were commercial metallocene and Ziegler-Natta polyethylene grades named therein as LLDPE1 and LLDPE2, respectively. Both

are copolymers of ethylene with 1-hexene (LLDPE1) and 1-octene (LLDPE2). Dow Chemicals Ibérica supplied all the materials used. Some of their molecular and physical features are collected in Table I. Both materials, with a thermal stabilizer, were mixed with 5% and 15% of a LDPE grade produced by tubular high-pressure process.

Mixing of LLDPE and LDPE samples was performed in a Haake mixer at a temperature of 180°C during 20 min. The individual pure components also have the same processing history. The sample sheets obtained were compression-molded at 160°C in a Schwabenthan Polystat 200T hot press for 5 min and a nominal pressure of 150 bar during 10 min, and then cooled to room temperature.

Sheets of around 1 mm of thickness have been molded and disks of suitable dimensions for rheological measurements have been obtained. It was confirmed that the rheological properties of the melts are stable during the measurement and no effects of the preparation procedure or degradation exist. The shear moduli, G′ and G″, were measured using the parallel-plates geometry (15 mm of diameter) in a stress-controlled Bohlin CVO rheometer at 130°C, 160°C, and 190°C. The oscillatory dynamic tests were carried out over the frequency range 10^{-2}–10^2 rad·s^{-1}. Deformation was set at around 10% or lower, which corresponds to the linear viscoelastic region in all the pure polymers and blends, identified through previous amplitude sweeps. The thermal stability of the samples was confirmed by means of time sweeps at low frequencies (0.6–6 rad·s^{-1}) in the temperature range of study. The data obtained at different temperatures were shifted at reference temperature using the Time-Temperature Superposition Principle (TTSP).

RESULTS AND DISCUSION

Rheology of the pure polymers

Figure 1 depicts the complex viscosity of the pure polymers listed in Table I as a function of frequency at a reference temperature 190°C after application of the TTSP. The data obtained at different temperatures
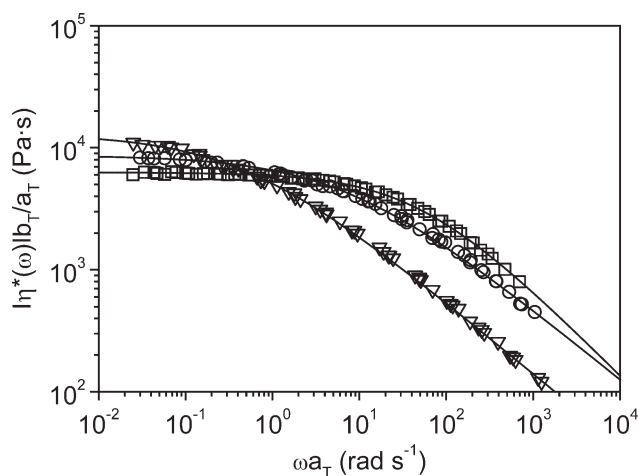
Figure 1 The complex viscosity curves of LLDPE and LDPE resins superposed to a reference temperature of 190°C. (□) LLDPE1; (○) LLDPE2, and (▽) LDPE. The lines are drawn to guide the eye.

were shifted at the reference temperature using the method developed by Mavridis and Shroff.[29] For the case of the two LLDPE samples (LLDPE1 and LLDPE2), the viscosity curve approaches the Newtonian viscosity value at low frequencies. LLDPE1 shows a clear Newtonian character as corresponds to a metallocene linear sample with a narrow molecular weight distribution (Table I). On the contrary, LLDPE2 sample exhibits a certain degree of shear thinning at high frequencies, as expected for a polydisperse Ziegler-Natta LLDPE. In the case of the LDPE sample a strong shear thinning behavior is observed. This behavior has been widely reported in the literature as due to the combined effect of polydispersity and high degree of long chain branching.[30] Lanfray and Marin reported an empirical method to analyze the dynamic rheological results of molten entangled polymers in order to obtain the Newtonian viscosity values.[31] They showed the suitability of the Cole-Cole representation of real and imaginary parts of the complex viscosity, $\eta^*(i\omega)$. In the complex plain the representation of η'' against η' is a circular arc described by three parameters: η_0, the limiting extrapolated viscosity at the intersection of the circular arc and the real axis, λ_0, a characteristic relaxation time that corresponds to the frequency at the maximum of η'' ($\lambda_0 = 1/\omega_{max}$), and β, the dispersion parameter defined as the angle between the diameter through the origin of the circular arc and the real axis:

$$\eta^*(i\omega) = \frac{\eta_0}{1 + (i\omega\lambda_0)^{1-\beta}} \qquad (1)$$

The Cole-Cole model provides an accurate fit to experimental data over the usual frequency range with only these three parameters for many flexible

polymers. The experimental results of the pure samples studied in the present work, fitted to obtain η_0 from eq. (1), are presented in Figure 2(a). The values of η_0 for the pure samples at 190°C are listed in Table I.

Time-Temperature Superposition Principle

The application of the TTSP allows to obtain the temperature shift factors, a_T and b_T, defined for the frequency and complex modulus, respectively. The horizontal shift factors (a_T) can be interpreted in terms of flow activation energy values (E_{aH}). Similarly, the vertical shift (b_T) was defined in terms of a vertical flow activation energy (E_{aV}).[29] The more commonly used equation to describe the thermal dependence of rheological properties of polymeric systems is the William-Landel-Ferry (WLF) expression.[32] This expression is generally applicable in the temperature range between the glass transition temperature, T_g, and $T_g + 100$ °C. For higher temperatures it can be closely approximated by an Arrhenius-type equation:
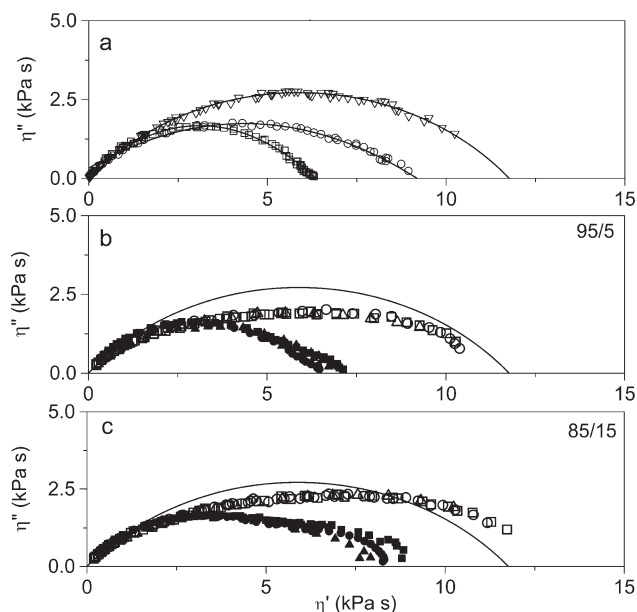
Figure 2 (a) Cole-Cole plot of the complex viscosity at a reference temperature of 190°C for the pure polymers. The symbols are the same than in Figure 1. The lines represent the fit to eq. (1). (b) Cole-Cole plot of the complex viscosity at a reference temperature of 190°C for 95/5 blends. Close symbols: LLDPE1/LDPE blends; open symbols: LLDPE2/LDPE blends; solid line: LDPE pure component. Different symbols mean different temperatures: (□) 130°C, (○) 160°C and (△) 190°C. (c) Cole-Cole plot of the complex viscosity at a reference temperature of 190°C for 85/15 blends. The symbols and lines are the same than in Figure 2(b).

TABLE II
Flow Activation Energy of Pure Polymer and Blends

Resin	E_{aH} (kcal/mol)	E_{aV} (kcal/mol)
LLDPE1	8.1 ± 0.1	0.60 ± 0.26
LLDPE2	8.2 ± 0.5	0.69 ± 0.40
LDPE	21.7 ± 1.5	3.3 ± 0.6
LLDPE1/LDPE 95/5	8.9 ± 0.2	0.86 ± 0.08
LLDPE1/LDPE 85/15	8.9 ± 0.4	1.73 ± 0.03
LLDPE2/LDPE 95/5	9.1 ± 0.7	0.59 ± 0.08
LLDPE2/LDPE 85/15	10.1 ± 0.5	0.44 ± 0.11

$$a_T = \exp\left(\frac{E_{aH}}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right)\right); \quad b_T = \exp\left(\frac{E_{aV}}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right)\right)$$

(2)

R is the gas constant, T the experimental temperature, T_0 the reference temperature. From the values of a_T and b_T and employing these expressions it is possible calculate the activation energy values, E_a. The values for the pure materials and the blends studied are listed in Table II. LLDPE presented no sings of thermorheological complexity ($b_T \approx 1$), being E_{aV} very low, close to zero. However, LDPE presented thermorheological complexity which means that the E_{aV} is non-zero and around 2–3 kcal/mol. Moreover, this sample shows E_{aH} values higher than LLDPE samples. The corresponding values for the LDPE sample is around 15.0–20.0 kcal/mol, typical of long chain branched polymer. This complex behavior has been attributed to the different relaxation mechanisms of the branched and linear chains in an entangled environment.[33] In general, for the LLDPE samples studied E_{aH} values are around 7.0–8.0 kcal/mol. Values in this range are characteristic of polyethylene with a few number of short chain branches (around 15 CH_3/1000 C atoms).[29,30]

The addition of LDPE causes an increase of the values of E_{aH} values. E_{aV} remains around values lower than 1 kcal/mol. This is also a common behavior in LLDPE/LDPE blends. The values obtained in our blends are listed in Table II. The LLDPE1/LDPE blends show values of E_{aH} close to those corresponding to the blend matrix. However, in the case of LLDPE2/LDPE blends, the values of E_{aH} clearly increase as LDPE content increases. In the case of polymer blends, the validity of the TTSP has been confirmed in some cases but not in others, independently of the miscibility or immiscibility of the blends. Thus, the TTSP cannot be considered a good test of miscibility.[34] Concerning the fulfillment of the TTSP principle, the result obtained in the blends studied is complex and interesting. Looking at the results obtained for the shear moduli, the TTSP seems to properly work in most of the cases. However, if we make use of a more sensitive function, like the out of phase component of the complex viscosity (η''), the

result obtained is completely different. In Figure 2 we can observe the Cole-Cole plots of the pure materials and blends studied. For the LLDPE1/LDPE blends (black symbols in Fig. 2(b,c)), it is clear that two different zones can be distinguished in the linear viscoelastic response. At high frequencies (low values of η') the TTSP fulfils, and the rheological response follows the same pattern than the LLDPE1 sample. The well defined maximum in η'' corresponding to the LLDPE1 in the blend is clearly distinguished. However, close to that region at which the relaxation of the pure LDPE sample occurs (high values of η'), the relaxation of the blends seems to be more temperature sensitive; a clear distinction between two different mechanisms is observed in these samples, more pronounced for the blend with the highest content in LDPE. On the contrary, for the LLDPE2/LDPE blends (the base polymer is the Ziegler-Natta LLDPE) the TTSP fulfils in the whole frequency range, even at that region within which the relaxation of the branched pure LDPE samples proceeds. In this case it is not possible to distinguish between different mechanisms, as a unique broad response proceeds (white symbols in Fig. 2(b,c)). What it is also very interesting is the fact that the blends in this case show Newtonian viscosities close (for the 95/5 blend) or even higher (for the 85/15 blend) than those corresponding to both pure LLDPE2 and LDPE samples.

The difference between both sets of blends is the base LLDPE polymer used. LLDPE1 is characterized by a well-defined relaxation spectrum (due to the narrow molecular weight and distribution). Also a narrower chemical composition is expected in this material in comparison to LLDPE2 sample, as it is obtained from a single-site catalyzed process. In fact, the standard deviation of the comonomer distribution obtained by Crystaf analysis is lower in LLDPE1 than in LLDPE2, as it can be judged by the data shown in Table I.

On the contrary, LLDPE2 shows a broader relaxation spectrum with higher relaxation times, and it is expected to posses a more heterogeneous composition, as a Ziegler-Natta multi-site catalyst is used in the polymerization process. This material not only has higher values of M_w and M_w/M_n than the LLDPE1 sample, but also shows a broader comonomer distribution.

As identical mixing conditions are used in all the cases, the molecular nature of the base LLDPE seems to play an important role in the temperature dependence of the molecular dynamics of the blends. However, for the blends with LLDPE1 a clear distinction between the relaxation modes is identified: a trend to a bimodal relaxation response with different temperature dependencies as the amount of LDPE increases. However, for the blends with LLDPE2, a unimodal broad relaxation response is clearly seen,
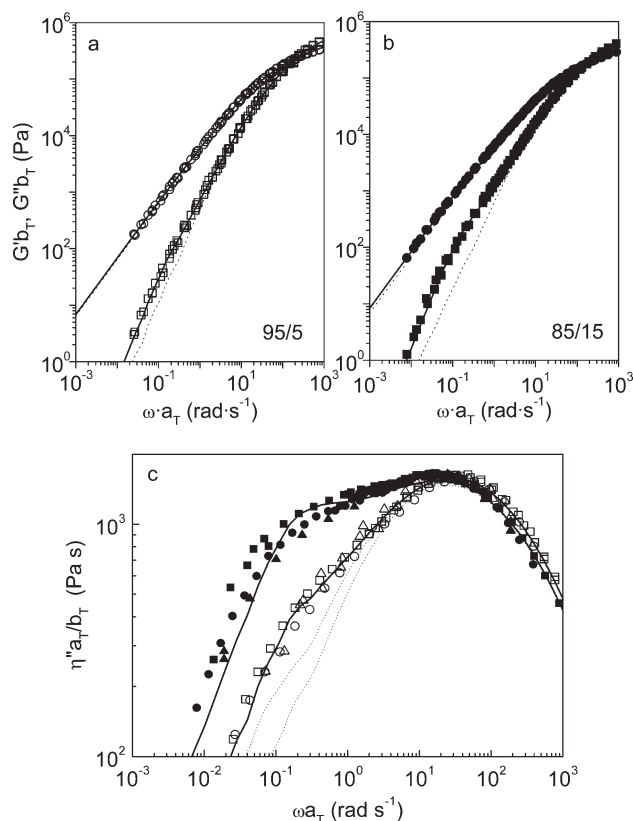
Figure 3 G′ (squares) and G″ (circles) versus the reduced angular frequency for (a) 95/5 and (b) 85/15 LLDPE1/LDPE blend at 190°C. Dotted lines represent the results of the additive model for miscible blends. Solid lines represent the results of the Palierne model for heterogeneous systems with $\alpha/R = 4 \times 10^3$ N/m². (c) Out of phase component of complex viscosity, η'', versus the reduced frequency of 95/15 LLDPE1/LDPE (open symbols) and 85/15 LLDPE1/LDPE blend (close symbols) superposed to $T_0 = 190$ °C. The different symbols correspond to different temperatures (□) 130°C, (○) 160°C and (△) 190°C. The lines mean the same than in Figure 3(a,b).

Analysis of the linear viscoelastic response

Application of models to the rheological response

For miscible blends, Groves et al.[3] found agreement between measurements and predictions derived from the double reptation theory, by empirically varying the exponent blending law C of the generalized form of the double reptation blending law:[28]

$$G(t) = \left[\sum_i \phi_i G_i^{1/c}(t) \right]^c \qquad (3)$$

In the case of high-density polyethylene and LDPE miscible blends (HDPE/LDPE), C depends on the viscosity ratio of blend components as follows:[3]

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

where η_{oB} and η_{oL} is the Newtonian viscosity of the branched and linear polymers, respectively. This model has been found to describe the linear rheology of miscible blends of linear and branched PEs for a range of C values between 1.25 and 4.[3,15] The variability in C was explained in terms of the different degrees to which branched and linear species cooperatively relax in the molten state. We have applied this model to the results obtained for the samples under study. The values of C are around 2, according to the corresponding ratio between the values of Newtonian viscosity values in our samples (listed in Table I). In Figures 3 and 4, we can observe that this additive model (dotted lines) is not able to explain the dynamic response of the LLDPE/LDPE
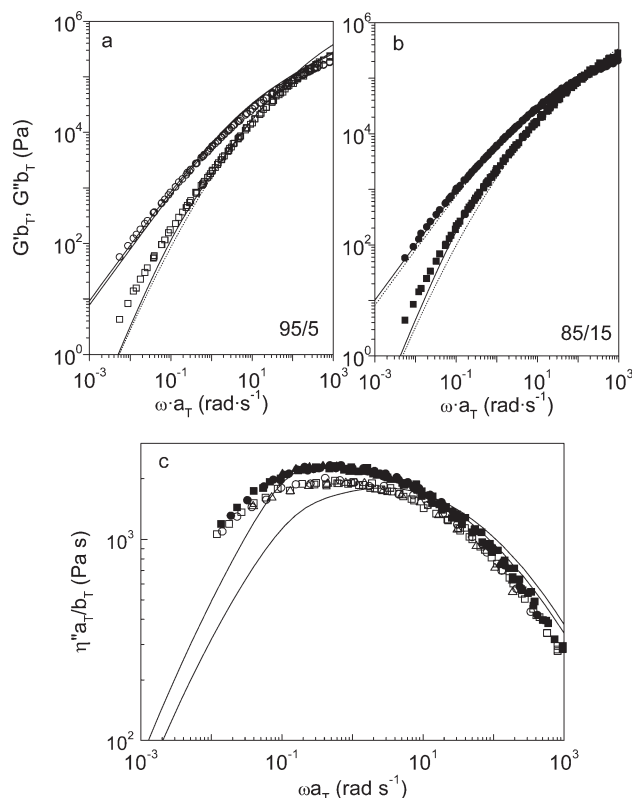
Figure 4 G′ (squares) and G″ (circles) versus the reduced angular frequency for (a) 95/5 and (b) 85/15 LLDPE2/LDPE blend at 190°C. Dotted lines represent the results of the additive model for miscible blends. Solid lines represent the results of the Palierne model for heterogeneous systems with $\alpha/R = 4 \times 10^3$ N/m². (c) Out of phase component of complex viscosity, η'', versus the reduced frequency of 95/15 LLDPE2/LDPE blends (open symbols) and 85/15 LLDPE2/LDPE blend (close symbols) superposed to $T_0 = 190$ °C. The different symbols correspond to different temperatures (□) 130°C, (○) 160°C, and (△) 190°C. The lines mean the same than in Figure 3(a,b).

with unique temperature dependence, pointing toward a cooperative relaxation mechanism between the involved species.

blends studied. This is especially true for the out of phase component of the complex viscosity, η'' (Fig. 3(c) and 4(c)). These results point toward the existence of at least one additional relaxation mechanism in the low frequency zone. The shift of the experimental viscoelastic fingerprint toward lower frequencies can be directly related to heterogeneous blend morphology. This response is characteristic of emulsion-like systems formed by viscoelastic materials. The additional slow relaxation mechanism has been interpreted as the disperse phase droplets deformation-relaxation process. The model developed by Palierne,[28] describes the linear response in this type of system in terms of the properties of each phase, the matrix (m) and the dispersed phase (d) by means of the expression:

$$G^*(\omega) = G_m^*(\omega)\frac{1 + 3\sum_i \phi_i H_i(\omega)}{1 - 2\sum_i \phi_i H_i(\omega)} \tag{5}$$

with $H_i(\omega)$ given by:

$$H_i(\omega) = \frac{4\left(\frac{\alpha}{R}\right)\left[2G_m^* + 5G_d^*\right] + \left[G_d^* - G_m^*\right]\left[16G_m^* + 19G_d^*\right]}{40\left(\frac{\alpha}{R}\right)\left[G_m^* + G_d^*\right] + \left[2G_d^* + 3G_m^*\right]\left[16G_m^* + 19G_d^*\right]} \tag{6}$$

This model predicts that the 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. In Figures 3 and 4 we can observe the results obtained upon the application of the model to G', G'', and η'' for the different compositions of the blends studied over a wide range of frequencies (5 decades). Exceptional agreement was shown between the experimental results and the calculations applied to LLDPE1/LDPE samples, with a value of $\alpha/R = 4.0 \times 10^3$ N/m². This value is in very good agreement with those reported in the literature for polyolefin's blends.[7,12,13,21,34] In these works, values of α/R varying between 0.5×10^3 and 4.0×10^3 N/m² can be found. In the case of LLDPE2/LDPE blends the Palierne model given by the simple formulation of eqs. (5) and (6), is not able to explain the experimental results obtained in the whole range of frequencies. When the matrix of the system is the Ziegler-Natta LLDPE2 polymer, and using the same value of $\alpha/R = 4 \times 10^3$ N/m², the Palierne model only fits the results obtained in the high frequency zone. The experimental linear viscoelastic fingerprint is further broadened toward lower frequencies than those predicted by the model. A change in the model parameter α/R does not improve the prediction. A decrease in α/R could account for a broadening of the response to lower
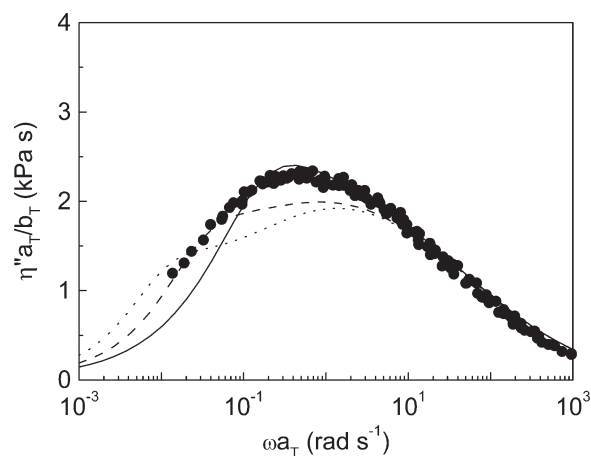
Figure 5 Application of the Palierne model to the out of phase component of the complex viscosity, η'', versus the reduced frequency of 95/15 LLDPE2/LDPE blend superposed to $T_0 = 190$ °C for different values of the model parameter α/R. Solid line $\alpha/R = 4 \times 10^3$ N/m², dashed lines $\alpha/R = 0.8 \times 10^3$ N/m², and dotted line $\alpha/R = 0.4 \times 10^3$ N/m².

frequencies, but in this case a characteristic bimodal response emerges, which is not present in the experiments, as it can be observed in Figure 5 for the 85/15 LLDPE2/LDPE blend. An explanation for the experimental results obtained would be a possible broad size distribution in LDPE domains, with the presence of large droplets with very high shape deformation relaxation times broadening the linear viscoelastic fingerprint to low frequencies. Decreased values in α/R up to one order of magnitude means a strong increase in the size of the dispersed particles, even considering small changes in α due to a better interaction between the molecular species at the interface. This possibility is questionable, taking into account that all blends, including those prepared with LLDPE1 sample, have been subjected to strong conditions during mixing operations.

Other relaxation mechanisms can be postulated to explain the broadening of the relaxation towards lower frequencies. It is important for further discussions to take into account that an interface could be eventually modified, and also should have its own viscoelastic properties. Besides the isotropic interfacial tension, α, such an interface is characterized by an interfacial elasticity. Jacobs et al. considered the emulsions of viscoelastic fluids from this point of view in the general framework of Palierne.[35] In this approach the interfacial stresses may be non isotropic and depend on deformation-induced variation of the interfacial area. In the equations, besides the interfacial tension, α, an additional complex contribution (β^*) emerges. Consequently, in a dynamic mechanical experiment, one would measure an apparent interfacial tension α_{ij} (the interfacial stress

tensor) composed by both the isotropic interfacial tension, α, and the additional complex contribution, β′ as the surface dilatation modulus (normally set to be zero), and β″ as the surface shear modulus. For well-interacting molecular species in a blend, as we postulate in our case, these interfacial properties could play an important role, giving rise to the broad relaxation spectrum observed the experiments. Some questions of great interest come out in our blends if we take into account this consideration.

Viscoelastic properties of the interface

The comparison of the weighted relaxation spectra is an interesting way to study the additional relaxation mechanisms associated with the presence of dispersed deforming droplets in a matrix.[21,25,36–38] The relationship between the relaxation spectrum $H(\tau)$ and shear dynamic moduli, G′ and G″ can be expressed by:[32]

$$G'(\omega) = \sum_i h_i \frac{\omega^2 \tau_i^2}{1 + \omega^2 \tau_i^2} \qquad (7)$$

$$G''(\omega) = \sum_i h_i \frac{\omega \tau_i}{1 + \omega^2 \tau_i^2} \qquad (8)$$

The transformation of dynamic mechanical data into a relaxation spectrum has been made for the pure samples and blends by a least-square fitting procedure. The relaxation times τ_i have been fixed at equally spaced intervals; τ_i / τ_{i-1} is a constant (with $\tau_{min} = 1/\omega_{max}$). In these conditions, the range of relaxation times should be related to the experimental range of frequencies. Then one can obtain the related continuous function, $H(\tau)$ from:[39]

$$h_i(\tau_i) = H(\tau)\Delta ln\tau \approx H(\tau)ln\left(\frac{\tau_i}{\tau_{i-1}}\right) \qquad (9)$$

The relaxation time spectra allow quantifying the characteristic times inherent in the observed relaxation behavior, for the pure materials and the blend series. These spectra are presented in Figure 6. The characteristic relaxation times are expressed as maxima, which can be easily analyzed quantitatively. Figure 6(a,b) show the weighted relaxation spectra of the LLDPE1/LDPE and LLDPE2/LDPE blends at 190°C, respectively. In Figure 6(a), it is seen that the relaxation spectra of the LLDPE1/LDPE blends develop a bimodal response as the amount of LDPE in the blend increases. It is clear that an additional peak in 95/5 LDPE1/LDPE is no evident due to the lower amount of the second component, but a clear broadening of the viscoelastic response is clearly identified. For the 85/15 LDPE1/LDPE blend the contribution of the second component is unambiguously single out at high relaxation times. Moreover,
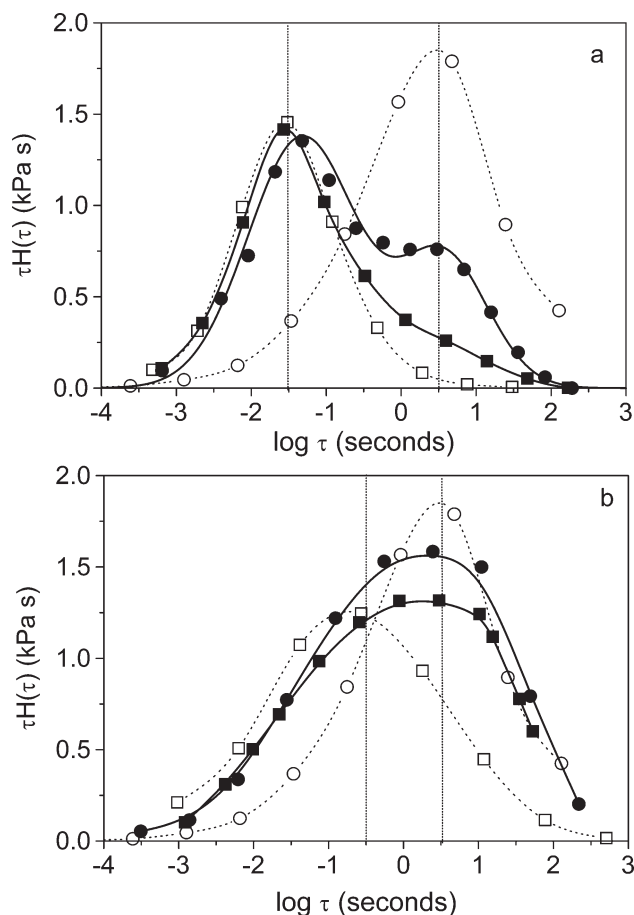
Figure 6 (a) Weighted relaxation spectra of (□) LLDPE1, (○) LDPE, (■) 95/5 LLDPE1/LDPE blend and (●) 85/15 LLDPE1/LDPE blend at a reference temperature of 190°C. (b) Weighted relaxation spectra of (□) LLDPE2, (○) LDPE, (■) 95/5 LLDPE2/LDPE blend, and (●) 85/15 LLDPE2/LDPE blend at a reference temperature of 190°C.

the main maximum corresponds to that relaxation time of the LLDPE1 matrix, whereas the high relaxation tail corresponds to that of the LDPE pure component. This suggests that LLDPE1 governs the rheological response of the blend at short times (high frequencies), whereas LDPE monitors the behavior of the blend at long time (low frequencies). The behavior described in Figure 6(a) implies immiscibility. As we have already pointed out in the previous section, the bimodal relaxation spectrum of the blends with LLDPE1 matrix can be explained by the Palierne approach, being the longest additional relaxation due to the shape deformation of the dispersed phase droplets. On the contrary, as it is shown in Figure 6(b), the spectrum curves for the LLDPE2/LDPE blends have a single peak that comprises both average relaxation times of LLDPE2 and LDPE pure components. Moreover, the relaxation time distributions of these blends show a longer tail than that corresponding to the pure LDPE sample.
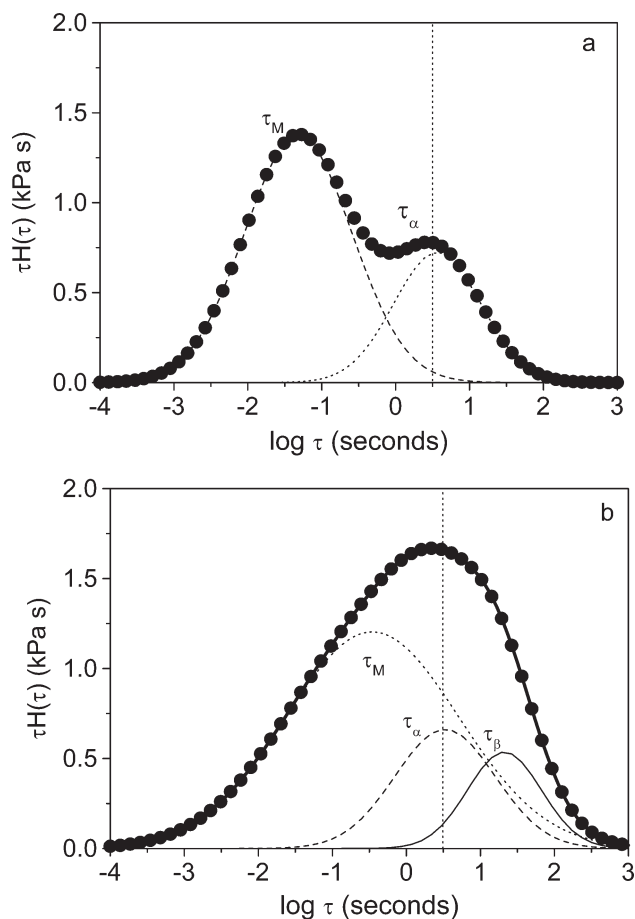
Figure 7 Identification of the different relaxation mechanisms by empirical gaussian splitting of the weighted relaxation spectrum: (a) 85/15 LLDPE1/LDPE blend, and (b) 85/15 LLDPE2/LDPE blend.

This is a clear indication of strongly cooperative or overlapped mechanisms in the whole time domain, as it is also suggested by the unique temperature dependence in the whole time range explored.

The relaxation behavior of the LLDPE1/LDPE samples can be empirically described by the sum of two gaussian functions [Fig. 7(a)], comprising both, the relaxation of the whole system (similar to that of the matrix LLDPE1 but shifted to slightly higher relaxation times) and the shape relaxation of the droplets. However, if we take into account similar two gaussian contributions (assuming similar α/R value, and then similar relaxation mechanism for the shape deformation of LDPE droplets) for the blend with the Ziegler-Natta matrix (LLDPE2), it is not possible to explain the relaxation spectrum completely [Fig. 7(b)]. To explain the whole relaxation spectrum, an extra contribution should be included, as it is observed in Figure 7(b). This relaxation appears at the longest relaxation times region and it could be interpreted as an interfacial contribution, β. The most o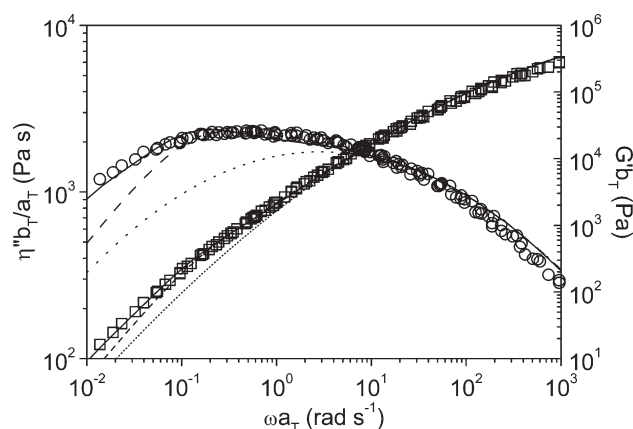f the heterogeneous systems generally exhibits bad phase adhesion as a consequence of a weak interaction between both components. This might not be the case in LLDPE2/LDPE blends. This interaction would promote the accumulation of certain molecular species preferentially at the interface causing changes in particle size and an improved adhesion between the blend components.[40,41] From a microscopic point of view, the presence of these molecular species enlarges the thickness of the interface. Friedrich's team was the first to obtain experimental evidences of viscoelastic features of an interface.[42–44] They found a characteristic signature of a thick interface in blends of PS/PMMA with 1 wt % of symmetric diblock copolymer poly(styrene-b-methyl methacrylate), P(S-b-MMA), or poly(cyclohexyl methacrylate-b-methyl methacrylate), P(CHMA-b-MMA). This additional relaxation process was characterized with a very large relaxation time, τ_β. This type of response has been observed in different blends by several authors.[42–47] However, the basic difference with our results is that all these authors observed the characteristic response of the interface when a third component is added to the blend. Moreover, all these authors have found that the properties of this interface strongly depend on the nature, molecular weight and amount of the third component.

The question that arises at this point is why this broader response only occurs in the case of the blends with the LLDPE2 sample. This material is a Ziegler-Natta copolymer, characterized by a more complex molecular architecture than its partner, the metallocene LLDPE1. LLDPE2 is actually a mixture of low molecular weight branched species and high molecular weight linear species. This linear high molecular weight tail possesses the highest relaxation time of the distribution. Moreover, the relaxation times of this tail spread to the same time region than the average relaxation time of the dispersed LDPE droplets [Fig. 6(b)]. It is well documented in the literature that linear polyethylene is miscible with LDPE.[6] Then we can expect some kind of interaction between the linear species from LLDPE2 and the lowest molecular weight species (almost linear) from LDPE, both having very high relaxation times. The case of metallocene LLDPE1 sample is different as the molecular species are characterized by homogeneous molecular size and chemical composition distributions. Moreover, the relaxation spectrum does not show any signature of a high molecular weight tail, as it can be observed in Figure 6(a). The high average value of randomly distributed short chain branches in this material should be the cause of the immiscibility and the existence of a sharper interface between the components. In this particular case the molecular species involved are highly dissimilar, then the interaction parameter should be
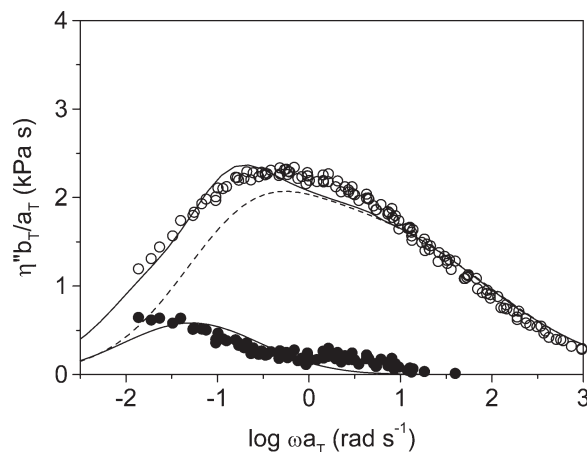
low and the diffusion movements very slow. Former systematic studies, in our team, found that molecular segregation occurs, in the solid state, for short chain branching content of around 20 branches/1000 C atoms.[48,49]

The morphological picture proposed for the LLDPE2/LDPE blends here is similar to that proposed by Wagner et al.[20] These authors suggested a two-phase system composed by one phase with the branched shortest chains of both LLDPE and LDPE polymers, and other phase with the longest chains of both components. We have considered the interface as an independent phase of the system, and consequently applied the Palierne model modified by Jacobs et al., which considers an additional term to the shape deformation of the droplets to account for the viscoelastic properties of the interface.[35] The approach used considers an interfacial dilatation modulus $\beta' = 0$, an interfacial shear modulus, β'', and a purely elastic interface, implying β'' to be independent of the frequency. Considering all of the above Van Hemelrijck et al. found the corresponding expression for the storage modulus, G' with only two parameters α/R and β''/R (see reference 45). The fits of the G' and η'' (G'/ω) experimental data with the Palierne model with $\beta''/R \sim 0.4 \times 10^3$ N/m^2 and $\alpha/R \sim 3.5 \times 10^3$ N/m^2 can be observed in Figure 8 for the 85/15 LLDPE2/LDPE blend. In this figure, the Palierne model with $\alpha/R \sim 3.5 \times 10^3$ N/m^2 and $\beta''/R = 0$ N/m^2 (which means only shape deformation mechanism in the blend) is also included. The characteristic frequency (relaxation time) domains along which the shape deformation and the viscoelastic response of the interface proceed

Figure 9 Identification of the β relaxation contribution in the out of phase component of the complex viscosity, η'', for 85/15 LLPDE2/LDPE blend at 190°C obtained from the Palierne model with an additional term for the viscoelastic response of the interface. Solid line ($\alpha/R = 3.5 \times 10^3$ N/m^2 and $\beta''/R = 0.4 \times 10^3$ N/m^2); dashed line ($\alpha/R = 3.5 \times 10^3$ N/m^2 and $\beta''/R = 0$); thick solid represents the mechanism assigned to the interface.

are clearly identified. In addition, from these fits the characteristic relaxation mechanism assigned to the response of the interface, τ_β, can be deduced, as it can be observed in Figure 9. The characteristic relaxation time domain for this relaxation mechanism is in very good agreement with the obtained with the empirical separation methodology applied for this blend in preceding lines (Fig. 7b).

The presence of the β contribution as ascribed to the elasticity of the interface in this type of blends should play an important role not only in processing operations in the melt state but also in the final properties (mechanical, optical, etc.) of the finished products such as films. Moreover, an effect of the LDPE molecular architecture (molecular weight and branching structure) can be anticipated in the viscoelastic response of the interface. The work is at this time in progress.

CONCLUSIONS

Small amounts of LDPE strongly affect to linear viscoelastic properties of LLDPE resins. In the range of 5–15% of LDPE in LLDPE, the characteristic response of heterogeneous polymeric blends has been observed. The melt dynamic functions in metallocene LLDPE/LDPE blends can be explained by the application of the Palierne model, which assumes an additional relaxation mechanism ascribed to the shape deformation of LDPE droplets in the blend. Ziegler-Natta LLDPE/LDPE blends show a broader linear response that cannot be described by only the shape deformation process of the dispersed LDPE droplets. We propose the existence of a thick

Figure 8 Application of the Palierne model with an additional term for the viscoelastic response of the interface for different values of α/R and β''/R to G' (squares) and η'' (circles) of 95/15 LLDPE2/LDPE blend. Dotted lines ($\alpha/R = 0$ and $\beta''/R = 0$), dashed lines ($\alpha/R = 3.5 \times 10^3$ N/m^2 and $\beta''/R = 0$); and solid lines ($\alpha/R = 3.5 \times 10^3$ N/m^2 and $\beta''/R = 0.4 \times 10^3$ N/m^2) to storage shear modulus, G', and the out of phase component of complex viscosity, η'', of 85/15 LLDPE2/LDPE blend.

interface with its own viscoelastic properties. This interface gives rise to a very long relaxation time tail, with one order of magnitude higher relaxation times than the shape deformation process. This long relaxation mechanism can be explained by a more complete viscoelastic model, which includes the effect of non-isotropic interfacial effects with a high elastic character. This interface is likely due to a strong interaction between the longest linear molecules of the Ziegler-Natta LLDPE and the smallest molecules of the LDPE component. The presence of the interfacial component in these systems may have an important impact in the their processing and final use. The additional long relaxation times associated to the interface could play a key role, for example in extensional properties, orientation phenomena and then in the final microstructure and physical properties of polymeric systems. This finding opens the possibility of modulate the physical properties of the blends, as it is expected that the properties of the interface depend on the molecular features and interaction of both the matrix and the dispersed phase.

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