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ORIGINAL CONTRIBUTION

Thermorheological properties of LLDPE/LDPE blends

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Abstract The thermorheological behavior of a number of linear low-density polyethylene and low-density polyethylene (LLDPE/LDPE) blends was studied with emphasis on the effects of long chain branching. A Ziegler–Natta, LLDPE (LL3001.32) was blended with four LDPEs having distinctly different molecular weights. The weight fractions of the LDPEs used in the blends were 1, 5, 10, 20, 50, and 75%. Differential scanning calorimetry (DSC) analysis has shown that all blends exhibited more than one crystal type. At high LDPE weight fractions, apart from the two distinct peaks of the individual components, a third peak appears which indicates the existence of a third phase that is created from the co-crystallization of the two components. The linear viscoelastic characterization was performed, and mastercurves at 150 °C were constructed for all blends to check miscibility. In addition, Van Gurp Palmen, zero-shear viscosity vs composition, Cole–Cole, and the weighted relaxation spectra plots were constructed to check the thermorheological behavior of all blends. In general, good agreement is found among these various methods. The elongational behavior of the blends was studied using a uniaxial extensional rheometer, the SER universal testing platform from Xpansion Instruments. The blends exhibit strain-hardening behavior at high rates of deformation even at LDPE concentrations as low as *1%*, which suggests the strong effect of branching added by the LDPE component.

Keywords Activation energy · PE Blend · Block copolymer · Mastercurve · Phase separation · Polymer blend

Introduction

The thermodynamic behavior of linear and branched polyethylene (BPE) blends using rheological methods has been the subject of many studies (Yamaguchi and Abe 1999; Lee and Denn 2000; Liu et al. 2002; Ho et al. 2002; Hussein et al. 2003; Hussein and Williams 2004a, b; Fang et al. 2005). It has been reported that the thermorheological and processing properties of the blend are largely determined by molecular parameters, which include: (1) long chain branching content (LCB), which is the number of long branches, typically branches which have a number of carbon atoms more than 13 (Wagner et al. 2004; Kissin 2005), (2) compositional distribution (CD), which is the number and length of long chain branches for a given LCB macromolecule, or the amount and type of comonomer in the case of LLDPE (Gabriel and Münstedt 2003; Hussein and Williams 2004b; Fang et al. 2005; Kissin 2005), (3) molecular weight, M_w (Hussein and Williams 2004b; Gabriel and Lilge 2006), and (4) molecular weight distribution (MWD; Dealy and Wissbrun 1990).

Most studies agree that linear low-density polyethylene and low-density polyethylene (LLDPE/LDPE) are miscible blends at low LDPE contents, which become immiscible at higher LDPE (Lee and Denn 2000; Ho et al. 2002). Hexene comonomer promotes immiscibility (Hussein et al. 2003; Hussein and Williams 2004b), whereas octene comonomer promotes miscibility (Fang et al. 2005). In addition, low molecular weight LLDPEs promote miscibility better than high M_w ones (Hussein and Williams 2004a). In a recent review, Zhao and Choi (2006) have reported that LLDPE/

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LDPE blends were immiscible in the melt state, with LCB being the determining factor of their immiscibility behavior.

Recently, Wagner et al. (2004) performed a quantitative analysis of melt elongational behavior of LLDPE/LDPE blends. They have reported that the complex behavior of these blends can be understood by assuming the existence of two phases; one phase composed of the highly branched low M_w chains of both polyethylenes and a second phase composed of the high M_w chains (mostly linear) of both polyethylenes. Differential scanning calorimetry (DSC) thermograms of LLDPE/LDPE blends reported by Fang et al. (2005) support the existence of a third phase composed of chains from the two polyethylenes that have the ability to co-crystallize; additionally, enhancement in the crystallization behavior of BPE blended with linear polyethylene (LPE) was explained in terms of co-crystallization due to the incorporation of the linear segments of BPE into rich-LPE lamellae and the segregation of the most branched chains (Puig 2001).

The LLDPE/LDPE blend miscibility studies mentioned above make use of thermal techniques, such as DSC, and rheometrical techniques, such as linear viscoelasticity of blends at different temperatures (Van Gurp and Palmen 1998; Mavridis and Shroff 1992; Hatzikiriakos 2000). Failure of time–temperature superposition can be interpreted as an immiscibility criterion (Van Gurp and Palmen 1998; Peón et al. 2003; Wagner et al. 2004; Pérez et al. 2005). Positive deviation of zero shear rate viscosity from the log-additivity-mixing rule is also an indication of immiscibility (Lee and Denn 2000; Liu et al. 2002; Hussein et al. 2003). The Cole–Cole plot, representation between the imaginary (η') and real part (η'') of the complex viscosity, has been used by several authors as criteria for miscibility in polyethylene blends (Kim et al. 2000; Ho et al. 2002).

The determination of the weighted relaxation spectra based on linear viscoelasticity is another method used to infer the thermorheological behavior of polyethylene blends. The spectra have been used to determine whether the blend components are immiscible due to an additional relaxation mechanism associated with interfacial tension (Gramespacher and Meissner 1992; Lacroix et al. 1997; Fang et al. 2005).

In this paper, we study systematically the thermorheological behavior of a LLDPE with four LDPEs that have viscosity curves that lie above, about the same, and below that of the LLDPE. The miscibility of the various blends is studied with DSC and linear viscoelastic measurements with the application of several thermorheological complexity criteria [time–temperature superposition (TTS), Van Gurp plot, Cole–Cole plot, zero-shear viscosity vs composition, and relaxation spectrum]. All the methods are compared to check consistency of the results. The extensional rheological properties of the blends are also studied to examine the effects of LCB.

Materials and methods

Polyethylene resins and blends

The LLDPE resin used in this study was a Ziegler–Natta, hexene copolymer, supplied by ExxonMobil (LL3001). The LDPE resins used in this work are LD200 by ExxonMobil, EF606A by Westlake Polymers, and 662I and 132I provided by Dow Chemicals. Table 1 lists all the polymers used along with their melt indices and densities. The LDPE resins have been labeled as LDPE-I to LDPE-IV in the order of decreasing melt index value.

The LLDPE resin was melt-blended respectively with each LDPE resin to create LLDPE/LDPE blends having weight compositions of 99:1, 95:5, 90:10, 80:20, 50:50, and 25:75. The blending was performed as follows: The original components were mixed and ground in a Brabrender mixer to reduce their pellet size. Then, the mixture in the form of flakes was blended into a single screw extruder, at low processing speed (3–4 rpm), using a screw having mixing elements near to the end of the metering zone. The temperature of the die was kept at 160 °C. The extrudates were then pelletized for easy handling. The blend 99:1 was produced in two dilution steps, the first being the 95:5.

Thermal analysis

A Shimadzu DSC-60 calorimeter was used to study the thermal behavior of the pure components and their blends. Measurements were made on samples of about 1–2 mg sealed in aluminum pans and nitrogen flow. The samples were heated from 30 to 180 °C, at a heating rate of 10 °C/min, to determine the melting temperature (T_m) and heat of fusion (ΔH_m). The calorimeter was calibrated periodically for melting temperature and heat flow using indium and zinc as standards.

Rheological techniques

Parallel-plate rheometry was performed to determine the linear viscoelastic properties of the pure components and their blends. The measurements were performed using a Rheometrics System IV (controlled-strain) and a Bohlin-

Table 1 Properties of polyethylene resins used in this study

Resin	Melt index (g/10 min) (190 °C)	Density (g/cc) (25 °C)	η_0 (Pa.s) (150 °C)
LLDPE (LL3001.32)	1	0.917	24,557
LDPE I (LD200)	7.5	0.915	8,272
LDPE II (EF606A)	2.2	0.919	44,234
LDPE III (662I)	0.47	0.919	72,780
LDPE IV (132I)	0.22	0.921	132,065

CVOR (controlled-stress rheometer). Experiments performed at different temperatures, namely, 130, 150, 170, 190, and 210 °C. Mastercurves were obtained, and most results are presented at the reference temperature of 150 °C.

Finally, the blends were rheologically characterized in simple extension using an SER universal testing platform (Sentmanat 2003, 2004) from Xpansion Instruments. As described by Sentmanat (2003, 2004), the SER unit is a dual windup extensional rheometer that has been specifically designed for use as a fixture on a variety of commercially available rotational rheometer host platforms. The particular SER model used in this study, a model SER-HV-B01, was designed for use on a VOR Bohlin rotational rheometer host system. Specimens were prepared by compression molding the polymer samples between polyester films to a gauge of about 1 mm, under 20 MPa and 170 °C, using a hydraulic press. Individual polymer specimens were then cut to a width of 6.4–12.7 mm. Typical SER extensional melt rheology specimens range from 40–150 mg in mass. Measurements were conducted at the reference temperature of 150 °C, more than 25° above the peak melting point of the polymers.

Results and discussion

Rheological characterization of pure resins

Figure 1 depicts the complex viscosity of all polymers listed in Table 1 as a function of frequency for the pure resins at 150 °C. For the case of LLDPE (LL3001), the viscosity curve approaches its zero-shear viscosity value at small frequencies and exhibits a certain degree of shear thinning at higher frequencies, a behavior that is typical of LLDPEs. The zero-shear viscosity values of the four LDPEs were not reached experimentally, as can be seen from Fig. 1. These were calculated by determining their relaxation spectrum of the resins using the linear viscoelastic mastercurves at the reference temperature of 150 °C. The values are listed in Table 1. Note that while LDPE-III (662I) and LDPE-IV (132I) possess a much higher zero-shear viscosity than that of LL3001, the presence of LCB causes significant shear thinning, and thus, their viscosity becomes considerably smaller at high frequencies.

The extensional rheological behavior of the pure resins is depicted in Fig. 2 at 150 °C. In all cases, the tensile stress growth coefficients, η_{E}^{+} are plotted for three different Hencky strain rates, namely, 0.1, 1, and 10 s^{-1}. For the sake of clarity, the material functions η_{E}^{+} have been multiplied by an appropriate factor (for convenience, a power of 10), as indicated on the plot. The LLDPE (LL3001) does not exhibit any degree of strain hardening at any extension rate, an observation consistent with polymers of linear architecture, and displays very little deviation from the linear viscoelastic envelope (LVE), $3\eta^{+}$. The latter was determined independently from linear viscoelastic shear rheology measurements, plotted as a dashed line in Fig. 2. On the other hand, the four LDPEs show significant strain hardening (deviation from the LVE, $3\eta^{+}$, also indicated for all resins by dashed lines), which is typically an indication of the presence of LCB. It is worth noting that the onset of strain hardening at a given rate occurs at approximately the same Hencky strain for all four LDPE resins, independent of the molecular weight of the resin. Also LDPE-I (LD200) shows a significantly higher deviation form LVE behavior, an indication of the presence of a higher degree of branching, which is a characteristic of coating LDPE resins.

Thermal analysis–DSC thermograms

Figure 3a–d depicts the melting thermographs of all blends obtained from DSC. For the LLDPE (LL3001)/LDPE-I (LD200) system and all other three systems, the melting

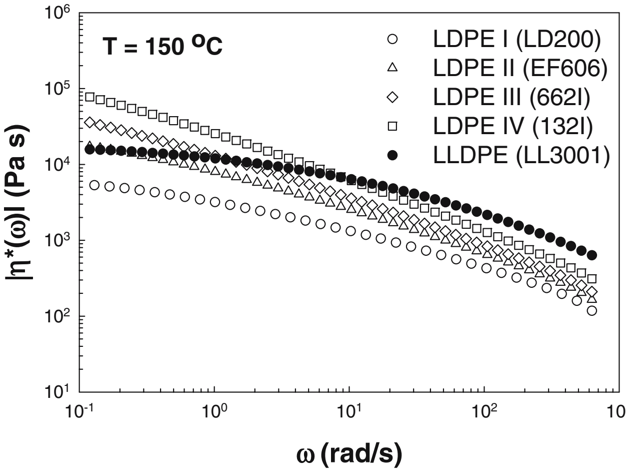


Fig. 1 The complex viscosity curves of LLDPE (LL3001) and those of all four LDPE resins (132i, 662i, EF606A, and LD200) at 150 °C

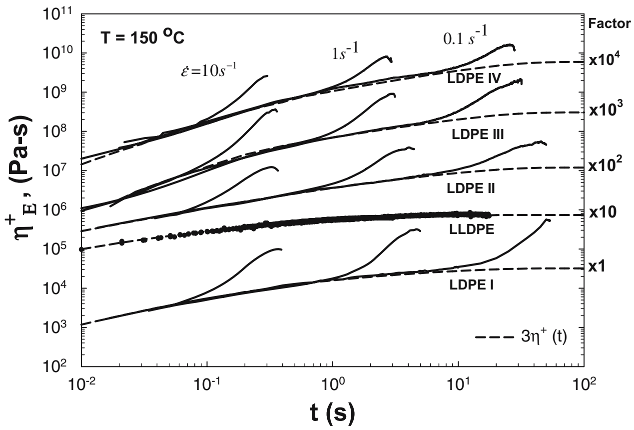


Fig. 2 The tensile stress growth coefficient for the LLDPE resin (LL3001) and the four LDPE resins (LD200, EF606A, 662I, and 132i) at three different Hencky strain rates: 0.1, 1, and 10 s^{-1}; at 150 °C

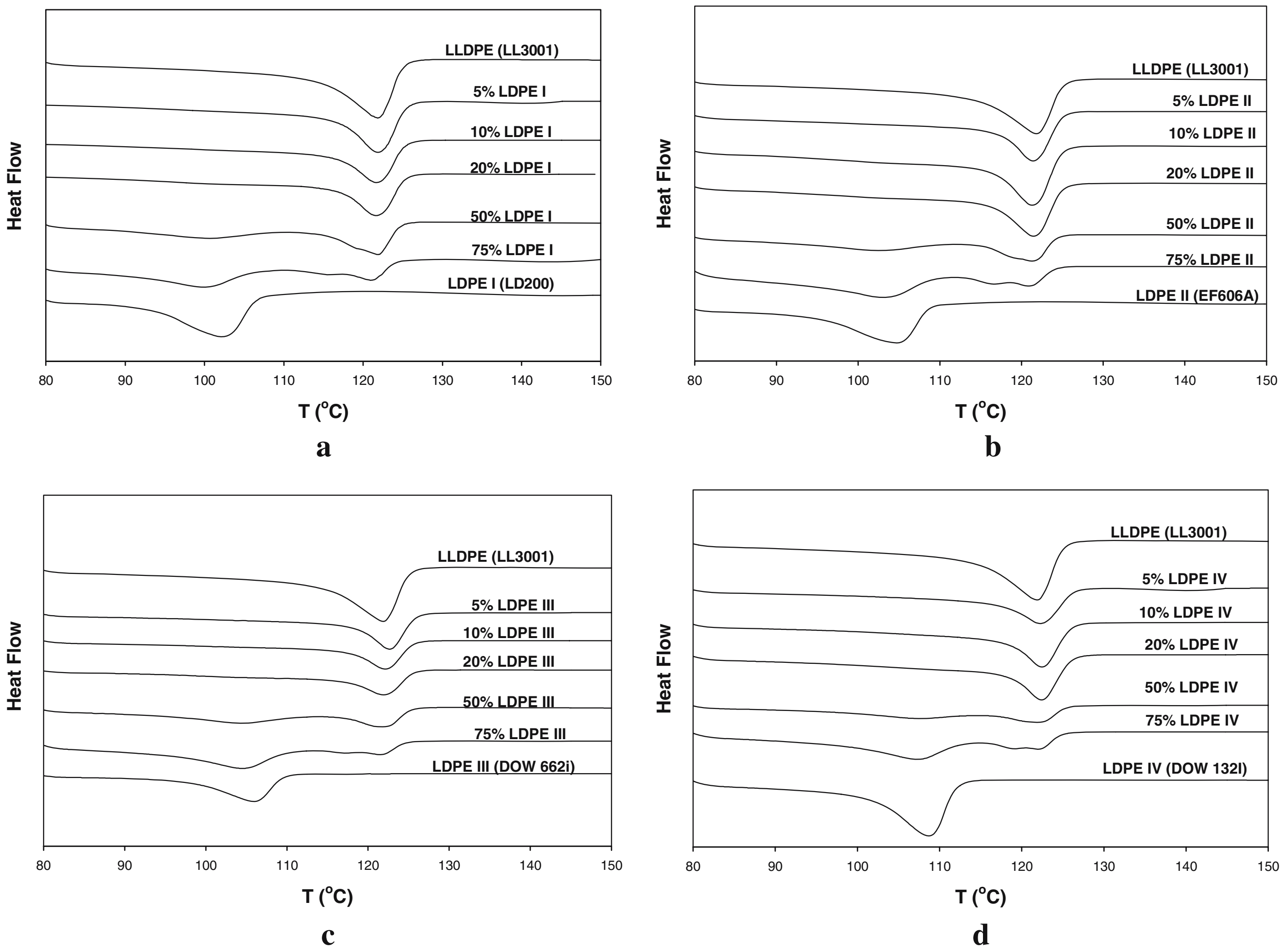


Fig. 3 DSC thermograms for the LLDPE/LDPE blend systems: **a** LL3001/LDPE I (LD200); **b** LL3001/LDPE II (EF606A); **c** LL3001/LDPE III (662I); **d** LL3001/LDPE IV (132I)

peak of LDPEs are lower than that of LL3001. At low weight fractions of LDPE, 5, 10, and 20% the melting is dominated by the LPE, LL3001, as such, the melting peak for these blends is the same as that of the pure LL3001. For the blends containing 50 and 75% LDPE-I, multiple melting peaks are observed denoting an immiscible system, with one peak corresponding to the melting of the LL3001 component, another corresponding to the melting of the LDPE-I component, and a third peak suggesting the existence of a transitional phase.

Co-crystallization was first proposed by Clampitt (1963) to explain the presence of an intermediate peak in differential thermal analysis (DTA) of linear and BPE blends. This is formed with chains segregated from the two polymers (linear and branched), which have the ability to co-crystallize and thus form distinct lamellae morphologies and thicknesses (Wignall et al. 2000; Puig 2001; Fang et al. 2005). This leads to multiple melting behavior (Zhang et al. 2002; Arnal et al. 2001; Mirabella et al. 1988). The formation of a third melting peak for LLDPE/LDPE blends has also been observed by Hussein and Hameed (2005) and Xu et al. (2001). As they have suggested, it is possible that the co-crystalline phase is formed from LLDPE and LDPE chains, which segregate selectively from their individual components. It is well known that Ziegler–Natta LLDPE resins segregate in fractions ranging from high molecular weight chains with low short chain branching content and low molecular weight chains with high amounts of short chain branching (Mirabella and Ford 1987; Mirabella et al. 1988; Schouterden et al. 1987; Karbashewski et al. 1992; Wignall et al. 1996, 2001; Zhang et al. 2001). Lee and Denn (2000) have suggested a hybrid system in which a small fraction of LDPE is miscible with LLDPE, forming the matrix phase; more recently, Wagner et al. (2004) explained the strain hardening of a LLDPE/LDPE system by assuming the existence of a phase composed of high molecular weight molecules from both LLDPE (linear) and LDPE (branched) segregated together to form a matrix phase.

The second set of blends, LL3001/LDPE-II (EF606A), exhibits similar behavior to the aforementioned blend, that is, dominated melting by the linear component up to a 20% LDPE-II blend composition, while the higher blend systems exhibit multiple melt peaks characterized by a second peak corresponding to the LDPE-II component and the occurrence of a third peak, likely resulting from the co-crystallization of chains from both polyethylene components and the possible formation of the third phase. Finally, the same behavior can be observed with regard to the third and fourth set of blends, namely, LL3001/LDPE-III (662i) and LL3001/LDPE-IV (132i).

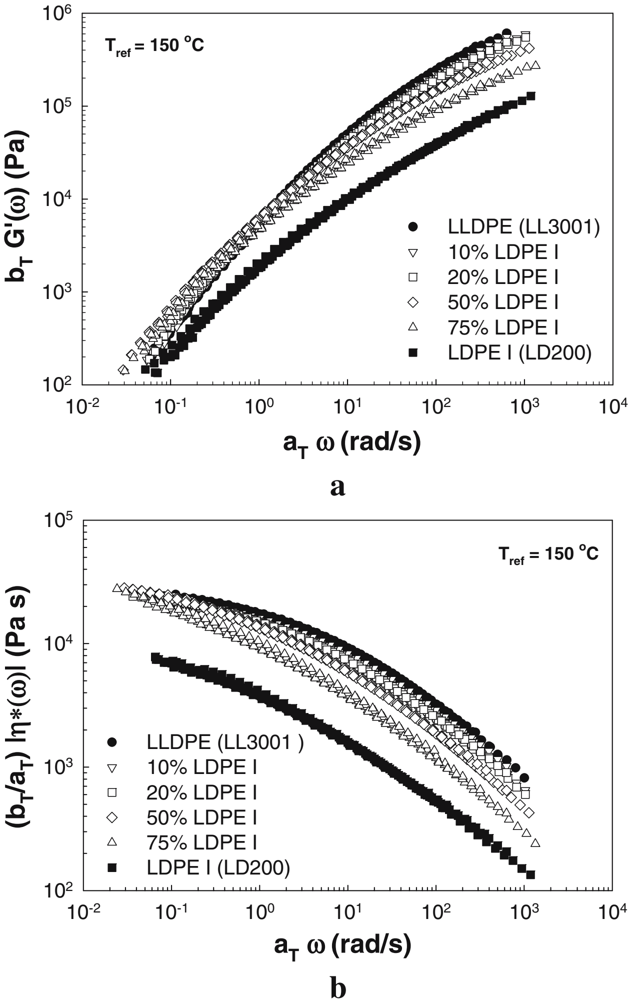
The thermograms plotted in Fig. 3a–d support the observation that LLDPE/LDPE blends form different crystal types at high LDPE weight fractions, typically more than 20 wt%. On the other hand, DSC is unable to resolve the thermodynamic behavior of blends at low LDPE concentrations, as the dominant melting peak at these compositions appears to be only that of the LLDPE component. These DSC results will be compared with several rheological techniques below. However, it should be realized that the DSC thermograms provide information on the crystal population of the various blend systems in the solid state, which might not be necessarily true in the melt state.

Linear viscoelastic measurements

The linear viscoelastic behavior of pure components and all their blends was studied in details over a wide range of temperatures 130–210 °C. TTS was applied to shift the data horizontally and vertically (whenever necessary) to obtain a mastercurve at a reference temperature, T_{ref}, in the present case 150 °C. Horizontal shift factors, a_T, which reflect temperature dependence of relaxation time, were obtained following the procedure proposed by Mavridis and Shroff (1992), where a_T is described by an Arrhenius equation as follows:

$$\log\left(a_T\right) = \frac{E_a}{R}\left(\frac{1}{T} - \frac{1}{T_{\mathrm{ref}}}\right) \tag{1}$$

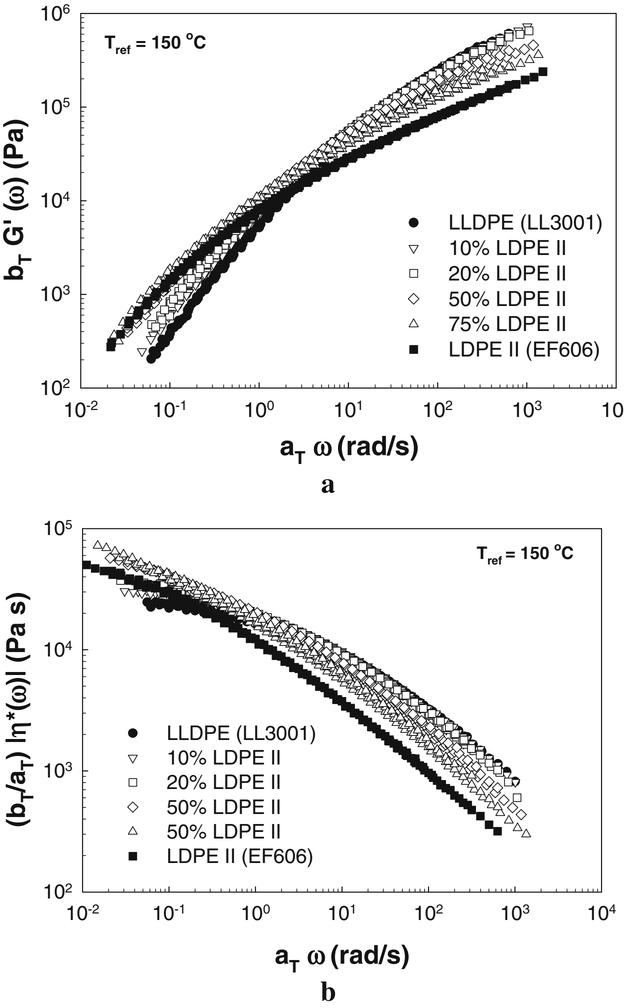
where E_a is the “horizontal activation energy,” and R is the universal gas constant. Due to the presence of LCB in the macromolecular structure of all LDPE resins, it was necessary to apply vertical shift factors (b_T) on the viscoelastic moduli to obtain better superposition (Mavridis and Shroff 1992).



a

b

Fig. 4 Mastercurves of **a** elastic modulus, G′, and **b** complex viscosity, $|\eta*(\omega)|$, for blend system I (LL3001/LD200)



a

b

Fig. 5 Mastercurves of **a** elastic modulus, G′, and **b** complex viscosity, $|\eta*(\omega)|$, for blend system II (LL3001/EF606)

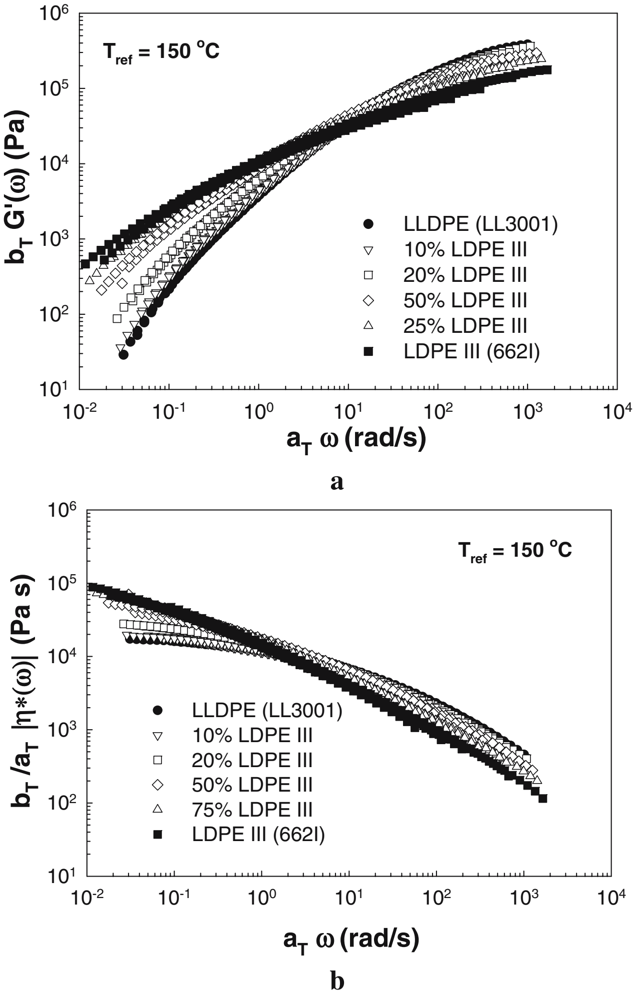


Fig. 6 Mastercurves of **a** elastic modulus, G′, and **b** complex viscosity, $|\eta*(\omega)|$, for blend system III (LL3001/662I)

Failure of TTS in the presence of LCB is typical (Malmberg et al. 1999; Wood-Adams and Costeaux 2001; present work). Mavridis and Shroff (1992) proposed the following expression for b_T, similar to Eq. 1.

$$\log\left(b_T\right) = \frac{E_v}{R}\left(\frac{1}{T} - \frac{1}{T_{\mathrm{ref}}}\right) \tag{2}$$

where E_v is the “vertical activation energy.” Materials showing high E_v values are said to be thermorheologically complex systems (Mavridis and Shroff 1992). In most cases, the superposition to obtain mastercurves was not perfect and may be attributable to two factors: (1) presence of LCB and (2) immiscibility of the blend systems studied (see DSC results above), which can both contribute to thermorheological complexity.

Figure 4a,b shows the shifted storage modulus, b_tG', and complex viscosity, $\left({}^{b_T}/_{a_T}\right)|\eta*(\omega)|$, vs reduced frequency, $a_T\omega$ for the pure resins and their blends with 10, 20, 50, and 75% of LDPE for the LL3001/LDPE I (LD200) system. LL3001 possesses a higher viscosity than that of LDPE-I (LD200) due to the inherently lower M_w of the LDPE. LL3001 apparently dominates the shear rheology of the blend with noticeable changes in shear viscosity only seen at 50% of LDPE and higher. Regarding TTS, no perfect mastercurve could be built for the 50 and 75% LDPE blends, which indicates thermorheologically complex behavior due to immiscibility. At smaller concentrations, mastercurves were obtained for the blends containing up to 20% of LDPE. This latter observation suggests that the lack of TTS for the blends with a higher LDPE concentration is not necessarily due to the presence of LCB, but it is rather due to immiscibility of the blend.

In the low frequency region, for the higher LDPE blend compositions, the values of the shifted storage modulus, b_TG' were observed to be higher than those of the pure components (elasticity enhancement). This implies the existence of an interface between two distinct phases, pointing to the conclusion that the system is immiscible at the high LDPE compositions. This elasticity enhancement also suggests that the lack of TTS is not necessarily due to the

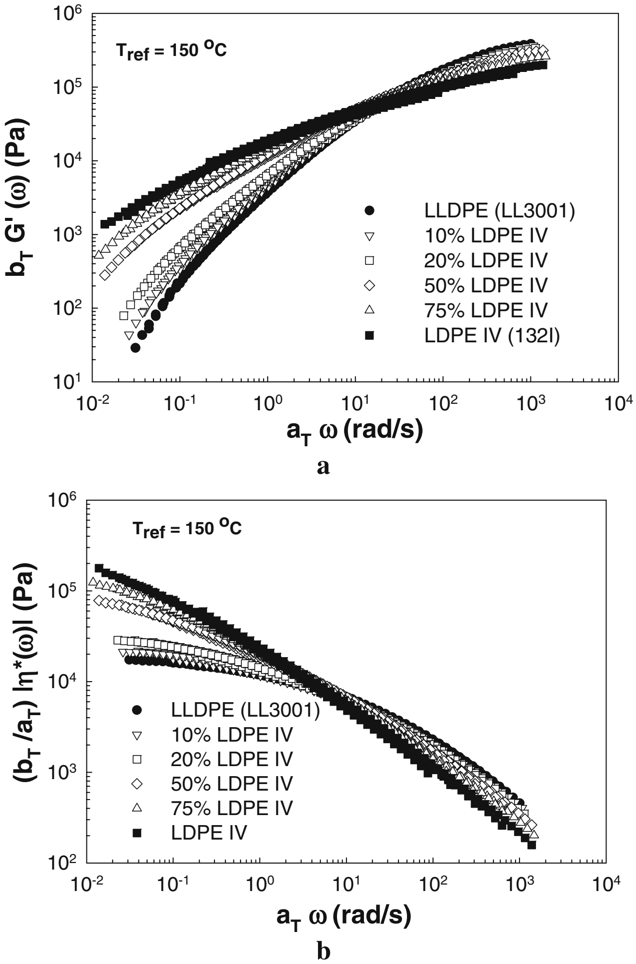
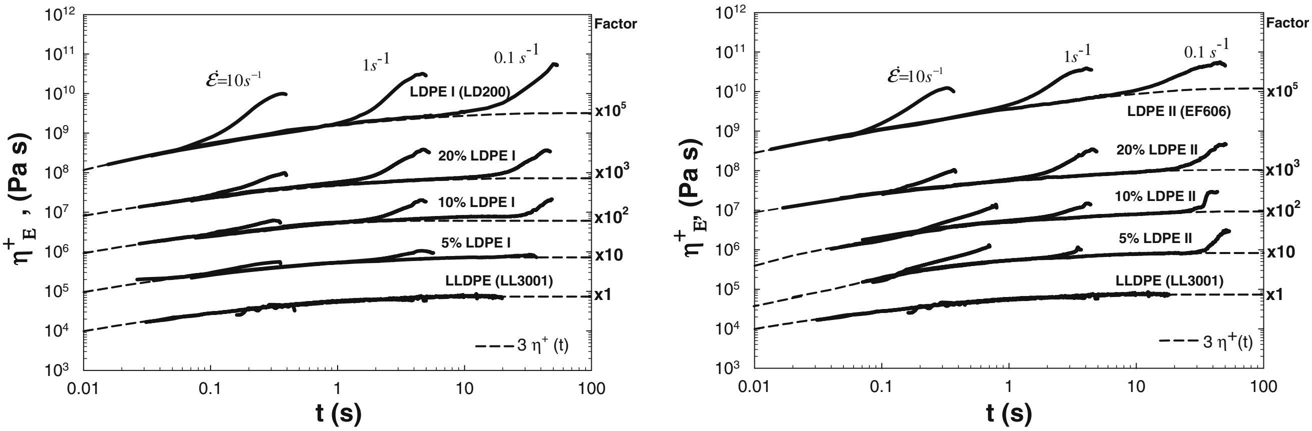
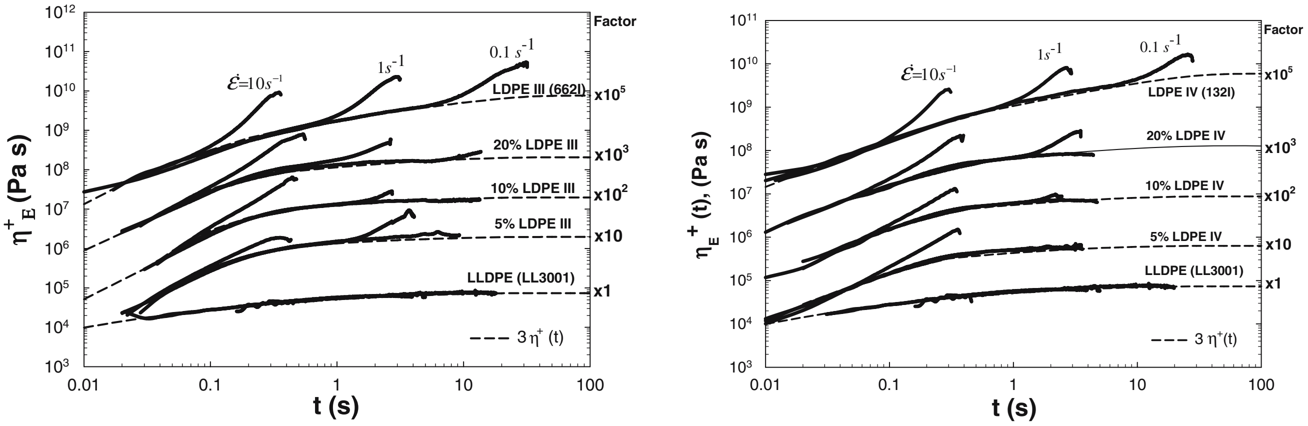


Fig. 7 Mastercurves of **a** elastic modulus, G′, and **b** complex viscosity, $|\eta*(\omega)|$, for blend system IV (LL3001/662I)



a LLDPE/LDPE I (LD200) **b LLDPE/LDPE II (EF606)**



c LLDPE/LDPE III (662I) **d LLDPE/LDPE IV (132I)**

Fig. 8 Tensile stress growth coefficient curves for 0.1, 1, and 10 s^{-1} Hencky strain rates at 150 °C for LLDPE/LDPE blend systems: **a** LL3001/LDPE I (LD200); **b** LL3001/LDPE II (EF606A); **c** LL3001/LDPE III (662I); **d** LL3001/LDPE IV (132I)

presence of the LCB but rather to the complex thermodynamic behavior of the blend.

Figure 5a,b depicts the mastercurves of the LL3001/LDPE-II (EF606A) blends, including the pure components. The shifted complex viscosity curves, $\left({}^{b_T}/_{a_T}\right)|\eta*(\omega)|$ vs reduced frequency, $a_T\omega$, of the two components of the blend are closer compared to those in the previous blend. Lack of good superposition particularly for 50 and 75% LDPE blends indicates that the systems are thermorheologically complex. In addition, elasticity enhancement can be seen

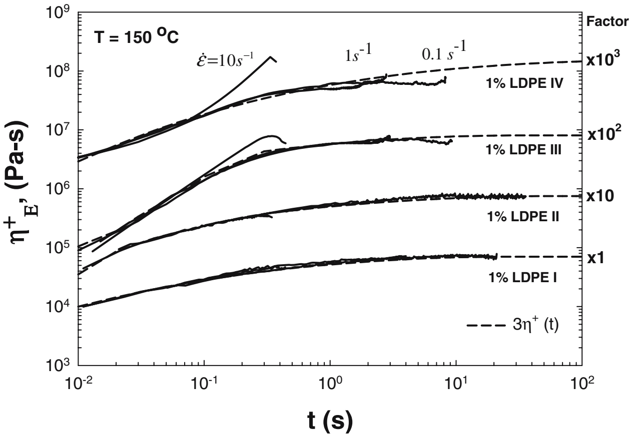


Fig. 9 Tensile stress growth coefficient curves at Hencky strain rates of 0.1, 1, and 10 s^{-1} for LLDPE/LDPE blend systems containing 1 wt% LDPE at 150 °C

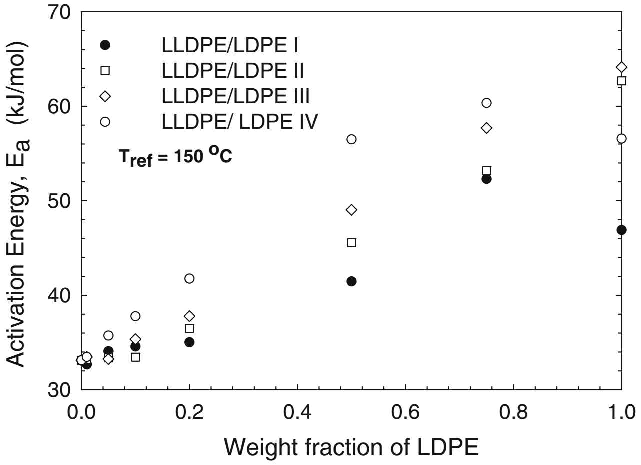


Fig. 10 Activation energy, E_a (Kcal/mol), as a function of weight fraction of LDPE for all blend systems at 150 °C

for 50 and 75% LDPE blends. Similar observations of elasticity enhancement were reported by Hussein and Williams (2004a, b) for ZN-LLDPE/LDPE blends at 90 and 70% LDPE compositions. Elasticity enhancement implies the existence of interface and thus immiscibility of the blends at these compositions.

For the third set of blends, LL3001/LDPE-III (662i), the storage modulus, $b_T G'$, and complex viscosity, $\left(b_T/\alpha_T\right)|\eta*(\omega)|$, mastercurves are plotted in Fig. 6a,b, respectively. Due to its high M_w, the values of $\left(b_T/\alpha_T\right)|\eta*(\omega)|$ for LDPE-III (662i) at low frequencies are higher than those of LL3001. Again, failure of TTS implies that the systems are immiscible at high LDPE compositions. No elasticity enhancement is seen for this system due to the much higher viscosity of LDPE-III. Similar conclusions can be drawn for the fourth set of blends LL3001/LDPE-IV (132i), where the viscosity and elasticity of LDPE-IV dominates the properties of these series of blends (see Fig. 7a,b). For example, with the addition of 10% of LDPE-IV into the LLDPE, significant changes are seen in the complex viscosity of the blend.

Extensional measurements

Extensional rheological measurements were conducted for all blends at 150 °C, the stress growth curves of which are plotted in Fig. 8a,d, using scaling factors as before (powers of 10). As observed in Fig. 8a,d, the strain-hardening behavior is a function of LDPE content with the degree of strain hardening increasing with LDPE weight fraction in the blend and becoming more evident at higher Hencky strain rates. In addition, at similar Hencky strain rates, the onset for strain hardening (deviation from LVE behavior) occurs at smaller Hencky strains with increasing LDPE content. Note that the presence of LDPE at a weight content of just 5% is clearly evident from the strain-hardening behavior witnessed in the tensile stress growth curves of the blends. Comparatively, differences in the linear viscoelastic shear rheology behavior of the polymer blends were only evident for LDPE weight contents greater than 20%.

Table 2 Thermodynamical behavior of LLDPE (LL3001)/LDPE-I (LD200) blends, at 150 °C, as concluded by various methods

	5% LDPE	10% LDPE	20% LDPE	50% LDPE	75% LDPE
DSC	U	U	U	I	I
η_0 vs w	M	M	I	I	I
TTS	M^1	M^1	M^1	I	I
van Gurp-Palmen	M	M	M	I	I
Relax. spectrum	I	I	I	I	I
Cole-Cole	M	M	M	I	I

U: Unable to resolve, *M*: miscible system, *I* immiscible system; M^1 : elasticity enhancement of $G'(\omega)$ observed

Figure 9 contains plots of the tensile stress growth coefficient curves for each blend with a LDPE weight of 1%. Although no strain-hardening behavior is observed with the LDPE-I and LDPE-II blends because of their inherently lower molecular weight, note that significant strain-hardening behavior is clearly evident with the LDPE-III and LDPE-IV blends at high rates of extension, an observation that could not be elucidated from the shear rheology data. It is therefore concluded that the extensional rheology is an extremely sensitive tool to describe and detect subtle macrostructural features in polymer blends.

Activation energy

The presence of LCB in the blend can also be reflected by its effect on the activation energy, E_a (Mark et al. 1986). This is seen in Fig. 10, where the activation energy is plotted as a function of weight fraction of LDPE, for all four systems. The activation energy of each LDPE resin is higher than the energy of the LL3001. The value for LL3001 is 33.5 kJ/mol, a value very typical for LLDPEs, whereas the LDPEs range from 46.6 to 64.9 kJ/mol, values again typical for LDPEs. In general, it can be seen that the activation energy increases monotonically with LDPE concentration in the blend systems with the exception of the blend systems I and IV at composition 75% LDPE that exhibit an activation energy higher than the corresponding value for pure LDPE (existence of maximum). The differences in these values are 9 and 6%, respectively, which might be due to elasticity and in general shear viscosity enhancement due to the presence of the interface (note that the blends are immiscible at these high LDPE compositions). However, as these effects are relatively small (less than 10% for a difference in composition of more than 25%), experimental error might also play a role.

It is noted that the vertical shift factors, b_T, applied to obtain the mastercurves for the various blend systems were small ranging from 0.72 to 1.14, with the higher values corresponding to the blends having higher amounts of

Table 3 Thermodynamical behavior of LLDPE (LL3001)/LDPE-II (EF606A) at 150 °C, as concluded by various methods

	5% LDPE	10% LDPE	20% LDPE	50% LDPE	75% LDPE
DSC	U	U	U	I	I
η_0 vs w	I	I	M	I	I
TTS	M^1	M^1	M^1	I	I
van Gurp–Palmen	M	M	M	I	I
Relax. spectrum	I	I	I	I	I
Cole–Cole	M	M	M	I	I

U: Unable to resolve, *M*: miscible system, *I*: immiscible system, M^1 : elasticity enhancement of $G'(\omega)$ observed

Table 4 Thermodynamical behavior of LLDPE (LL3001)/LDPE-III (662I) at 150 °C, as concluded by various methods

	5% LDPE	10% LDPE	20% LDPE	50% LDPE	75% LDPE
DSC	U	U	U	I	I
η_0 vs w	M	M	M	I	I
TTS	M	M	M	I	I
van Gurp–Palmen	M	M	M	I	I
Relax. spectrum	I	I	I	I	I
Cole–Cole	M	M	M	I	I

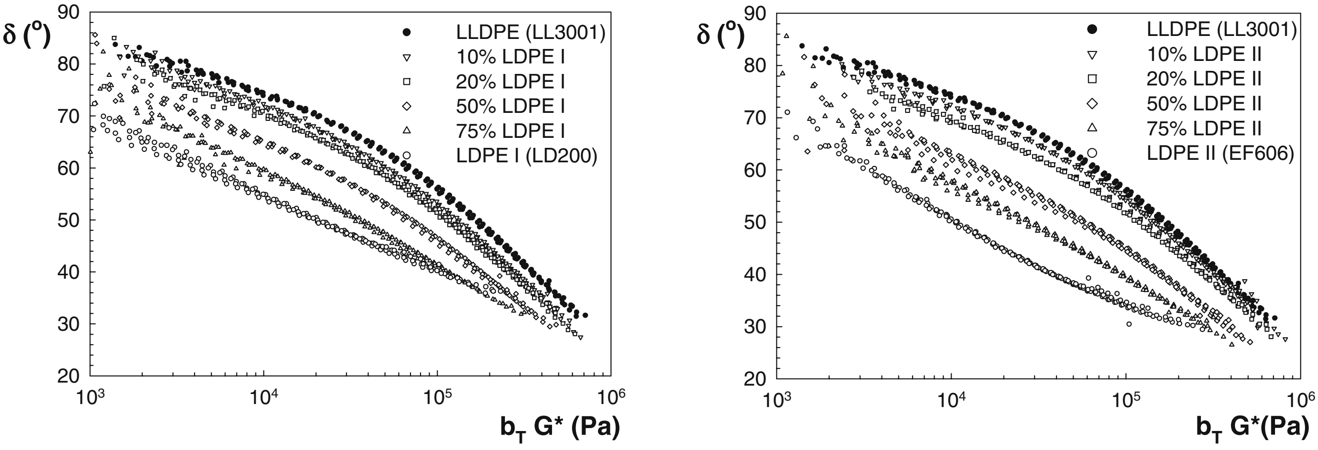
U: Unable to resolve, *M*: miscible system, *I*: immiscible system

LDPE. The corresponding calculated vertical activation energies, E_v, ranged from 1.76 to 8 kJ/mol for the various compositions of all four blend systems with no particular trends worthy of reporting.

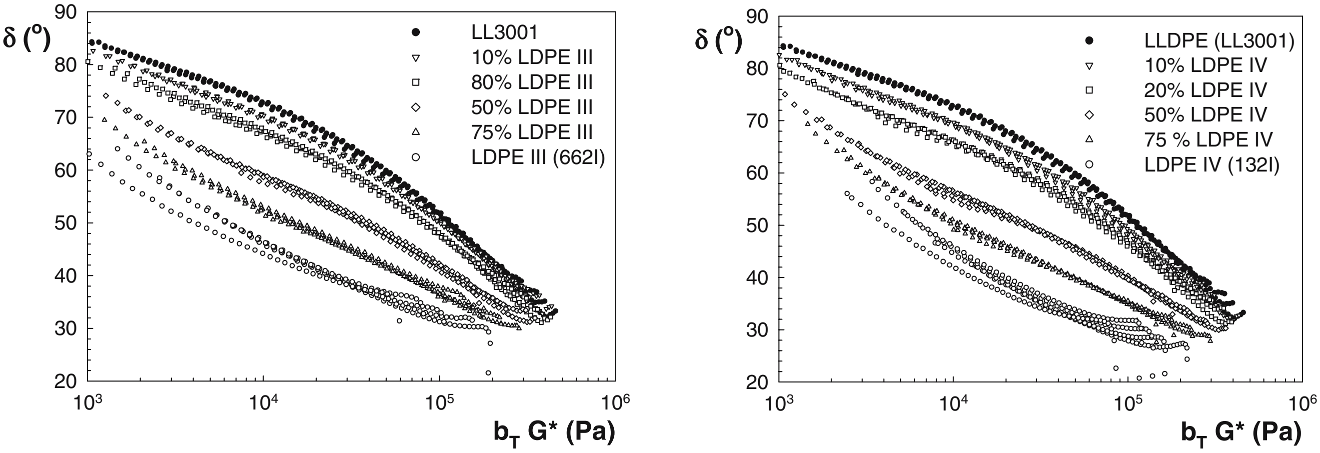
Rheological criteria for miscibility

In this section, several rheological criteria for miscibility will be examined for the various blends systems. First, TTS has already been used as a method to assess miscibility in LLDPE/LDPE blends (Yamaguchi and Abe 1999; Pérez et al. 2005). As discussed before, the blends rich in LDPE composition have shown difficulty in applying the TTS principle. This is an indication of different relaxation times, possibly due to the existence of different phases comprised by linear and branched chains, respectively. In addition, elasticity enhancement for certain blends was observed, pointing to the conclusion that some these blends were immiscible as well (see Tables 2, 3, and 4). A possible third phase exists in these blends composed of chains from both pure components that have the ability to co-crystallize, i.e., high M_w branched chains from LDPE with high M_w of linear chains from LLDPE.

Use of the Van Gurp–Palmen plots has been used in the past to infer miscibility of the blends. These are phase angle ($\delta°$) vs complex modulus ($b_T G^*$) plots. Figure 11a,d depicts such plots for all four sets of blends. First, it is clear that for the pure LL3001, the time–temperature superposition (TTS) is excellent. For low LDPE blend composition (10%), in all the



a LL3001/LDPE I (LD200) **b** LL3001/LDPE II (EF606)

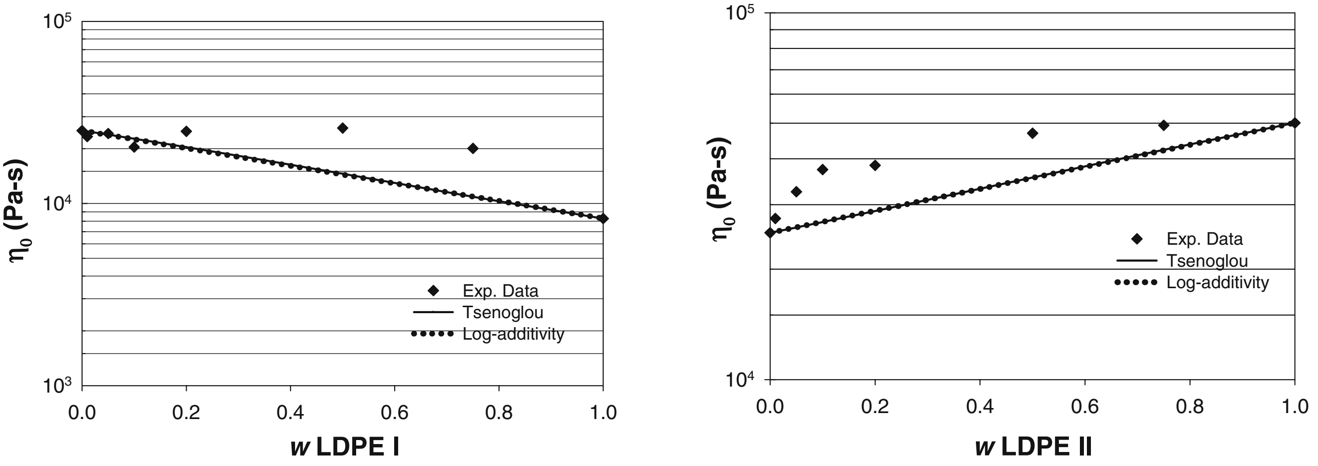


c LL3001/LDPE III (662I) **d** LL3001/LDPE IV (132I)

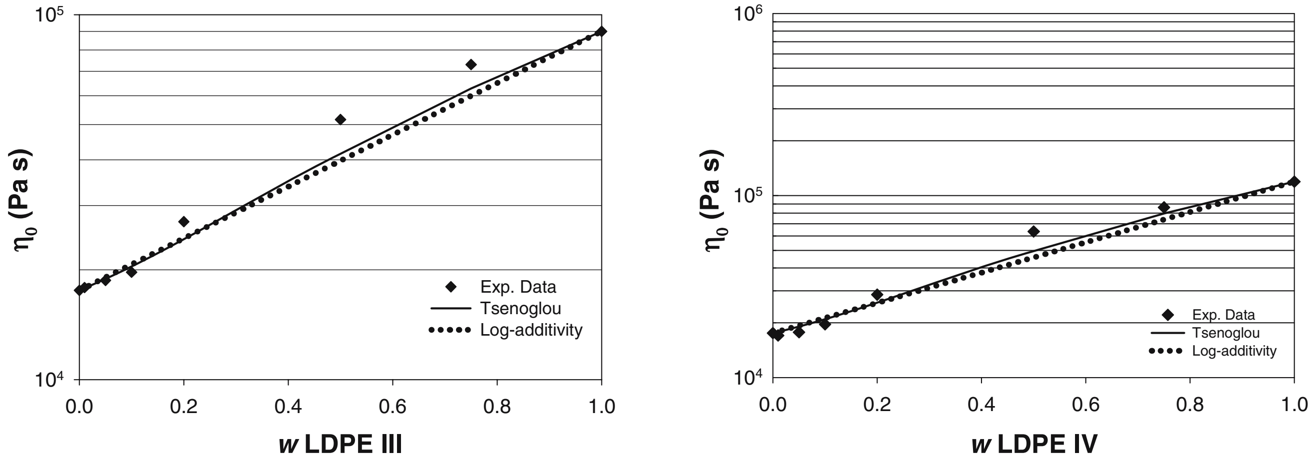
Fig. 11 van Gurp–Palmen plots for all four LLDPE/LDPE blend systems using linear viscoelastic data at 130, 150, 170, 190, and 210 °C blend systems of this study, TTS is obtained. For systems III and IV, failure of superposition was clearly observed at 20% LDPE composition, perhaps due to the higher molecular weights of LDPE III and IV compared to that of LLDPE. For high LDPE composition, i.e., 50 and 75% of LDPE, all blend systems exhibit lack of superposition. Hence, these blends are thermorheologically complex fluids.

Another criterion commonly used to check the miscibility/immiscibility of blends is the zero shear viscosity, logη_0, vs weight fraction plot. The graphs shown in this study compare experimental data of the zero-shear viscosity determined by calculating the parsimonious relaxation spectra of all blends from fitting the linear viscoelastic data (Baumgaertel and Winter 1989; Baumgaertel et al. 1990, 1992). The log-additivity and Tsenoglou mixing rules (Tsenoglou 1988, 1991) are also plotted in Fig. 12. It should be mentioned that as this method uses model predicted rather than measured data, it could be a source of error especially when reliable experimental data is limited to the shear thinning part of the viscosity curve. Positive deviation behavior (PDB) from the log-additivity rule means immiscibility, while the opposite implies miscibility (Utracki 1989). In most cases, positive deviation is clearly observed for LDPE compositions of 20% and higher, which means immiscibility, an observation also drawn from DSC and failure of TTS, as well as from the van Gurp–Palmen plots. Small negative deviation can only be seen at small LDPE concentrations, and perhaps, it is reasonable to assume that at small LDPE compositions, the blends are miscible with LLDPE (also concluded by Lee and Denn 2000). Similar plots at 130, 170, 190, and 210 °C (not shown here) show similar behavior for all blend systems. Positive deviations from the log-additivity mixing rule of blends of linear and branched PP have been recently reported by Stange et al. (2005), also concluding immiscibility of these blends.

Weighted relaxation spectra, $\tau H(\tau)$ as a function of log (τ), were constructed to extract further information on the miscibility of the blends. The relaxation spectrum, $H(\tau)$ was determined by fitting experimental $G'(\omega)$ data, following a numerical differencing procedure developed by Ninomiya

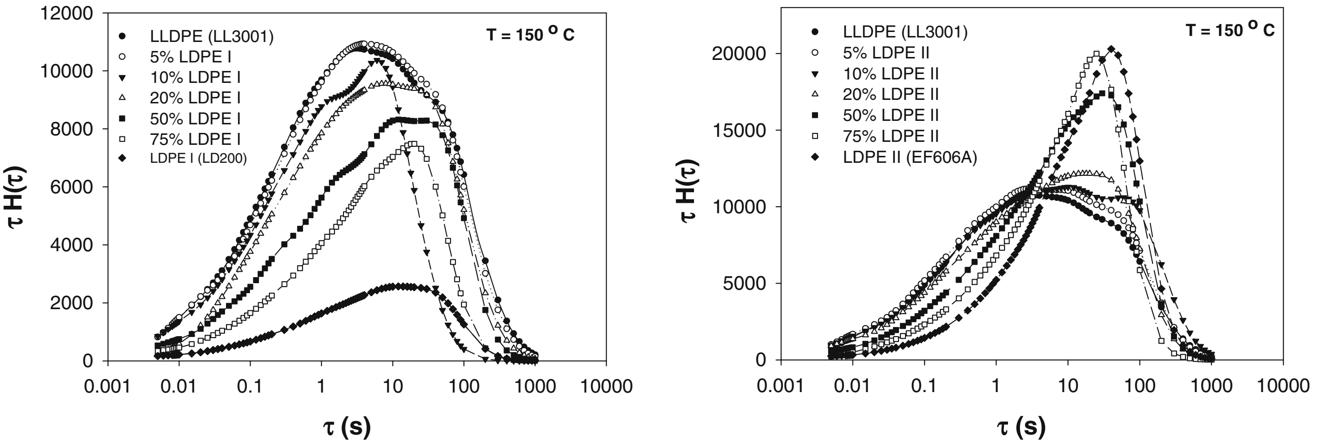


a LL3001/LDPE I (LD200) **b** LL3001/LDPE II (EF606)

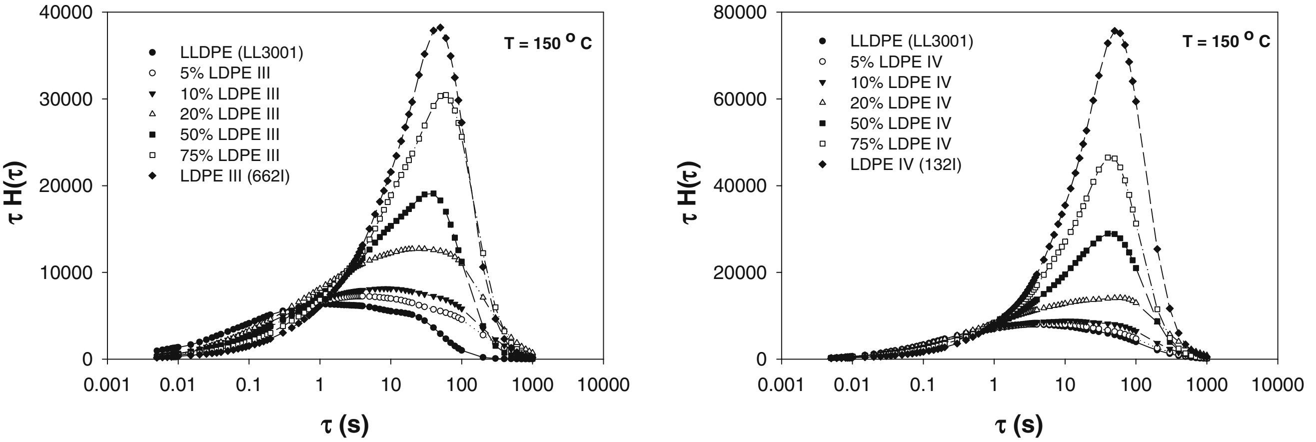


c LL3001/LDPE III (662I) **d** LL3001/LDPE IV (132I)

Fig. 12 Zero shear viscosity, η_o, vs LDPE weight fraction, *w*, for all four LLDPE/LDPE blend systems at 150 °C



a LL3001/LDPE I (LD200) **b** LL3001/LDPE II (EF606)



c LL3001/LDPE III (662I) **d** L3001/LDPE IV (132I)

Fig. 13 Weighted relaxation spectra for all four LLDPE/LDPE blend systems at 150 °C

and Ferry (Ferry 1980). All spectra were calculated from linear viscoelastic data at 150 °C. Figure 13a shows the weighted relaxation spectra of LL3001/LDPE-I (LD200). Pure LLDPE (LL3001) shows a very broad spectrum as well as a "shoulder" at the high M_w end. This is possibly due to phase separation that results from non-uniform branch content distribution previously observed in Ziegler–Natta LLDPE resins (Mirabella and Ford 1987; Mirabella et al. 1988; Schouterden et al. 1987; Karbashevski et al. 1992). On the other hand, weighted relaxation spectrum for LDPE-I (LD200) shows a much smaller peak than LL3001, which is due to their apparent difference in molecular weight. The weighted spectra for 5 and 10% LDPE blends were observed to be identical as that of pure LLDPE, which indicates that the relaxation of the blends is dominated by the major component. For the rest of the blends, with 20, 50, and 75% compositions of LDPE, the distribution of the spectrum is narrower; however, they do not show single peak and smooth peak transitions from one pure component to the other, conditions required for a blend to be considered as miscible as discussed by Gramespacher and Meissner (1992). Thus, based on the weighted relaxation spectra data, all the blends are suggested to be immiscible by this method. Similar conclusions can be drawn for the rest of blends LL3001/LDPE-II (III) (IV).

Finally, Cole–Cole plots, η'' vs η', were constructed for all the blend systems to check for immiscibility. It is said that for a miscible blend, Cole–Cole plots give semicircular relationships of almost identical radii (Utracki 1989; Cho et al. 1998; Kim et al. 2000; Kwag et al. 2000). Cole–Cole plots were constructed for the four blend systems using the reduced

Table 5 Thermodynamical behavior of LLDPE (LL3001)/LDPE-IV (132I) at 150 °C, as concluded by various methods

	5% LDPE	10% LDPE	20% LDPE	50% LDPE	75% LDPE
DSC	U	U	U	I	I
η_0 vs w	M	M	M	I	I
TTS	M	M	M	I	I
van Gurp–Palmen	M	M	M	I	I
Relax. spectrum	I	I	I	I	I
Cole–Cole	M	M	M	I	I

U: Unable to resolve, *M*: miscible system, *I*: immiscible system values of η'' vs η' at all temperatures by applying their respective vertical shift factors $\left({}^{b_T}/_{\alpha_T}\eta',\ {}^{b_T}/_{\alpha_T}\eta\right)$. The Cole–Cole plots for LL3001 gave a semicircle, demonstrating its thermorheological simplicity (also concluded from other rheological methods). On the other hand, Cole–Cole plots for all the LDPE resins did not result in semicircular shapes, suggesting a different signature due to the presence of LCB (thermorheological complexity). Regarding the blends systems, for 1, 5, 10, and 20% LDPE compositions, Cole–Cole plots (not shown here for the sake of simplicity) observed circular relationships, thus suggesting miscible blends. However, for 50 and 75% LDPE compositions, the behavior is similar to the LDPE resin and thus suggesting immiscibility. This was observed to be the case for all four blend systems.

The results of all the methods for examining miscibility are shown in Tables 2, 3, 4, and 5 for the different blend systems: All methods agree that at high LDPE composition, the blends are immiscible. At low LDPE composition, the agreement is only partial among the various methods; most methods appear to indicate a transition from miscibility to immiscibility for all the blend systems studied, and therefore, we can conclude that miscibility at smaller LDPE concentrations exist, which changes to immiscibility at higher LDPE concentrations (essentially higher than 20%). As the failure of TTS might be due to the presence of LCB, TTS is not a good indicator for miscibility unless elasticity enhancement is observed that points immiscibility (blend systems I and II). Overall, it is reasonable to conclude that LDPEE (hexane)–LDPE blends are immiscible at high LDPE concentrations (Lee and Denn 2000).

Conclusions

The rheological effects of LCB was studied using several LDPE resins as pure and as blends with a hexene copolymer of LLDPE by means of linear viscoelastic measurements, i.e., shear thinning and strain hardening in tensile stress growth behavior. While LLDPE essentially follows the LVE of $3\eta^+$, the LLDPE/LDPE blends exhibit clearly strain hardening, which is found to be a function of LDPE concentration; moreover, strain hardening was observed even for some blends with only a 1% LDPE weight fraction for blend with the higher M_w LDPE's. At these low compositions of LDPE, linear viscoelastic experiments in simple shear have shown no effect; hence, the rheological characterization of polymers in uniaxial extension could be used as a very sensitive tool for detecting and describing subtle differences in blend composition and morphology.

DSC thermographs for high LDPE compositions have shown the presence of a third melting peak, possibly due to the existence of a co-crystallization reaction. At low LDPE compositions, the thermographs exhibit a single melting peak suggesting that the LLDPE is dominating the melting, thus yielding inconclusive results with regard to the issue of miscibility.

Several rheological criteria were applied to all blends for assessing polymer miscibility. First, by inspection of viscoelastic moduli mastercurves, failure of TTS was observed for all blends at high LDPE compositions; the same behavior was corroborated with van Gurp–Palmen plots. Therefore, it can be concluded that LCB promotes thermorheologically complex behavior at high compositions of LDPE. Positive deviation behavior (PDB) from log-additivity rule was observed, in the whole range of temperatures, for all blend systems with LDPE compositions in LDPE of 20% and up.

Finally, the broad distribution of the weighted relaxation spectrum in pure LLDPE suggests an inherent and non-homogeneous chain composition and immiscibility for all blends. In general, all blends of hexene–LLDPE were immiscible with amounts of LDPE greater than 20%, regardless of the molecular weight.

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