Elongational Rheology of LLDPE / LDPE Blends

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ABSTRACT: The objective of this study is to investigate the effect of low density polyethylene (LDPE) content in linear low density polyethylene (LLDPE) on the crystallinity and strain hardening of LDPE / LLDPE blends. Three different linear low density polyethylenes (LL-1, LL-2 and LL-3) and low density polyethylenes (LD-1, LD-2 and LD-3) were investigated. Eight blends of LL-1 with 10, 20, 30 and 70 wt % of LD-1 and LD-3, respectively, were prepared using a single screw extruder. The elongational behavior of the blends and their constituents were measured at 150°C using an RME rheometer. For the blends of LL-1 with LD-1, the low shear rate viscosity indicated a synergistic effect over the whole range of concentrations, whereas for the blends of LL-1 with LD-3, a different behavior was observed. For the elongational viscosity behavior, no significant differences were observed for the strain hardening of the 10–30% LDPE blends. Thermal analysis indicated that at concentrations up to 20%, LDPE does not significantly affect the melting and crystallization temperatures of LLDPE blends. In conclusion, the crystallinity and rheological results indicate that 10–20% LDPE is sufficient to provide improved strain hardening in LLDPE. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 88: 3070–3077, 2003

Key words: polyolefins; blends; rheology

INTRODUCTION

The film blowing process is widely used for the manufacturing of polyethylene films in a wide range of applications. Many of these films involve polyolefin blends. In particular, blends of linear low density polyethylene (LLDPE) and low density polyethylene (LDPE) are used because of the good mechanical and optical properties of LLDPE and the stability and processability of LDPE. It is generally recognized that strain hardening during film elongation provides for easier processing and better bubble stability.[1–3] The purpose of this article is to investigate the elongational rheological behavior of different LDPE and LLDPE resins and some of their blends.

In blends of high density polyethylene (HDPE) with LDPE, crystallization and extensional rheology are the most important parameters governing the film formation during processing.[1] Other studies have found that blowability is increased as the resin's molecular weight distribution (MWD) becomes narrower and the degree of long chain branching (LCB) smaller.[2–3] However, these studies also concluded that a resin having lower elongational viscosity tends to give a better blowability and that a more uniform tensile strength in the machine direction (MD) and transverse direction (TD) is achievable with an LLDPE resin than with an LDPE resin. This may be due to the absence of long side chain branching in LLDPE.

Minoshima and White investigated a series of LLDPEs, HDPEs and LDPEs in shear and uniaxial elongation, as well as in film blowing performance.[4–5] Increasing long chain branching and, to a lesser degree, broadening the molecular weight distribution, seemed to enhance the bubble stability during tubular film blowing. Similar results were found in later studies on LDPE, HDPE, and LLDPE film blowing behavior on commercial production lines.[6–7] It was suggested that the bubble stability in film blowing is related to rheological properties, and strain hardening might work as a stabilizing factor. Ghijsels and Ente used the melt strength as an identifier to assess the bubble stability in the film blowing process.[7] Bubble stability was found to increase with melt strength and LDPE was identified as the polyethylene with the highest melt strength for a given shear viscosity. Ghijsels and Ente suggested that the molecular weight and the LCB are the two most important molecular structural factors governing the melt strength, and therefore the blowability of polyethylenes.

Ramesh and Malwitz[8] used a simple rheological technique based on the entrance pressure drop method[9] to obtain a value for the elongational viscosity in order to predict the blowability of new resins. They pointed out that an increased slope in the elongational viscosity versus elongational rate curve, followed by a flat elongational viscosity describes the best conditions for achieving a stable bubble. Micic et al[10] investigated the transient elongational viscosity of LLDPE and its

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blends with 10% and 20% of LDPE at two temperatures. They suggested that the bubble behavior is mostly determined by the strain hardening characteristics of the polymer. Increasing strain hardening characteristics could improve the bubble stability. Shear curves seem to be of limited use in predicting the bubble stability as a function of temperature in film blowing.

Metallocene catalyzed polyethylenes (mPE) are the latest addition to the polyethylene family and have a narrower molecular weight distribution and a more uniform co-monomer distribution than conventional Ziegler-Natta catalyzed polyethylenes. However, as LLDPE, they exhibit less shear-thinning than branched polyethylene and are more difficult to process. In order to overcome these difficulties, mPEs are often blended or coextruded with other polyethylenes.

Beagan et al[11] compared monolayer blended films of mPE and LDPE to three layer coextruded films with mPE in the center and found that incorporation of mPE into an LDPE film will result in an increase in tensile properties both for the monolayer blended film and the three layer coextruded film. They also found that, generally, the coextruded films exhibit higher break strengths than blended films for the same mPE content and that blending of even relatively small amounts of mPE into an LDPE film leads to a significant decrease in crystallinity. Later, they investigated the effect of blending two grades of mPEs with conventional LDPE for use in thin films.[12] They observed that increasing the mPE content in the film improved the mechanical properties.

In other studies on the properties and performance of LDPE / LLDPE blends,[13] positive synergistic effects were observed in melt tension, elongation, Elmendorf tear strength, toughness and initial tear strength of blown film. Castillo and Grossman investigated the addition of LDPE to other polyolefin resins for use in the film blowing process and found that, with the addition of LDPE, film extrusion processability increased, blockiness decreased and tensile strength improved without a decrease in flexibility.[14] At the same time, roughness, elongation and impact resistance increased. These results were interpreted to be the result of higher intermolecular entanglements.

Cho et al. investigated crystallinity and mechanical properties of LLDPE / LDPE, LLDPE / HDPE, and HDPE / LDPE blends.[15] All three blends were miscible in the melt, but the LLDPE / LDPE and HDPE / LDPE blends exhibited two crystallization and melting temperatures, indicating that those blends phase-separated upon cooling from the melt. The melt strength of the blends increased with the increasing molecular weight of the LDPE used. The mechanical properties of the LLDPE / LDPE blend were higher than those calculated from a simple rule of mixtures, while those of the LLDPE / HDPE blend conformed to the rule of mixtures. The properties of HDPE / LDPE were less than those predicted by the rule of mixtures.

In this study, we investigated the rheological behavior of LDPE, LLDPE and some of their blends. We examined elongational rheology, shear rheology and thermal behavior in order to evaluate the effects of co-monomer type and molecular weight (in terms of melt index, MI) on the elongational behavior of LLDPEs and LDPEs, the degree of strain hardening in LLDPE / LDPE blends and the effect of LDPE addition on the crystalline structure of LLDPE.

EXPERIMENTAL

Materials

The polymers used in this study are presented in Table I. Three LLDPEs (LL-1, LL-2 and LL-3) with melt indices between 0.5 and 1 and co-monomers of octene, hexene and butene, respectively, were selected to look at the effect of co-monomer type on their rheology. Three LDPEs (LD-1, LD-2 and LD-3) with similar densities, around 0.924 g/cm^3, and with an increasing melt index, i.e. decreasing molecular weight, were used to investigate the effect of the LDPE molecular weight.

Blending and blends composition

Two series of blends were prepared from LL-1 with LD-1 and LL-1 with LD-3. Their compositions are shown in Table II. The blends were extruded in 1.5 mm thick sheets using a 25 mm single screw extruder operated at 200°C with a screw rotation speed of 80 rpm. Specimens for rheological testing were cut from this sheet and annealed to remove residual stresses.

Rheological measurements

A first set of rheological measurements was carried out in the dynamic mode on a Rheometric Scientific RMS-32 apparatus. Discs of 2.5 cm were tested under the parallel plates configuration at 150°C using a deformation of 15%. Preliminary strain sweeps at this

TABLE I
LLDPE and LDPE Materials Used in this study

Designation	Trade name	Comonomer	Melt flow index (MFI)	Density
		LLDPE		
LL-1	2021D	Octene	1.0	0.920
LL-2	L72113	Hexene	0.5	0.925
LL-3	PFY821	Butene	0.9	0.934
		LDPE		
LD-1	Ld133		0.3	0.924
LD-2	611		0.9	0.924
LD-3	913		2.5	0.923

TABLE II
Blends' Designation and Composition

Blend No.	LLDPE content	LDPE content
1	100% LL-1	
2	100% LL-2	
3	100% LL-3	
4		100% LD-1
5		100% LD-2
6		100% LD-3
7	90% LL-1	10% LD-1
8	80% LL-1	20% LD-1
9	70% LL-1	30% LD-1
10	30% LL-1	70% LD-1
11	90% LL-1	10% LD-3
12	80% LL-1	20% LD-3
13	70% LL-1	30% LD-3
14	30% LL-1	70% LD-3

temperature were performed (although not shown here), and deformation was determined to be well within the linear viscoelastic region. Frequency sweeps from 0.01 to 100 rad/s were performed. The dynamic behavior of the blends was then modeled using the following equation:

$$\eta' = \eta_0[1 + (\omega\tau)^{m1}]^{-m2}$$

Then, this equation was used to obtain the gross relaxation spectrum, used later to determine the linear viscoelastic growth function and the elongational viscosity using the equation below:

Figure 1 Complex viscosity as a function of frequency for the pure resins at 150°C.

Figure 2 Complex viscosity as a function of frequency for LL-1 / LD-1 blends at 150°C.

$$\eta_E^+ = 3\eta_0 \int_{-\infty}^{\infty} H_G [1 - \exp(-\omega\tau)]d\ln\omega$$

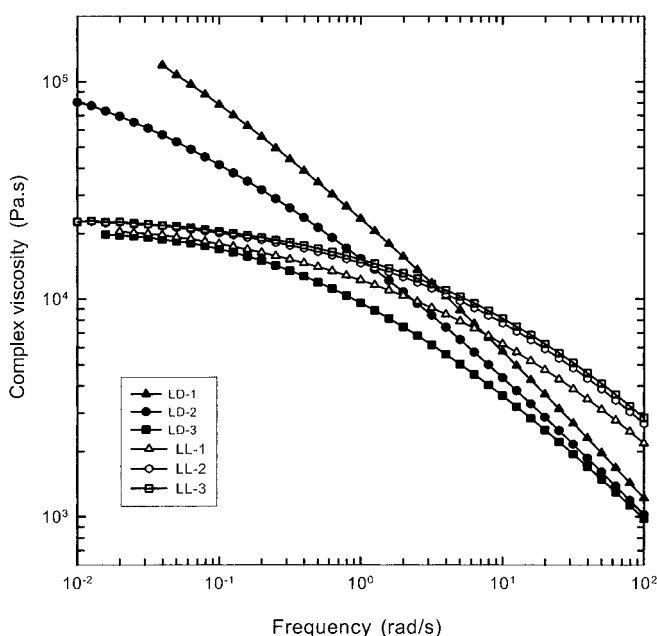Experimental determinations of the linear viscoelastic stress growth in shear, using the cone and plate configurations, were also performed in some cases. In those cases, a cone angle of 0.1°, shear rates between 0.005 and 0.1 s^{-1}, a temperature of 150°C and a diameter of 2.5 cm were used.

Elongational flow measurements were carried out on a Rheometric Scientific RME extensional rheometer. The deformation was uniaxial on strips 1 mm thick, 1.0 cm wide and about 10 cm long, which were initially stress free because of the annealing process. Strain rates from 0.05 to 1.0 sec^{-1} were used at a temperature of 150°C. The maximum Henky strain achieved was about 7.

Thermal analysis of the blends

The crystallinity of the blends was determined using a Perkin-Elmer DSC-7 calorimeter. The samples were heated from 15°C to 200°C at a rate of 10°C/min. They were held for 2 min at 200°C and then cooled to 15°C at 10°C/min. Crystallinity results obtained both during heating and cooling are reported, using a heat of fusion of 280 J/g for fully crystalline polyethylene (PE).

RESULTS AND DISCUSSION

Figure 1 presents the complex viscosity of the resins as a function of frequency at 150°C. As expected, because of their close melt flow indexes, the LLDPEs have similar behavior. The viscosity curves of LL-2 and LL-3 are almost indistinguishable, and LL-1 shows an only slightly lower viscosity. On the other hand, LDPEs show dissimilar behavior, as expected from their different melt flow indexes. LD-1 is the most viscous, and the zero shear viscosity plateau was not reached. LD-2 is slightly less viscous, and the plateau was not reached for it either. LD-3 is even less viscous and has a zero shear viscosity similar to that of the LLDPEs but with a large shift at higher frequencies, which reflects both its molecular weight distribution and likely branching differences.

Figures 2 and 3 show the complex viscosity as a function of frequency, also conducted at 150°C, for the LL-1 / LD-1 blend and the LL-1 / LD-3 blend, respectively. The addition of LD-1 to LL-1 significantly increases the viscosity of LL-1 because of LD-1's higher viscosity. The reverse is observed in LD-3 blends, which are slightly less viscous than the LLDPE. In order to quantify any synergistic effect, viscosity was plotted as a function of composition in LL-1 and is shown in Figures 4 (a) and (b). The LL-1 / LD-3 blend shows positive deviation from a simple log-additive mixing rule for the whole composition range, whereas the LL-1 / LD-1 viscosity curve is much closer to
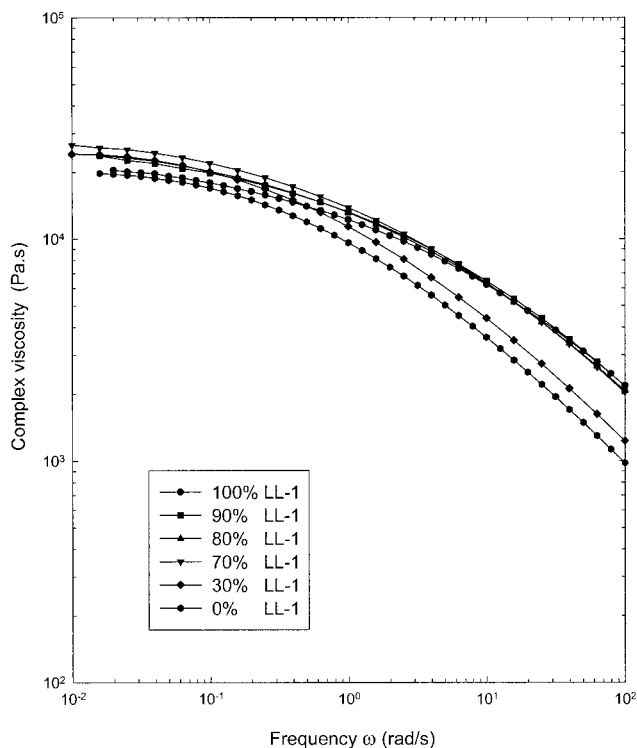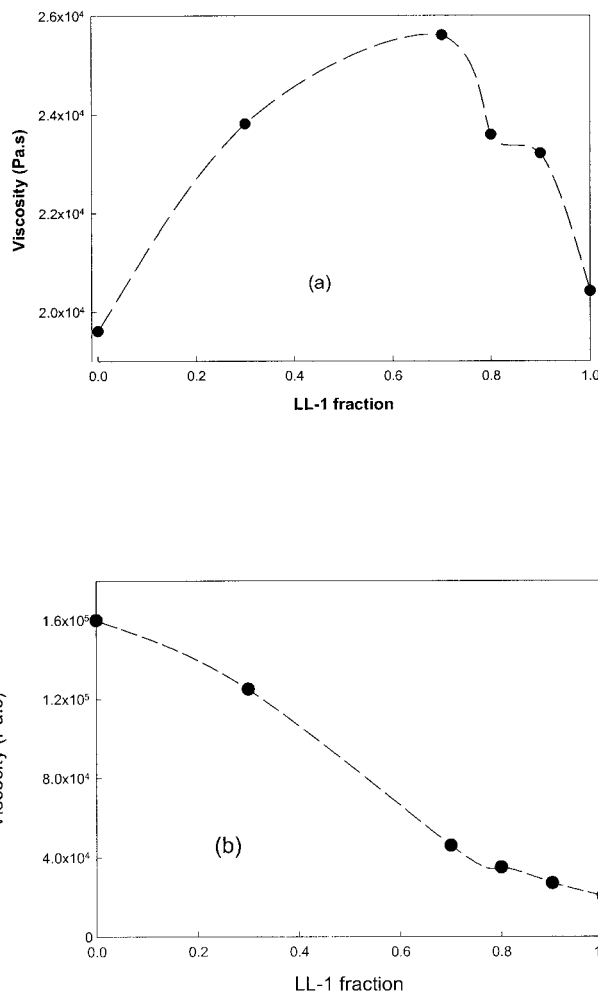

Figure 4 Viscosity as a function of LL-1 content at a frequency of 0.02 s^{-1} for: (a) LL-1 / LD-3 blends and (b) LL-1 / LD-1 blends.

additivity for the chosen frequency. In LL1 / LD-3 blends, the maximum deviation is around 30% at an LL-1 fraction of 70 wt %. This suggests that the molecular weights of the resins can play a role in the type of behavior that can be observed, possibly by preventing complete miscibility in the melt state for the mismatched viscosity blends. The presence of a blend interface modifies the relaxation spectrum of the polymer melt and can result in the presence of a shoulder in the storage modulus of the blends at low frequency. In the case of immiscible polyolefin blends, the interfacial tension is so low that this effect is difficult to observe. In fact, no storage modulus (G') plateau or shoulder was observed for these blends, as shown in Figure 5.

The elongational rheology of the LLDPE resins is presented in Figure 6. The curves for LL-2 and LL-3 are shifted for the sake of clarity (one decade for LL-2 and two decades for LL-3). At strain rates below 0.3 s^{-1}, no strain hardening was observed. It is well known that strain hardening depends mostly on short chain

Figure 3 Complex viscosity as a function of frequency for LL-1 / LD-3 blends at 150°C.
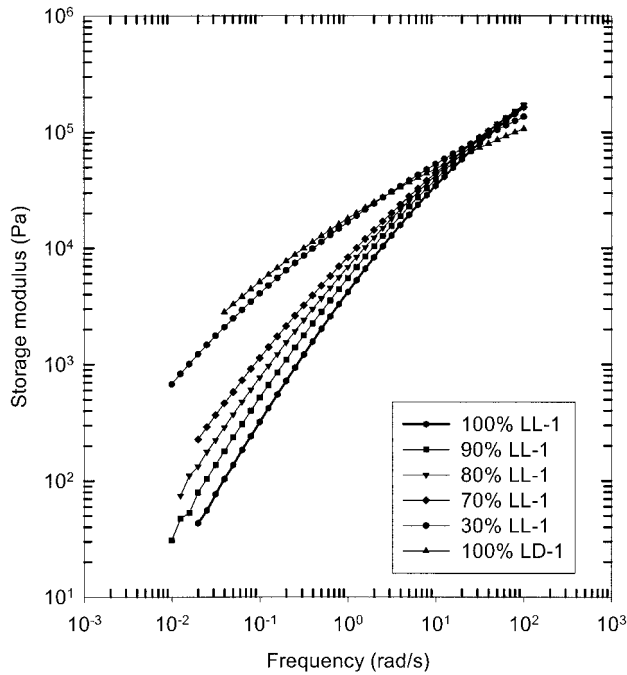
Figure 5 Storage modulus as a function of frequency for LL-1 / LD-1 blends at 150°C.

branches.[1–3,6,7] The longer they are, the more strain hardening observed.[6,7] LL-1 shows the most strain hardening, as expected from the longer side-branches obtained with the octene co-monomer. Figure 7 shows
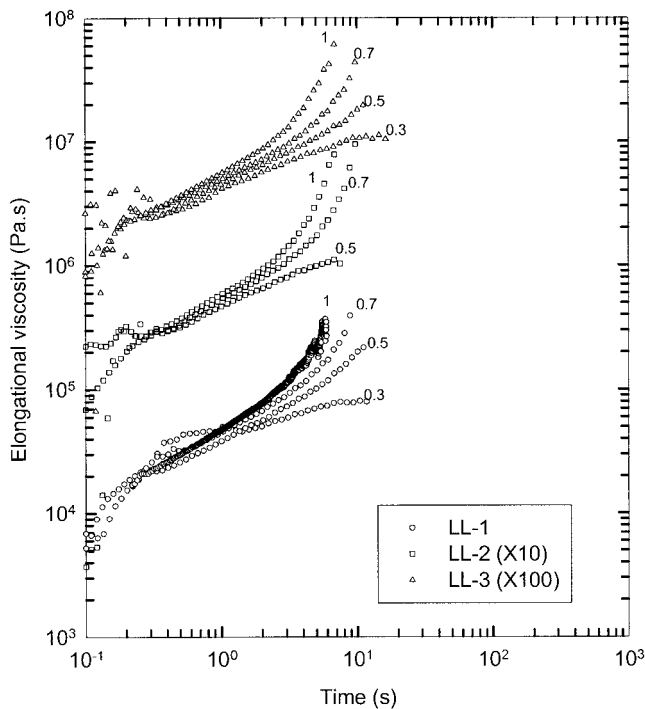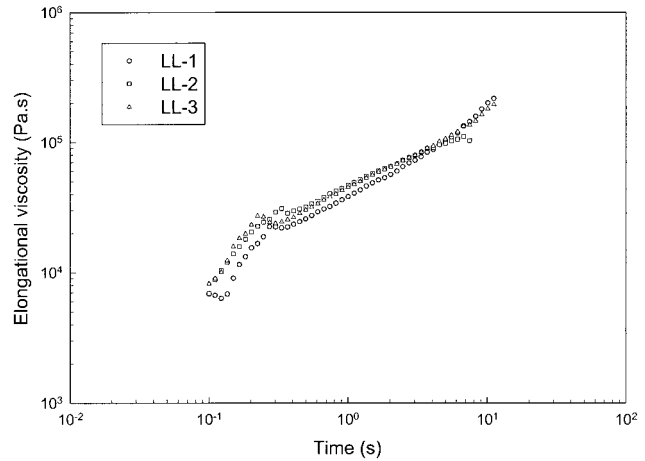

Figure 7 Comparison of the elongational viscosity of the LLDPE materials at 150°C and a strain rate of 0.5 s^{-1}.

a comparison of the three LLDPEs at a strain rate of 0.5 s^{-1}.

Figure 8 shows a plot of elongational viscosity as a function of time for the LDPE resins. The curves for LD-2 and LD-3 are also shifted for the sake of clarity. Strain hardening occurs much faster and the viscosity increase is much higher compared to LLDPE resins. For LD-1, strain hardening was observed starting at strain rates of 0.03 s^{-1} (possibly lower, which would be impossible to measure because of transducer sen-

Figure 6 Elongational viscosity of LLDPE resins at 150°C for different strain rates. The curves for LL-2 and LL-3 are shifted vertically by factors of 10 and 100, respectively.
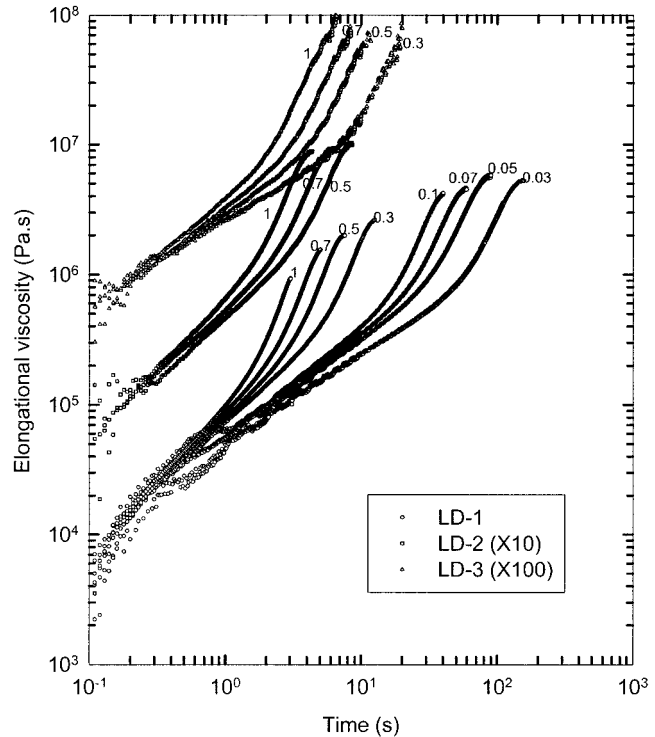

Figure 8 Elongational viscosity of LDPE resins at 150°C for different strain rates. The curves for LD-2 and LD-3 are shifted vertically by factors of 10 and 100, respectively.
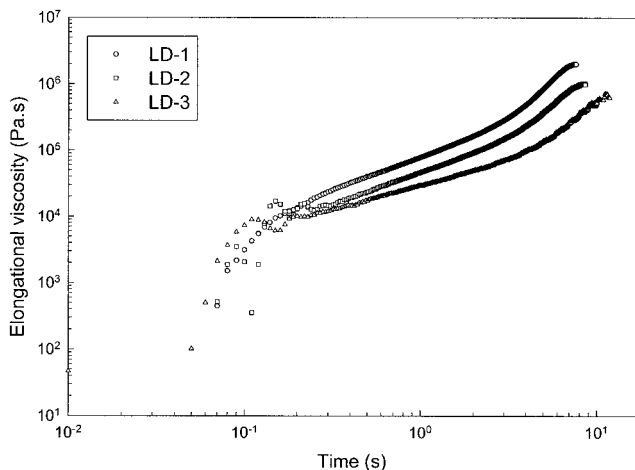
Figure 9 Comparison of the elongational viscosity of the LDPE materials at 150°C for a strain rate of 0.5 s^{-1}.

sitivity limitations). Figure 9 compares the three LDPEs at the same strain rate of 0.5 s^{-1}. The strain hardening is most significant for the low melt index LD-1, as expected from its higher molecular weight.

Figure 10 presents the elongational viscosity of the LL-1 / LD-1 90 / 10 blend at different strain rates in addition to stress growth results obtained from shear and dynamic data, as described in the experimental section. Strain hardening occurred starting at a strain rate of 0.1 s^{-1} (possibly lower, but as above, impos-
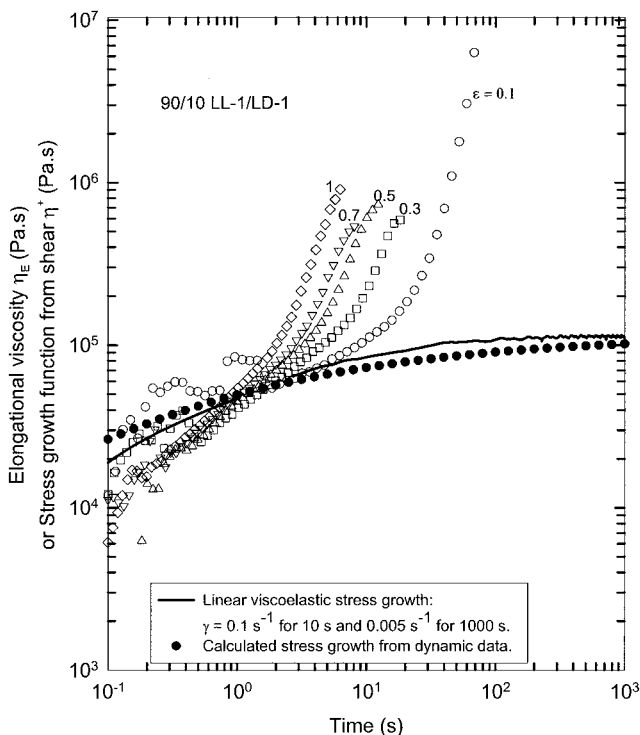

Figure 10 Elongational viscosity and stress growth function of a 90 / 10 LL-1 / LD-1 blend at 150°C for different strain rates.
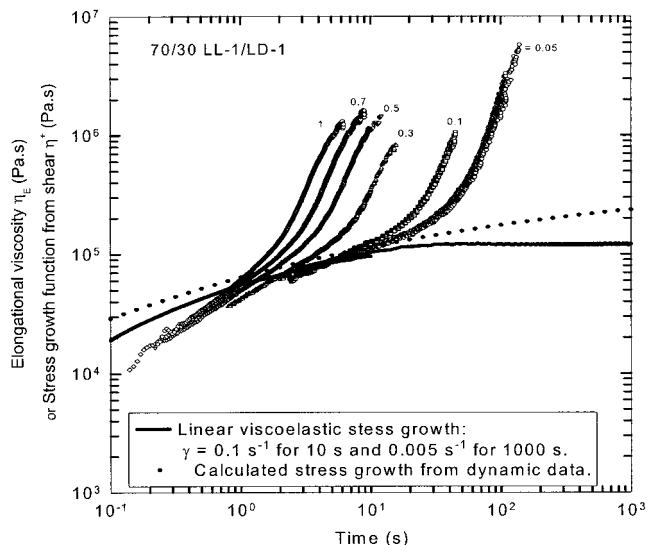

Figure 11 Elongational viscosity and stress growth function of a 70 / 30 LL-1 / LD-1 blend at 150°C for different strain rates.

sible to measure because of transducer sensitivity limitations). The envelope for the linear viscoelastic response is similar for all the data except at very short times and high strain rates, which may be due to an artifact in the time response of the transducer and the actual strain rate applied at those times. This study clearly suggests that the addition of as little as 10% LD-1 to LL-1 significantly improves its stress hardening, which usually translates into improved processability in the film blowing process.

When larger amounts of LD-1 are added, such as 30 wt %, an even earlier strain hardening is observed, as shown in Figure 11 for the 70 / 30 LL-1 / LD-1 blend. However, the envelope for the linear viscoelastic response is significantly different for the different measurements, which may be due to the fact that the deformation rates used for the shear and dynamic data were not in the linear viscoelastic region, as can be observed in the dynamic data shown in Figure 2. The differences from the 10 wt % blend are not large, apart from the earlier mentioned strain hardening (at 0.05 s^{-1} for the 30% blend instead of 0.1 s^{-1} for the 10%).

Figure 12 presents the elongational viscosity for the different blend compositions of the LL-1 / LD-1 blend. The addition of only 10% of LD-1 to the linear material increases the strain hardening significantly. Further increasing the LD-1 concentration up to 30 wt % produces a slightly earlier strain hardening (at 0.05 s^{-1} for the 30% blend instead of 0.1 s^{-1} for the 10%) and a higher strain hardening, but most of the strain hardening gain is already observed at the 10 wt % level.

Similar experiments were conducted using LL-1 / LD-3 blends. LD-3 shows less strain hardening than
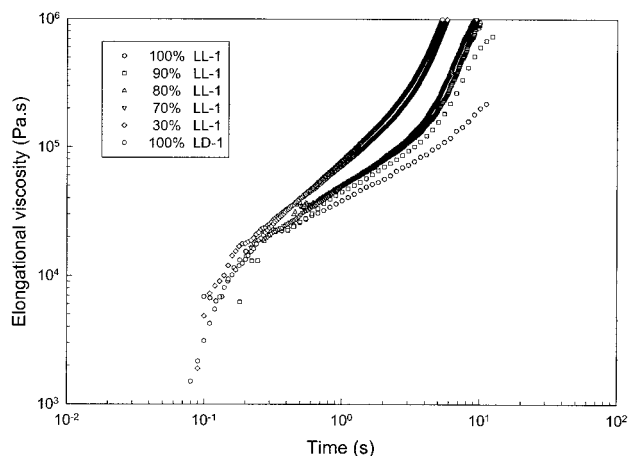
Figure 12 Elongational viscosity of LL-1 / LD-1 blends at 150°C and a strain rate of 0.5 s^{-1} for different compositions.

(a)

LD-1 and has a shear viscosity close to that of LL-1. The results are presented in Figure 13 for a strain rate of 0.5 s^{-1}. Observations similar to the previous system can be made, but with a less pronounced strain hardening.

Finally, the elongational viscosities were plotted as a function of LL-1 composition at a total deformation of 2.5 for the strain rates of 0.5 and 1 s^{-1}, shown in Figures 14 (a) and (b) for LD-1 and LD-3 blends, respectively. Data are close to compliance with the additivity rule, with a small positive deviation in particular for the LL-1 / LD3 blends.

From the above results, it is clear that addition of LDPE to LLDPE improves its strain hardening behavior, which usually translates into better processability in the film blowing process. Furthermore, it was observed that approximately 10% LDPE addition is sufficient for a significant change in the elongational behavior of LLDPE. A question that may rise at this stage
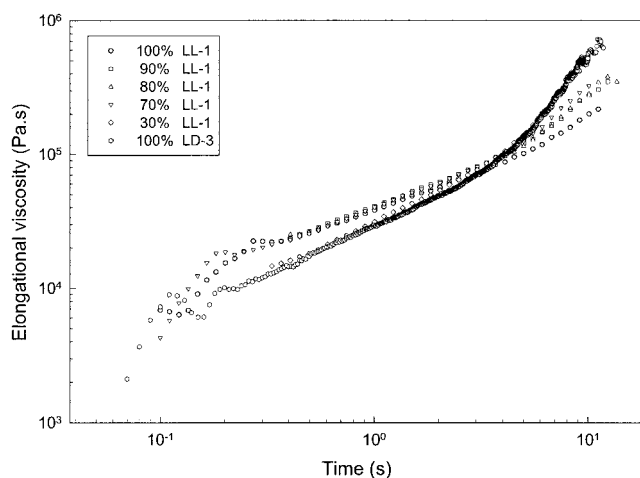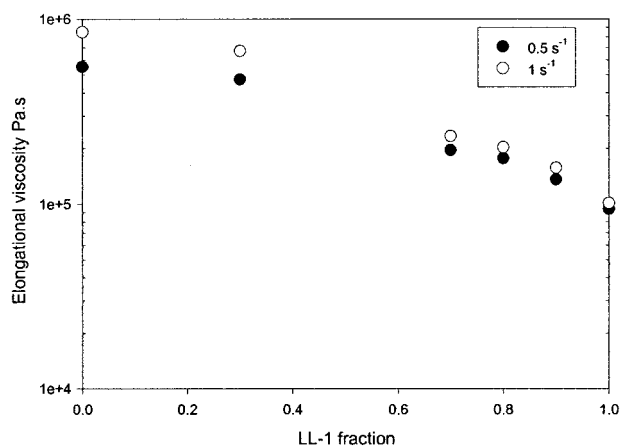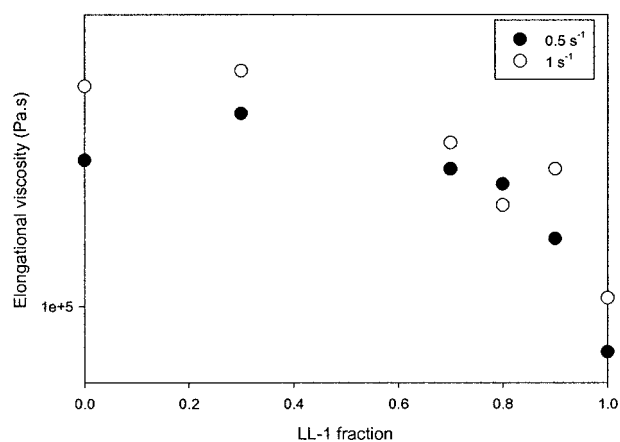

(b)

Figure 14 Elongational viscosity of the blends at 150°C as a function of LL-1 content. The total deformation was 2.5 and the strain rates were 0.5 and 1 s^{-1}. (a) LD-1 / LL-1 blends, (b) LD-3 / LL-1 blends.

is the effect of this addition on the structure and hence the properties of the LLDPE.

LLDPE is used generally because of its better properties in terms of strength, clarity and tear compared to LDPE. In order determine any structural changes in the blends, the melting and crystallization behavior of the pure materials and of the blends were investigated. Table III presents the thermal analysis results obtained for the pure resins and their blends. The melting peak temperature of the blends is for the most part similar to that of LLDPE for the 10 and 20% LDPE

Figure 13 Elongational viscosity of LL-1 / LD-3 blends at 150°C and a strain rate of 0.5 s^{-1} for different compositions.

TABLE III
Thermal Analysis Results of LLDPE/LDPE Materials and Blends

Sample	Tm (Peak) melting-heating mode (°C)	Heat of fusion (J/g)	% Crystallinity heating mode (%)	Tc (Peak) crystallinity cooling mode (°C)	Heat of crystallinity cooling mode (%)	Crystallinity cooling mode (%)
LL-1	123.3	135.1	48.3	106.4	136.9	48.9
LL-2	126.0	149.3	53.3	111.6	166.6	59.5
LL-3	122.7	120.1	42.9	108.1	146.5	52.3
LD-1	112.6	120.5	43.0	99.1	150.8	53.9
LD-2	114.5	134.1	47.9	98.8	163.1	58.3
LD-3	114.5	126.3	45.1	98.2	157.5	56.3
LL-1-/LD-1 90/10	122.9	112.9	40.3	108.4	162.3	58.0
LL-1/LD-1 80/20	122.8	122.1	43.6	108.6	149.1	53.3
LL-1/LD-1 70/30	114.6	117.1	41.8	108.3	138.2	49.4
LL-1/LD-1 30/70	112.5	124.2	44.4	98.6	135.9	48.5
LL-1/LD-3 90/10	122.7	119.2	42.6	106.4	143.5	51.3
LL-1/LD-3 80/20	121.7	124.4	44.4	105.8	149.4	53.4
LL-1/LD-3 70/30	116.8	125.5	44.8	105.3	141.7	50.6
LL-1/LD-3 30/70	114.8	121.3	43.3	101.1	145.0	51.8

blends. The crystallization peak temperature upon cooling from the melt in the DSC is almost the same for pure LLDPE and for its 10, 20 and 30% blends with LDPE. For crystalline content, no significant difference between the pure materials and the blends can be outlined from the data obtained.

CONCLUSIONS

A small amount of LDPE enhances the strain hardening of LLDPE resins. In the range of 10–30% of LDPE in LLDPE, no significant differences are observed in the strain hardening of the blends; thus, to take advantage of the improved strain hardening behavior of the blend, 10–20% of LDPE should be sufficient from a rheological perspective. The melting and crystallization temperatures of the blends are not significantly affected by LDPE concentrations below 20 wt %.

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