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Influence of Composition Distribution and Branch Content on the Miscibility of m-LLDPE and HDPE Blends: Rheological Investigation[†]

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ABSTRACT: The miscibility of metallocene linear low-density polyethylene (m-LLDPE) and Ziegler−Natta LLDPE (ZN-LLDPE) with linear high-density polyethylene (HDPE) was studied. The influences of composition distribution (CD) and branch content (BC) on the miscibility of m-LLDPE and ZN-LLDPE with HDPE were investigated with rheological methods. The m-LLDPEs (BC = 13.2 CH_3/1000 C) and ZN-LLDPE (BC = 14.5 CH_3/1000 C) of similar molecular weights were paired to study one molecular variable at a time. Melt blending was carried out in a Haake PolyDrive at 190 °C in the presence of 1000 ppm of antioxidants. Dynamic and steady shear measurements were performed in a Rheometrics ARES at 190 °C. The miscibilities of blends were revealed by the dependence of their η_o, η', N_1 and G' on blend composition and from predictions of rheological models. The CD was found to have no effect on the miscibility of low-BC ZN-LLDPE and m-LLDPE blends with linear HDPE, and both blends were miscible at all compositions. Increasing the branch content (BC = 42.0 CH_3/1000 C) resulted in an increased immiscibility of m-LLDPE-rich blends with linear HDPE. The rheology of immiscible blends suggests a layered morphology and agreement with Bousmina−Palierne−Utracki's and Lin's models was obtained with slip parameters $k = 2.85 \times 10^{-5}$ and $\lambda = 0.72$, respectively.

1. Introduction

In general, high-density polyethylene (HDPE) is used for applications that require stiff products, and linear low-density polyethylene (LLDPE) is usually blended to improve flexibility.[1] Also, LLDPE is blended in small amounts (5−10 wt %) to reduce extruder back-pressure and increase output.[2] The miscibility of LLDPE and HDPE blends has received wide attention in the literature.[3−6] The Hill's group used mainly transmission electron microscopy (TEM) and differential scanning calorimetry (DSC), while the Graessley, Wignall, and Alamo group employed small-angle neutron scattering (SANS). The TEM and SANS groups suggest that blends of LLDPE and HDPE were miscible if the branch content of LLDPE is < 40 CH_3/1000 C. Also, Lee and Denn[7] studied the miscibility of LLDPE in HDPE by rheological methods and concluded that the studied system was miscible. The branch content of the LLDPE used in that study was < 40 CH_3/1000 C. Other techniques[8,9] have also been used, and miscibility was suggested.

Unfortunately, most of the previous studies on the miscibility of LLDPE/HDPE blends made use of Ziegler−Natta (ZN) LLDPEs. In addition to its heterogeneity in size, ZN-LLDPE is known for its structural heterogeneity ranging from linear to highly branched chains with branches randomly distributed on the chain.[10−12] The diversity of composition, molecular structure, molecular weight (M_w), and molecular weight distribution (MWD) has a strong influence on miscibility of PE/PE blends.[3−6,13] Further, the details of the molecular structure are becoming more important in view of the immiscibility of LLDPE/LLDPE systems and suggested or suspected liquid−liquid-phase separation in ‘pure’ LLDPE.[14−18] LLDPE produced by a single-site metallocene catalyst (m-LLDPE) is now available with more even distribution of branching and a narrower MWD.

Recently, Tanem and Stori[19,20] used TEM and DSC to investigate the miscibility of m-LLDPE (BC = 14;20 CH_3/1000 C) and linear polyethylene blends and their results indicated phase separation in butene LLDPE-rich blends up to 210 °C. It was found that M_w had strong influence on miscibility (see Figure 10 of ref 19). Also, Lee and co-workers[9] used SEM, DSC, and mechanical testing to study the miscibility of ZN-LLDPE and m-LLDPE in HDPE. They concluded that ZN-LLDPE/HDPE are more miscible than m-LLDPE/HDPE blends. However, Hill and Barham[21] suggested no influence for the catalyst type (ZN vs metallocene) on the miscibility of LLDPE and HDPE. On the other side, blends of different M_w fractions of HDPE/HDPE and LDPE/LDPE were observed to be miscible and the viscosity, η, vs composition, ϕ, relationship followed the log-additivity ($\eta = \sum\phi_i \log \eta_i$) rule.[22−24]

Because of emulsion morphology, phase separation causes the storage and loss moduli G' and G'' to exceed values for the matrix phase. Even in a mixture of two Newtonian liquids, the emulsion morphology gives rise to a nonzero G'. That is, their emulsion exhibits elastic behavior due to interfacial tension[25−28] and viscosity vs composition show positive deviation behavior (PDB). However, miscible systems are expected to follow linear additivity ($\eta=\sum\phi_i\eta_i$) or log additivity[13] with smooth variation of rheological properties as functions of composition.[29]

Also, immiscibility can lead to negative deviation behavior (NDB), which is believed to be a result of interlayer slip,[13] which was first observed for low-M_w liquids by the fluidity-additivity equation[30]

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$$\frac{1}{\eta} = \frac{\phi_1}{\eta_1} + \frac{\phi_2}{\eta_2} \tag{1}$$

where η is the viscosity of the blend and η_1 and η_2 are the viscosities of the pure components. For polymeric liquids, Lin[31] introduced a slip parameter, λ, to account for the NDB rheology:

$$\frac{1}{\eta} = [1 + \lambda(\phi_1\phi_2)^{0.5}]\left[\frac{\phi_1}{\eta_1} + \frac{\phi_2}{\eta_2}\right] \tag{2}$$

Recently, Bousmina−Palierne−Utracki[32] (BPU) derived another expression that predicts slip in layered morphology

$$\frac{1}{\eta} = \frac{\phi_1}{\eta_1} + \frac{\phi_2}{\eta_2} + k(\phi_1\phi_2)^{0.5} \tag{3}$$

where k is the slip parameter, and it is related to the number of layers. The above literature review introduces different deductions about the miscibility of LLDPE and HDPE blends. However, the effects of branch content (BC) and composition distribution (CD) on the miscibility of LLDPE/HDPE blends are yet to be explored by rheological tools. Here, the matrix of resins used as blend components was designed to study one variable at a time. Two LLDPE resins of comparable molecular weight (one ZN-LLDPE and one m-LLDPE) and HDPE were selected to study the effect of CD. Both ZN-LLDPE and m-LLDPE were blended with the same HDPE. The two resins were selected in a way that other molecular parameters such as M_w, BC, and MWD remain very close to each other. Hence, the CD will be the *only* molecular parameter that is varied. To study the effect of BC, two m-LLDPEs of the same M_w and MWD and of different densities (BC) were blended with the same HDPE, and results were compared for the effect of BC. This approach that isolates the effect of other molecular variables was not followed in most of the previous studies.

2. Experimental Section

2.1. Materials. Three commercial samples of butene LLDPE and one HDPE were used in this study. Two of the LLDPEs were metallocene resins of different branch contents (density) and the third is a Ziegler−Natta product. All samples were ExxonMobil products. Table 1 provides characterization data such as density at room temperature, melt index (MI) at 190 °C as provided by ExxonMobil. Details about the GPC and NMR characterization were given in a recent publication.[33] The number-average (M_n) and weight-average (M_w) molecular weights were obtained by GPC using a GPC2000 from WATERS. The resins with low and high BC were labeled as m-LLDPE1 and m-LLDPE2, respectively. The same HDPE was used in all of these blends. The effect of BC of LLDPE on the miscibility was investigated by studying m-LLDPE1/HDPE and m-LLDPE2/HDPE systems. Results from the low-BC pair (m-LLDPE1/HDPE) were compared to those of the high-BC pair (m-LLDPE2/HDPE). Resins m-LLDPE1 (BC = 14.5 CH_3/1000 C) and m-LLDPE2 (BC = 42.0 CH_3/1000 C) were selected in a way that branch content would be the *only* molecular parameter in this comparison. As given in Table 1, m-LLDPE1 and m-LLDPE2 have about the same M_w and MWD. Also, both resins were butene-based and made by metallocene Exact technology, and hence, composition distributions are expected to be similar. Hence, comparison of m-LLDPE1 and m-LLDPE2 blends with HDPE will disclose the effect of BC on the miscibility of m-LLDPE/HDPE blends. On the other hand, ZN-LLDPE was chosen to have about the same molecular parameters (M_w or MI, MWD, density or BC) as m-LLDPE1. Comparison of ZN-LLDPE and m-LLDPE1 blends with HDPE would reveal the influence of composition distribution on the miscibility of LLDPE/HDPE blends. The HDPE used in all of these blends has a density higher than 0.960 and hence should have no branches.[34]

Table 1. Characterization of Resins

resin	density, g/cm^3	MI, g/10 min	M_n, kg/mol	M_w, kg/mol	MWD	branch content, CH_3/1000 C
ZN-LLDPE	0.9180	1.0	39	118	3.1	13.2
m-LLDPE1	0.9100	1.2	55	108	2.0	14.5
m-LLDPE2	0.8800	0.80	69.4	125	1.8	42.0
HDPE	0.9610	0.70	15.2	102	6.7	0

2.2. Melt Conditioning and Sample Preparation. The HDPE and LLDPE resins used in this study were conditioned (or blended) in a Haake PolyDrive melt blender for 10 min at 190 °C and 50 rpm. Pure resins as well as blends of 10, 30, 50, 70, and 90% LLDPE were all conditioned in the presence of 1000 ppm of additional antioxidant (AO) to avoid degradation. Test for degradation during melt blending was performed for all pure resins. The rheology of as-received resins was compared to the rheology of the same sample conditioned at 190 °C in the presence of extra AO.[33] For example, dynamic viscosity, η', and elastic modulus, G', were obtained as a function of frequency, ω, for sample ZN-LLDPE. Results for η' and G' for the "pure" ZN-LLDPE are shown in Figure 1a. Excellent reproducibility of data for conditioned and as-received resin indicates prevention of degradation during melt blending and conservation of both viscous and elastic nature of the melt as discussed in the previous study of Hussein et al.[35] All PE samples obtained from melt blender were molded in a Carver press. Details of the molding procedure were given elsewhere.[36] The PE disk was then inserted between the rheometer platens.

2.3. Measurements in ARES. All tests were carried out using a cone-and-plate fixture; the cone angle was 0.1 rad, and the platen diameter was 25 mm. Sample loading and testing procedures were the same as those discussed in one of the author's previous work[35] on Rheometrics Mechanical spectrometer (RMS 800). Strain amplitude, $\gamma°$, of 15% was selected for all polymers used in this study. As suggested earlier by Hussein et al.,[35] a check for degradation and reproducibility of rheological measurements *should* use samples prepared from different batches. Hence, samples of a 50/50 blend of ZN-LLDPE with HDPE were obtained from different batches following melt blending at the same conditions. Results for η' and G' on these samples are shown in Figure 1b. In both cases, extra AO was added. The agreement of data shows the excellent reproducibility of the rheological measurements.

In all measurements, fresh samples were always used. Steady-shear tests began at the lowest shear rate (usually $\dot{\gamma}$ = 0.01 s^{-1}) and continued up to 5 s^{-1} to avoid the known hydrodynamic instabilities caused by secondary flow, which leads to radial ejection of the sample.[37] The details of steady shear measurements of $\eta(\dot{\gamma})$, first normal stress difference, $N_1(\dot{\gamma})$, and $N_1(t)$ were given in a recent publication.[33]

3. Results and Discussion

3.1. Effect of Composition Distribution on the Miscibility of LLDPEs in HDPE. The effect of composition distribution on the miscibility of LLDPE and HDPE was studied by blending one ZN-LLDPE and one m-LLDPE with the same HDPE. As shown in Table 1 the two resins have about the same M_w, BC, and MWD, and the CD is the only molecular variable in this comparison. For blends of m-LLDPE1 with HDPE the dynamic shear data was measured and results for $\eta'(\omega)$ and $G'(\omega)$ are given in Figure 2. Data were shown

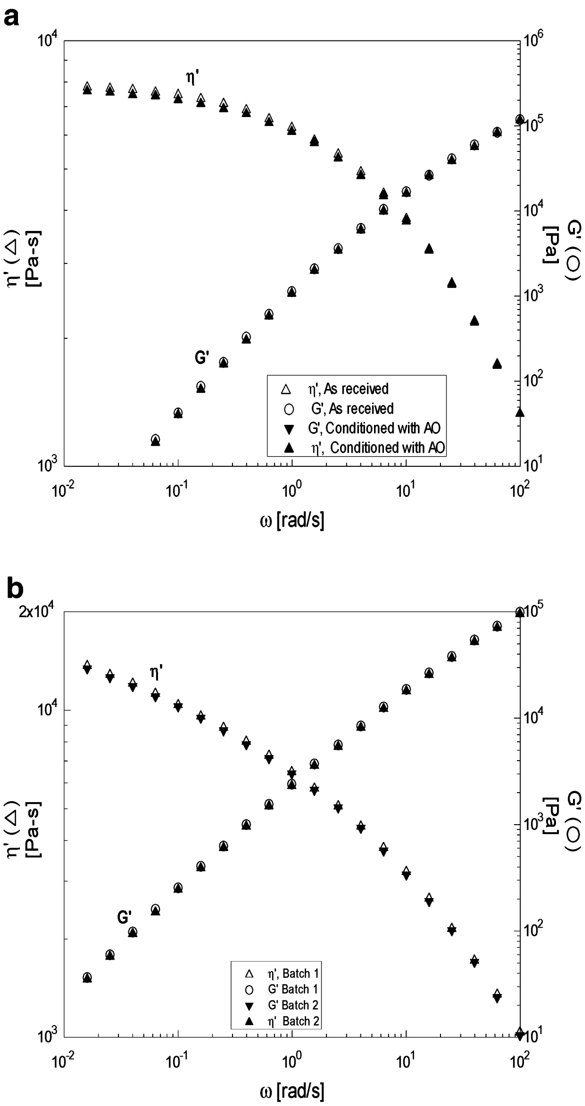

Figure 1. (a) Comparison of the rheology of as-received and conditioned ZN-LLDPE (T_{mix} = 190 °C, T_{test} = 190 °C, $\gamma°$ = 15%). (b) $\eta'(\omega)$ and $G'(\omega)$ for 50% ZN-LLDPE blend with HDPE (T_{mix} = 190 °C, T_{test} = 190 °C, $\gamma°$ = 15%).

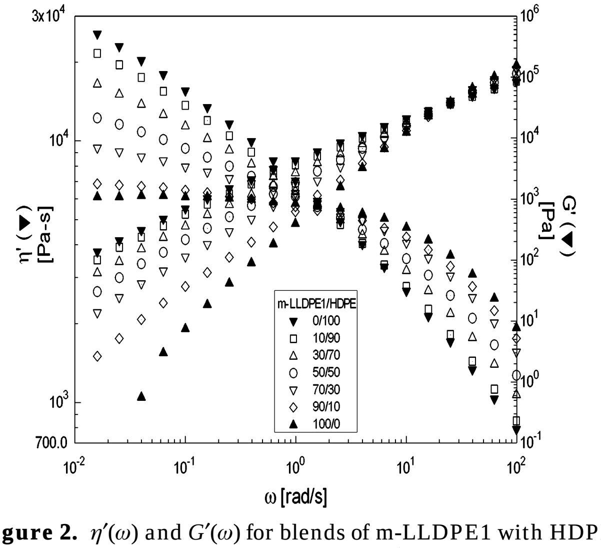

Figure 2. $\eta'(\omega)$ and $G'(\omega)$ for blends of m-LLDPE1 with HDPE (T_{mix} = 190 °C, T_{test} = 190 °C, $\gamma°$ = 15%).

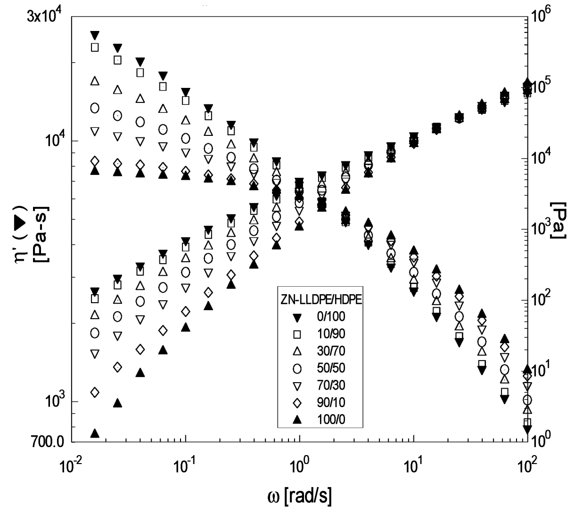

Figure 3. $\eta'(\omega)$ and $G'(\omega)$ for blends of ZN-LLDPE with HDPE (T_{mix} = 190 °C, T_{test} = 190 °C, $\gamma°$ = 15%).

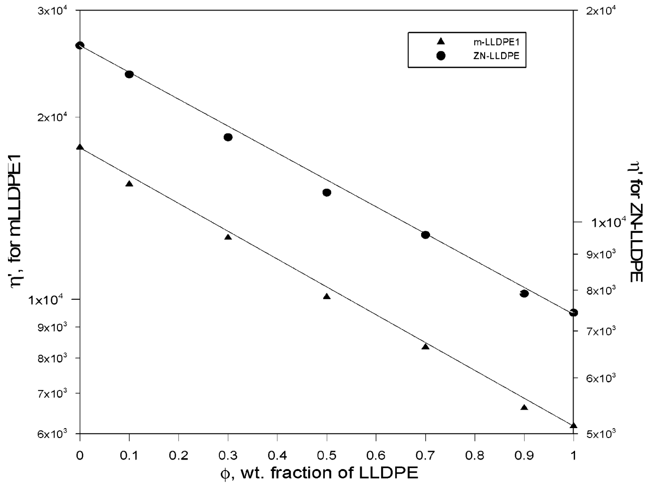

Figure 4. $\eta'(\phi)$ for blends of m-LLDPE with HDPE (T_{mix} = 190 °C, T_{test} = 190 °C, $\gamma°$ = 15%, ω=0.06 rad/s).

on the same plots for the 10, 30, 50, 70, and 90% m-LLDPE1 blends with HDPE as well as for the pure resins. Likewise, plots of $\eta'(\omega)$ and $G'(\omega)$ for blends ZN-LLDPE with HDPE are given in Figure 3. (Filled symbols were used for pure polymers, while open symbols represent the different blends. The same symbol was used for the same composition in all figures that display data on different blends.)

A Newtonian plateau that extended over a period of 2 decades was observed for the metallocene resin, m-LLDPE1. Also, m-LLDPE1 and ZN-LLDPE resins showed thelowest values for both $\eta'(\omega)$ and $G'(\omega)$. Over a wide range of ω, the increase in both η' or G' for blends of m-LLDPE1 and ZN-LLDPE with HDPE was found to be proportional to the increase in the fraction of the more viscous or elastic component.

For the determination of the morphology of the blend, low-shear data should be used. Experimental data for $\eta'(\phi)$ of blends of m-LLDPE1 and ZN-LLDPE with HDPE at low-ω near-Newtonian regime (ω=0.06 rad/s) were extracted from Figures 2 and 3 and plotted in Figure 4. The results show that the two different blend systems produced similar rheology and suggest no influence for the CD on the miscibility of LLDPE with HDPE. Also, $\eta'(\phi)$ for both blends of m-LLDPE1 and ZN-LLDPE with HDPE followed the log-additivity rule suggesting the miscibility[22−24] of both ZN-LLDPE and m-LLDPE1 in HDPE at all compositions. Plots of η'-

$(\phi)|_{\tau=\text{const}}$ at constant shear stress, τ, obtained through curve fitting of $\eta'(\tau)$ data (suggested by Van Oene[38] due to the continuity of τ) produced similar results that are not shown here.

The behavior of $G'(\phi)$ for blends of m-LLDPE1 and ZN-LLDPE with HDPE were very similar (see Figures 2 and 3). In both cases the magnitudes of G' lie between the predictions of the linear and the log-additivity rules suggesting miscibility. The results of $G'(\phi)$ suggest no significant role for CD on the miscibility of butene LLDPE with HDPE and reinforce the previous findings from $\eta'(\phi)$ data.

Further, dilute emulsion models developed by Palierne[39] and Bousmina[40] for viscoelastic fluids under small-amplitude dynamic shear were used to predict the complex modulus, $G^*(\omega)$. Expressions for $G'(\omega)$, $G''(\omega)$ and more details about both models were given in previous publications.[36,39] For miscible blends, the interfacial tension, α, is expected to be zero. For the comparison of the effect of the CD on miscibility, the HDPE-rich (10% LLDPE) and the LLDPE-rich (90% LLDPE) blends of both ZN and metallocene systems were examined.

In Figure 5a, $G^*(\omega)$ are shown for both the 10% ZN-LLDPE and the 10% m-LLDPE1 blends with HDPE. Both models produced the same predictions; hence, the predictions of only one model were shown in the figure. Experimental data were represented by solid and open circles and Bousmina model predictions ($\alpha = 0$) were shown with a solid line. The agreement between the experimental data and model predictions suggest the miscibility of both blends. On the other hand, the LLDPE-rich regime was also checked. Results for the 90% blends of ZN-LLDPE and m-LLDPE1 with HDPE are given in Figure 5b. Similarly, agreement between experimental data and model predictions for $\alpha = 0$ was obtained.

Furthermore, measurements of steady shear viscosity as a function of time (transient) were performed on all blends of ZN-LLDPE and m-LLDPE with HDPE using a cone-and-plate geometry at a steady shear of 1 s^{-1}. Results of $N_1(t)$ for the m-LLDPE and the ZN-LLDPE pairs are shown in Figures 6a and 6b, respectively. For both systems, the values of N_1 at $t = 190$ s ($N_{1,\text{ss}}$) were about the same as shown in Figure 6c suggesting no influence for the CD. A weak PDB from linear additivity rule was observed around the 50/50 composition. The relaxation part of the $N_1(t)$ experiments followed the same trend of the step rate (results not shown here) and the increase in $N_1(t)$ was proportional to the increase in the fraction of HDPE. Also, the trends of the $N_1(\dot{\gamma})$ data for the ZN-LLDPE and m-LLDPE1 blends with HDPE were similar and results for the m-LLDPE1 pair will be shown later when the effect of BC is discussed.

Hence, both the dynamic and steady-shear measurements suggest no influence for the CD (or catalyst type) on the miscibility of butene LLDPE with HDPE with both blend systems being miscible at *all* compositions. These rheological findings are in agreement with TEM measurements of Hill and Barham[21] and the recent SANS results of Wignal et al. The disagreement with the SEM and DSC experiments of Lee et al.[9] is likely due to the effect of BC since the BC of their samples ($\rho_{\text{ZN-LLDPE}} = 0.909$; $\rho_{\text{m-LLDPE}} = 0.896$) was higher than those used in this study (see Table 1).

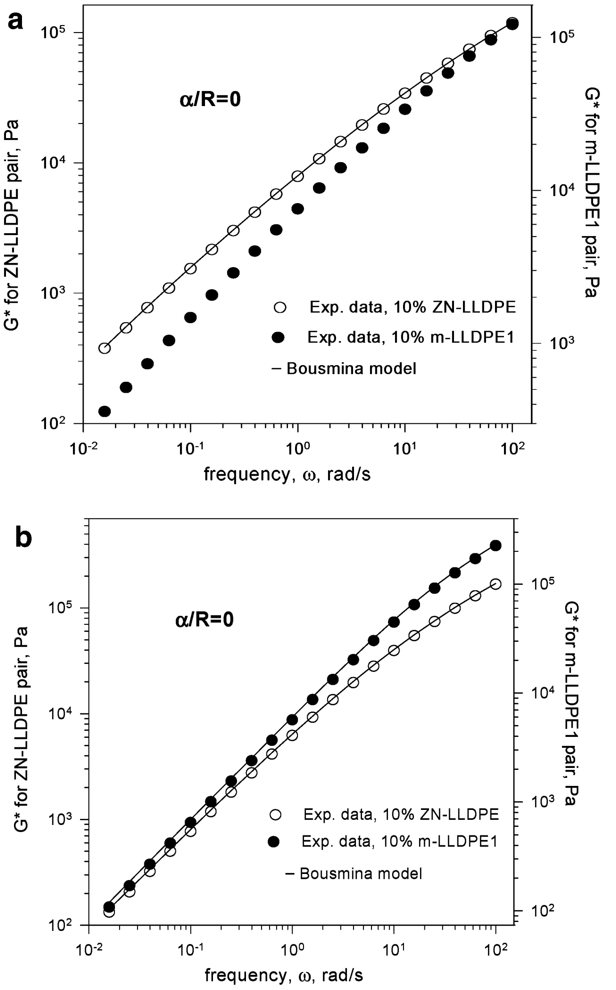

Figure 5. (a) Predictions of the Bousmina model for 10% ZN-LLDPE and m-LLDPE1 blends with HDPE ($T_{\text{mix}} = 190$ °C, $T_{\text{test}} = 190$ °C, $\gamma° = 15\%$). (b) Predictions of the Bousmina model for 90% ZN-LLDPE and m-LLDPE1 blends with HDPE ($T_{\text{mix}} = 190$ °C, $T_{\text{test}} = 190$ °C, $\gamma° = 15\%$).

3.2. Effect of Branch Content on the Miscibility of m-LLDPEs in HDPE. The effect of BC on the miscibility of LLDPE/HDPE blends was investigated by comparing the dynamic and steady-shear rheology of two m-LLDPE pairs. Blends of m-LLDPE1 (BC 14.5 CH_3/1000 C) and m-LLDPE2 (BC = 42.0 CH_3/1000 C) with the same linear HDPE were studied. Other molecular parameters (MWD, M_w) were about the same (see Table 1), and both resins were butene-based. Dynamic and steady-shear measurements were performed on the high- and low-BC pairs. For the low-BC pair, plots of $\eta'(\omega)$ and $G'(\omega)$ are given in Figure 2. Results for m-LLDPE1/HDPE blends (low-BC pair) were discussed earlier and the different dynamic and steady-shear measurements suggested the miscibility of the low-BC pair at all compositions. Here, the blend miscibility of m-LLDPE2 with HDPE (high-BC pair) will be emphasized.

Results for $\eta'(\omega)$ and $G'(\omega)$ for blends of m-LLDPE2 (high-BC pair) with HDPE are shown in Figure 7. The plot of $\eta'(\omega)$ showed a Newtonian plateau for pure m-LLDPE2. As can be observed from Figure 7, m-LLDPE2 possessed the lowest viscosity and elasticity in comparison with HDPE. In the low-ω range, the viscosities of the 50, 70, and 90% m-LLDPE2 blends were shifted toward the m-LLDPE2 and $\eta'(\omega)$ for the 90% m-LLDPE2 blend was even lower than the lowest viscosity component. This behavior was not observed for blends of m-LLDPE1 with HDPE given earlier in Figure

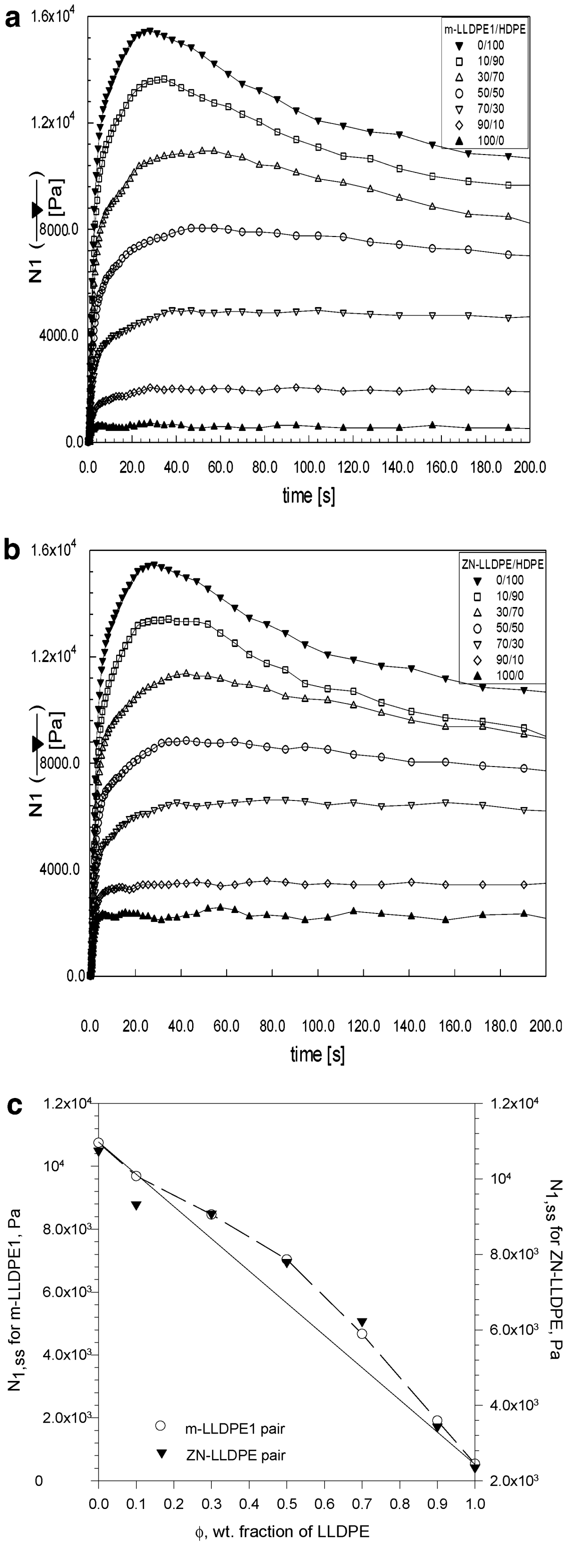

Figure 6. (a) $N_1(t)$ for blends of m-LLDPE1 with HDPE (T_{mix} = 190 °C, T_{test} = 190 °C, $\dot{\gamma}$ = 1 s^{-1}). (b) $N_1(t)$ for blends of ZN-LLDPE with HDPE (T_{mix} = 190 °C, T_{test} = 190 °C, $\dot{\gamma}$ = 1 s^{-1}). (c) $N_{1,\mathrm{ss}}(t)$ for blends of m-LLDPE1 and ZN-LLDPE with HDPE. (T_{mix} = 190 °C, $\dot{\gamma}$ = 1 s^{-1}).

2, suggesting an influence for the BC especially in the m-LLDPE-rich blends.

Plots of $\eta'(\phi)$at low ω (ω = 0.06 rad/s) are shown in Figure 8a for blends of m-LLDPE1 and m-LLDPE2 with HDPE. The m-LLDPE1 blends with HDPE followed the log-additivity rule (solid line) suggesting the miscibility of the low-BC pair. For the high-BC pair, log-additivity (dotted line) behavior was followed in HDPE-rich blends. However, the m-LLDPE2-rich blends showed a NDB from log-additivity rule suggesting[13] the immiscibility of these blends. Interlayer slip is believed to be the reason for NDB behavior. A comparison of the two blend systems suggests the influence of BC on the miscibility of m-LLDPE/HDPE blends specially in the m-LLDPE-rich regime.

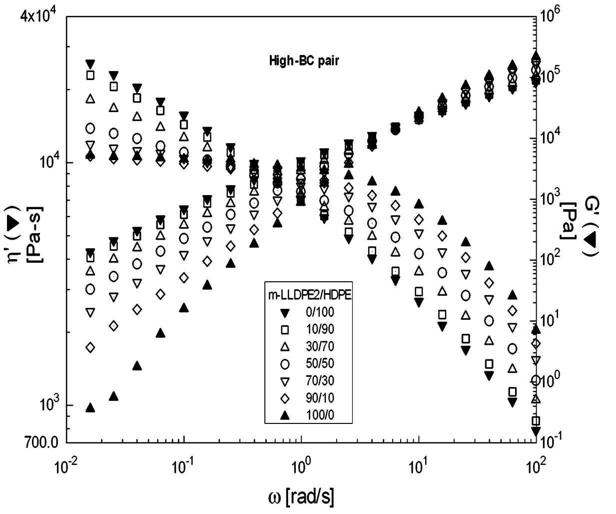

Figure 7. $\eta'(\omega)$ and $G'(\omega)$ for blends of m-LLDPE2 with HDPE (T_{mix} = 190 °C, T_{test} = 190 °C, $\gamma°$ = 15%).

Further, zero-shear viscosities of the pure polymers and their blends were calculated; using ARES software, by fitting the data to the Cross model. Computed $\eta_o(\phi)$ were plotted in Figure 8b for the low- and high-BC pairs. Results of $\eta_o(\phi)$ followed the same trend of previous plots of $\eta'(\phi)$at low ω suggesting the melt immiscibility of the high-BC pair for the 50/50 and m-LLDPE2-rich blends. The experimental data were lower than the predictions of the inverse additivity of viscosity (fluidity) rule ($(1/\eta) = (\phi_1/\eta_1) + (\phi_2/\eta_2)$), which was developed[30] for multiphase systems with multi layered morphology. Therefore, the $\eta_o(\phi)$ data support the immiscibility of m-LLDPE2-rich blends and the miscibility of the HDPE-rich blends.

Also, both BPU and Lin's models[31,32] (eqs 2 and 3 above) suggested the presence of layered morphology in LLDPE-rich blends with slip parameters k and $\lambda = 2.85 \times 10^{-5}$ and 0.72, respectively (see Figure 8b). For HDPE-rich blends, predictions of both models are different from experimental data, which suggest miscibility in that composition range. The miscibility of HDPE-rich blends was further supported by the agreement between the G*(ω) experimental data and Bousmina model predictions ($\alpha = 0$) for the 10% m-LLDPE2 blend with HDPE (see Figure 8c). Hence, dynamic-shear measurements suggest the influence of high BC on the miscibility of m-LLDPE/HDPE blends.

Furthermore, steady shear measurements were carried out on all blends of m-LLDPE1 and m-LLDPE2 with HDPE. Results of $N_1(\dot{\gamma})$ for blends of m-LLDPE1 (low-BC pair) and m-LLDPE2 (high-BC pair) with HDPE are displayed in Figure 9, parts a and b, respectively. Data are shown for both pairs in the range $\dot{\gamma}$ = 0.6–4.0 s^{-1}. The lower and upper $\dot{\gamma}$ limits were dictated by the instrument sensitivity and material flow instability, respectively. For blends of m-LLDPE1 with HDPE, $N_1(\dot{\gamma})$ for all blends (Figure 9a) was bounded by the $N_1(\dot{\gamma})$ for the pure resins, and it increased in

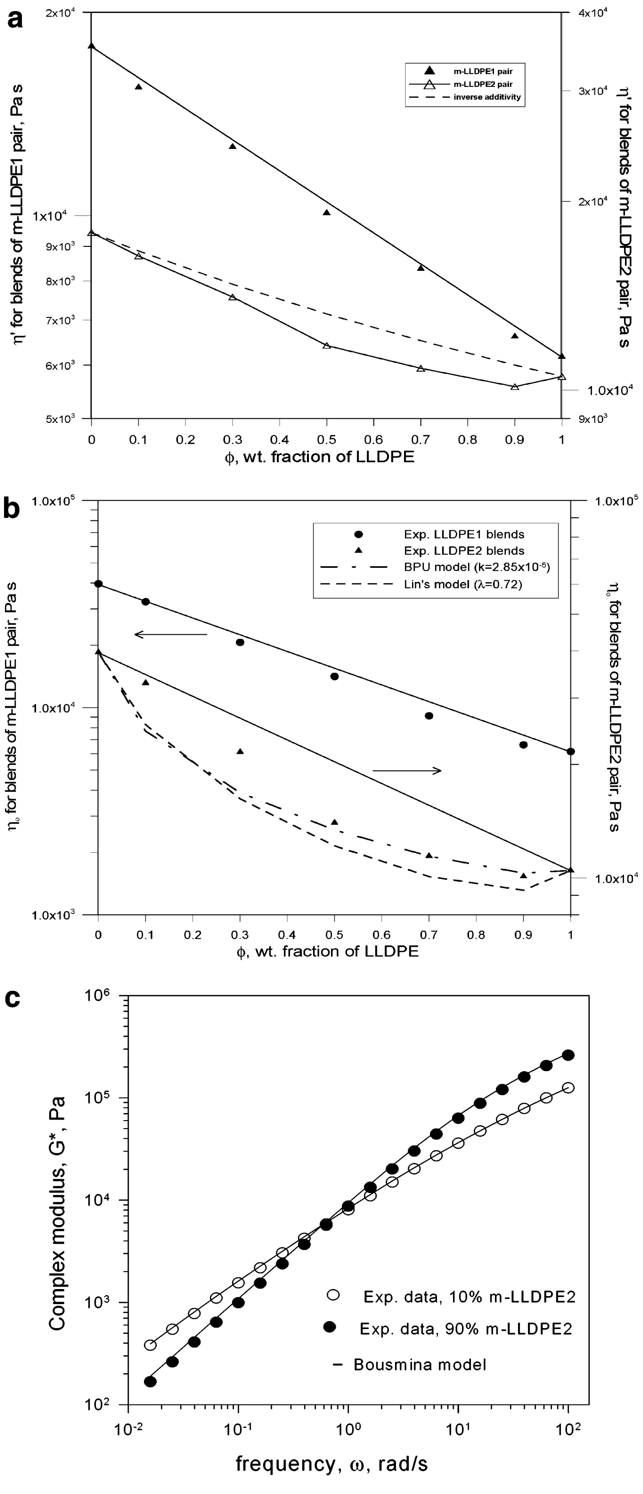

Figure 8. (a) $\eta'(\phi)$ for blends of m-LLDPE1 and m-LLDPE2 with HDPE (T_{mix} = 190 °C, T_{test} = 190 °C, $\gamma°$ = 15%, ω=0.06 rad/s). (b) $\eta_o(\phi)$ for blends of m-LLDPE1 and m-LLDPE2 with HDPE computed from the Cross model. (T_{mix} = 190 °C, T_{test} = 190 °C, $\gamma°$ = 15%). (c) Predictions of the Bousmina model for 10% and 90% m-LLDPE2 blends with HDPE (T_{mix} = 190 °C, T_{test} = 190 °C, $\gamma°$ = 15%).

proportion to the increase of HDPE (the more elastic component).

However, for blends of m-LLDPE2 with HDPE the behavior is different (see Figure 9b). It was observed that the $N_1(\dot{\gamma})$ for the 90% m-LLDPE2 blend with HDPE was lower than the m-LLDPE2 which is the blend component that possesses the lowest elasticity (N_1 and G') as discussed earlier. Also, $N_1(\dot{\gamma})$ for both the 50% and the 70% m-LLDPE2 blends with HDPE was higher than the 30% blend. This PDB of the 50% and 70% blends as well as the NDB of the 90% blends of the high-BC pair suggest[13] the immiscibility of these systems. Hence, the steady-shear data of $N_1(\dot{\gamma})$ suggests the immiscibility of the m-LLDPE-rich blends and supports the previous results obtained from dynamic shear data.

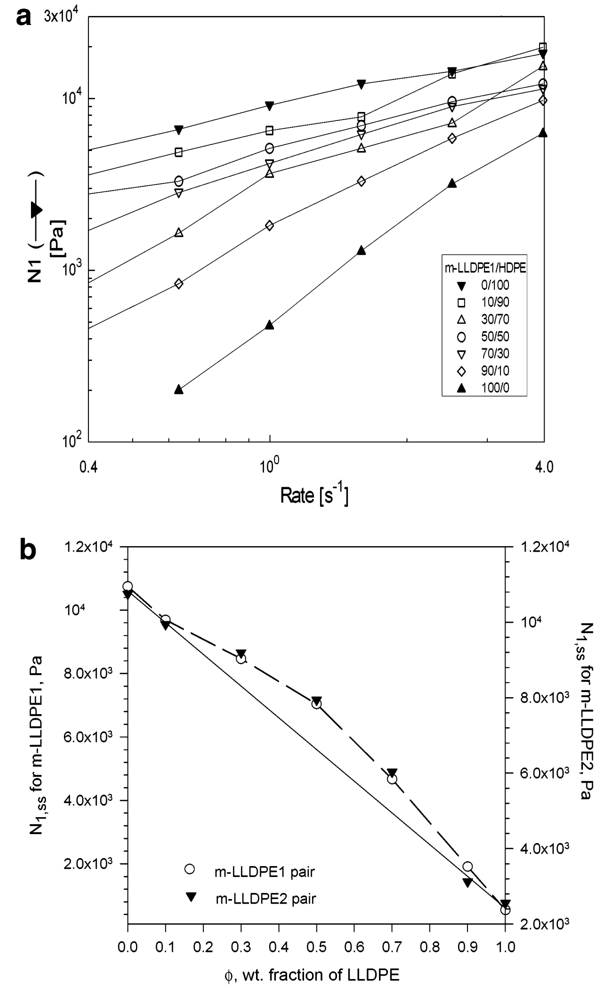

Figure 9. (a) $N_1(\dot{\gamma})$ for blends of m-LLDPE1 with HDPE (T_{mix} = 190 °C, T_{test} = 190 °C, tbm = 100 s, mt = 30 s). (b) $N_1(\dot{\gamma})$ for blends of m-LLDPE2 with HDPE (T_{mix} = 190 °C, T_{test} = 190 °C, tbm = 100 s, mt = 30 s).

The slope of N_1 vs $\dot{\gamma}$ for the 50/50 blend of the high-BC pair was found to be 0.76 ($\dot{\gamma} = 0.4-1\ \mathrm{s}^{-1}$), while Doi–Ohta theory[41] predicts a slope of 1. In addition, the slope of log N_1 vs log $\dot{\gamma}$ for both the 10% and the 90% m-LLDPE2 blends is in disagreement with Yu et al. theory[42] that predicts a slope of 2 at low $\dot{\gamma}$. Both theories were developed for emulsion systems. The disagreement of the current results with emulsion theories is another support for the layered morphology suggested by both experimental data (Figure 8b) and suggested by rheological models.[31,32] Therefore, both dynamic and steady shear measurements suggest the influence of BC on the miscibility of m-LLDPE/HDPE blends specially in the LLDPE-rich range. Furthermore, the current observation of non symmetric effect of composition on blend immiscibility of the highly branched m-LLDPE2 with HDPE is consistent with theoretical predictions of Fredrickson and co workers.[43,44]

In the first part of this study, it was found that the branching distribution has no influence on the miscibility for low-BC blends. However, in the second part it was observed that high BC ($\sim$40 CH_3/1000 C) resulted in partial immiscibility of m-LLDPE/HDPE blends. So, as long as the BC of LLDPE is low, blends of LLDPE (metallocene or ZN) with HDPE will be miscible. However, ZN-LLDPEs can contain a highly branched fraction as well as a linear fraction.[10] Such types of "pure" ZN-LLDPEs can be looked at as blends of linear (similar to HDPE used in this study) and branched molecules; hence, phase separation is possible. The current findings explain the previous reports[14−18] that suggested or suspected phase separation in "pure" ZN-LLDPE resins. The current rheological results are in agreement with the previous findings from SANS and TEM techniques mentioned earlier.

Now, it is clear why previous studies that examined the miscibility of LLDPE/HDPE using ZN-LLDPE resins might result in different conclusions about blend miscibility. Furthermore, why can some ZN LLDPE/LLDPE blends[13] phase separate? The determining factor in the miscibility of ZN-LLDPE/HDPE or ZN LLDPE/LLDPE blends is the presence of a highly branched fraction in ZN-LLDPE resins. The reasons for the immiscibility of PEs were discussed in previous publications.[33,45−47] HDPE is suggested by different techniques[41−45] to have molecular order in the melt (chain folded structure) that turns into more random coillike chain at high branch content. In a recent molecular dynamics simulation study[42] it was observed that the critical BC for this transformation in molecular conformation is $\sim$40 CH_3/1000 C. This explains the results of MD simulations of Choi[45] on LLDPE/HDPE blends where the same critical BC was observed. Below the critical BC, the chain-folded conformations are dominant for both linear HDPE and LLDPE and conformational match is likely the reason behind the miscibility. However, blends of LLDPE containing fractions of high BC with linear HDPE are expected to result in a conformational mismatch. Consequently this mismatch can lead to immiscibility of LLDPE/HDPE blends as suggested by theoretical predictions.[43,44]

All of the above results support the argument that the use of ZN-LLDPE in previousmiscibility studies was inconclusive due to the possibility of having highly branched fractions in the heterogeneous structure of ZN-LLDPE, which could lead to phase separation.

4. Conclusions

In this study, the effect of CD (influenced by catalyst type) and BC on the miscibility of m-LLDPE and ZN-LLDPE with HDPE was studied. It was found that blends of m-LLDPEs with HDPE were likely to be miscible at all compositions at low BCs (much less than 40 CH_3/1000 C) with no effect for CD. However, increasing the BC of m-LLDPE to 40 CH_3/1000 C resulted in partial immiscibility of the blend system. Immiscibility was observed in the m-LLDPE-rich blends regime. Dynamic and steady shear rheological measurements as well as rheological models supported the above arguments on the miscibility/immiscibility of the ZN-LLDPE and m-LLDPE blends with HDPE. For the immiscible blends, layered morphology was suggested by both experiment and BPU and Lin's model predictions with slip parameters $k = 2.85 \times 10^{-5}$ and $\lambda = 0.72$, respectively.

The dissimilarities in molecular structure are likely to be the reason behind the partial immiscibility. Highbranching in LLDPE chains is expected to produce conformations different than that of the linear chain[47] and hence induce immiscibility of LLDPE/HDPE blends. The current study suggests the strong influence of BC on the miscibility of LLDPE/HDPE blends.

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