Rheological Study of Heterogeneities in Melt Blends of ZN-LLDPE and LDPE:

Influence of M_w and Comonomer Type, and Implications for Miscibility

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ABSTRACT

The influences of molecular weight and LLDPE comonomer type on the heterogeneity (immiscibility) of Ziegler-Natta LLDPE and LDPE blends are investigated with rheological methods. Dynamic and steady shear measurements were carried out in a Rheometrics Mechanical Spectrometer 800.

Blends of low-M_w ($<10^5$)LLDPE (butene) and LDPE are likel*y* homogeneous and *miscible* as revealed by the dependence of their η' on blend composition at 140^oC. Blends of high-M_w (10^5)LLDPE (butene) and LDPE mixed and tested at 190^oC were only *partially* miscible; cheterogeneity and i*mmiscibilty* was likely to occur around the 50/50 composition and in the LDPE-rich blends. Blends were likely *miscible* in the LLDPE-rich range. Increasing the LLDPE branch length (comonomer) from butene to octene slightly increased the miscibility of LLDPE/LDPE blends. It is suggested that the molecular order in polyethylenes (see Hussein and Williams, J. Non-New. Fluid Mech., 86, 105-118, 1999a; Macromol. Rapid Commun., 19, 323-325, 1998) and mismatch of the molecular conformations of different polyethylene structures provide explanations for the immiscibility of polyethylenes. Agreement was observed between the measured $G'(\omega)$ and $G''(\omega)$ and theoretical predictions of Palierne and Bousmina-Kerner models, which are based on two-phase emulsion behavior.

I. Introduction

It is estimated that 60 to 70% of LLDPE enters the market as blends (Utracki, 1989a), primarily with other members of the polyolefin family, e.g. LDPE or polypropylene (PP). Despite the long history of polyethylene (PE) blending and its widespread use, many questions about the homogeneity of such blends, with obvious implications for thermodynamics and for the rheology, are still not answered to everyone's satisfaction.

We here employ rheology to address specifically one of the most common types of blends, namely those using LLDPE and LDPE, where Ziegler-Natta (ZN) LLDPE is used. Even within this type of blend, there can be enormous variations due to volume fraction, ϕ, molecular weight, choice of LLDPE comonomer (i.e., branch length) and branch content as well as distributions of both molecular weight and branching along the LLDPE main chain.

For polyethylenes the simple study of the phase morphology of the melt tends to be unhelpful, and in general, individual methods are inconclusive (Groves et al., 1996). The rheology of various kinds of polyolefin blends was surveyed by Plochocki (1978) and that of polyethylenes in particular was reviewed by Utracki (1989b). Blends of PE/PE components show a quite diverse range of behavior as discussed below.

A. Blends of "Homopolymers"

Blends of HDPE/HDPE and LDPE/LDPE (different M_w fractions) were reported to be miscible and homogeneous [Munoz-Escalona, (1997); Utracki (1989a,b); Hill and Barham, (1995)] and the viscosity vs. composition relationship followed the log-additivity rule. For LLDPE/LLDPE systems studied by Utracki (1989b), one pair was found miscible; however, another blend was reported to be *immiscible*.

B. HDPE/LDPE Blends

Dobrescu (1980) studied HDPE/LDPE blends of different M_w using a capillary rheometer. In most cases the $\eta(\phi)$ plot showed positive deviation behavior (PDB) relative to various linear mixing rules, such as the arithmetic "rule of mixtures", $\eta=\eta_A+\phi\eta_B$, and the log-additivity rule (log $\eta=\sum\phi_i$ log η_i); and the stronger the mismatch between the component viscosities η_A and η_B the larger was the PDB. Deviations from the linear mixing rules for $\eta(\phi)$ has generally been taken to imply emulsion-like behavior and thus immiscibility. Garcia-Rejon and Alvarez (1987) reported the incompatibility (immiscibility) of HDPE/LDPE blends, too. They observed that low concentrations of low-G′ HDPE (10%) had increased the blend G′ by 50% over that of the higher-G′ LDPE (strong PDB). Martinez-Salazar and co-workers [Martinez-Salazar et al, (1991); Plans et al., (1991)] correlated PDB of HDPE/LDPE systems to the branch content of LDPE, and reported a critical branch content below which miscibility was assured for their components. Furthermore, Curto et al. (1983) indicated good superposition of reduced $\eta(\dot{\gamma})$ capillary flow data for a series of HDPE/LDPE blends at T=160° to 200°C, interpreted as support for likely miscibility (or stable morphology). Similarly, the results of Lee and Denn (2000) and Lee et al. (1997) supported the miscibility of HDPE/LDPE blends.

C. HDPE/LLDPE Blends

The miscibility of certain HDPE/LLDPE pairs was reported by: Hu et al. (1987); Lee et al. (1997); and Lee and Denn (2000). However, liquid-liquid phase separation with HDPE/LLDPE systems was detected by Hill and co-workers [Thomas et al., (1993); Hill and Barham, (1995)] using heavily branched LLDPE (branch content > 40 CH_3/1000 C).

D. LDPE/LLDPE Systems

Utracki and Schlund (1987) found that a blend of LLDPE/LDPE was immiscible; however, other blends of LLDPE/LDPE were reported to be partially miscible [Datta and Birley, (1983); Utracki, (1989b); Muller and Balsamo, (1994); Lee and Denn, (2000)]. The molecular weight and branching information for LLDPE and LDPE used in the previous studies are given in Table 1. It is clear that most of the previous reports did not provide the branching information, which makes comparisons with our current work very difficult.

Therefore, due to the diversity of composition, molecular structure, M_w and MWD the LLDPE/LDPE blends may or may not be miscible in specific cases. Hence, blends of LLDPE with other LLDPE or LDPE may show a widely diverse behavior, dependent on small changes in molecular structure caused by e.g., different catalyst, polymerization method or composition [Utracki, (1989b)]. It should be noted that Ziegler-Natta (ZN) catalysis produces simultaneously linear and branched chains, so these linear LLDPE products are suspected of being intrinsically multiphase even before blending with HDPE or LDPE components.

Blends of LLDPE and LDPE combine the favorable mechanical properties of the LLDPE with the ease of processing of LDPE. Yet, the rheological consequences of blending LLDPE and LDPE have received far less attention than have linear/linear or linear/LLDPE or linear/LDPE blends.

The aim of this investigation is to examine the effects of M_w, molecular architecture (branch type, branch content), MWD, catalyst type (ZN or Metallocene which influence several structural factors in LLDPE), and mixing temperature, T_{mix}, on the miscibility of LLDPE blends with LDPE in the melt state. The metallocenes produce random copolymers as opposed to the ZN ones that tend to have higher degrees of short chain branching in the lower M_w components

(Freed and Dudowicz, 1996). The matrix of resins used as blend components was designed to study one variable at a time.

In this paper, only the effect of M_w and branch type will be discussed; the influence of T_{mix} is discussed elsewhere [Hussein and Williams, (1999c)]; and other parameters will be treated in future publications. Two pairs of LLDPE and LDPE were selected to study the effect of M_w. S229 (LLDPE) and S216 (LDPE) composed the high-M_w pair; and S227 (LLDPE) and S231 (LDPE) were chosen as the low-M_w pair. The effect of the LLDPE branch type was investigated by testing blends of S226 (octene LLDPE) and S216 and comparing results to those of S229 (butene LLDPE) and S216, where both pairs had the same high-M_w nature.

II. Rheology & Miscibility of Multiphase Systems

For immiscible blend systems, the state of dispersion and specifically the shape of the dispersed phase (i.e. droplets) greatly influence the rheological responses. As illustrated by Chuang and Han (1984) rheological behavior of immiscible blends is strongly affected by the type of applied shear. While shear-induced mixing that alters blend morphology is observed in some steady shear experiments (Larson, 1992; Minale et al., 1997), no such effects are reported for small amplitude dynamic shear (Utracki, 1988; Chuang and Han, 1984). We therefore favor the latter in this study.

Generally, phase separation causes the storage and loss moduli G′ and G′′ to exceed values for the matrix phase, due to the presence of droplets of the dispersed phase. This increase is a result of "emulsion morphology" present in phase separated systems. Another representation of the effect of emulsion rheology is shown in Figure 1, taken as behavior typical of ϕ-dependent data for either miscible (soluble) blends or immiscible blends. For the miscible systems, one expects data to follow the linear "Rule of Mixtures" or something close to this. For the

morphology-dependent emulsions, however, $\eta(\phi)$ is distinctly nonlinear and often a maximum is seen near the high-η end of the ϕ-range. Indeed, the latter can be taken as evidence that the blend is immiscible (We will later show that theoretical models predict both of the effects displayed in Figure 1). Even in a mixture of two Newtonian liquids, the emulsion morphology gives rise to a non-zero G'. That is, the emulsion exhibits elastic behavior due to surface tension between the phases, in addition to the enhanced viscosity (Taylor, 1932; Oldroyd, 1953).

Earlier hydrodynamic calculations [Taylor, (1932); Fr$\ddot{o}$hlich and Sack, (1946)] for such systems were for dilute emulsions, and an extension to concentrated emulsions (to order ϕ^2) was given by Choi and Schowalter (1975). They derived expressions for G' and G'' for an emulsion of two Newtonian liquids, which can also be applied to a phase separated polymeric system in the low-ω Newtonian regime (Scholz et al., 1989; Gramespacher and Meissner, 1992), where the G' had increased due to the presence of droplets. Scholz et al. (1989) derived a constitutive equation for dilute emulsions of noninteracting, spherical and monodisperse droplets of Newtonian liquids. The two liquids were assumed to be incompressible, and totally immiscible. For the linear viscoelastic range of deformation, the emulsion was shown to have dynamic moduli given by:

$$\frac{G''(\omega)}{\omega} = \eta' = \eta_m \left[1 + \phi \left(\frac{2.5k+1}{k+1} \right) \right] \tag{1}$$

$$G'(\omega) = \frac{\eta_m^2 \phi}{80(\alpha/R)} \left(\frac{19k+16}{k+1} \right)^2 \omega^2 \tag{2}$$

where, η_m = the viscosity (Newtonian) of the matrix liquid; η_d = the viscosity (Newtonian) of the

dispersed droplets; k = $\dfrac{\eta_d}{\eta_m}$; R = radius of the dispersed domains; α = surface tension between

the two liquids; ϕ = volume fraction of the dispersed phase.

The storage modulus G′(ω) obtained experimentally at low ω for immiscible polymer blends

was reported [Fujiyama and Kawasaki, (1991); Graebling et al., (1993); Gramespacher and

Meissner, (1992); Chuang and Han, (1984); Scholz et al., (1989)] to be higher than those of the

components. Similar to the concentrated-emulsion model, Ajji and Choplin (1991) found the

effects of phase separation on G′ to be more pronounced than on G″. Earlier work of the

Williams group (Martinez and Williams, 1980) showed similar increase in η′(ϕ) and η($\dot{\gamma}$) for an

immiscible HDPE/PMMA system. Their rheological measurements were supported by SEM

micrographs. The low-shear data showed excellent agreement with the predictions of η$_o$(ϕ) by

the dilute Newtonian emulsion model [Taylor, (1932); Oldroyd, (1953)]. None of the above-cited

experimental studies employed PE/PE blends.

It is recognized that eq. (1) and (2) cannot be entirely adequate for polymer melt blends

because those equations can accommodate only Newtonian fluids. However, Palierne (1990,

1991) developed a general expression for the complex shear modulus of an emulsion of

viscoelastic fluids. For an emulsion of two viscoelastic phases with a uniform spherical particle

size and constant interfacial tension, the complex modulus of a blend, $G_b^*(\omega)$, was given by:

$$G_b^*(\omega) = G_m^* \frac{1 + 3\phi H(\omega)}{1 - 2\phi H(\omega)} \tag{3}$$

Expressions for G′ and G″ and H(ω) are given elsewhere [Carreau et al., (1997)]. Recently,

Bousmina (1999a) extended Kerner's model for modulus of composite solid elastic media

(Kerner, 1956) to predict the dynamic moduli of an emulsion of viscoelastic liquid phases. Bousmina obtained the following expression for $G_b^*(\omega)$:

$$G_b^* = G_m^* \frac{2(G_d^* + \alpha/R) + 3G_m^* + 3\phi(G_d^* + \alpha/R - G_m^*)}{2(G_d^* + \alpha/R) + 3G_m^* - 2\phi(G_d^* + \alpha/R - G_m^*)} \tag{4}$$

and corresponding expressions for G'(ω) and G''(ω) were also transmitted to us (Bousmina, 1999b). Bousmina (1999a) showed that his model (Bousmina-Kerner model) gave predictions similar to those of the Palierne model.

In addition to experimental observations of the sort described in Figure 1, other types of data have been used to identify the immiscibility of binary blends. One example is a test of so-called Cox-Merz behavior.

The similarity of dynamic and steady shear properties [e.g., between $\eta(\dot{\gamma})$ and $\eta^*(\omega)$, and between $N_1(\dot{\gamma})$ and $2G'(\omega)$] must *not* be expected for inmmiscible blends [Utracki and Schlund, (1987); Chuang and Han, (1984)]. However, while the lack of superposition of dynamic and steady shear viscosities does indicate immiscibility, success of superposition cannot be taken as a proof of miscibility [Utracki and Schlund, (1987)].

III. EXPERIMENTAL

A. Materials

All polyethylene resins used in this study (see Table 2) were supplied by NOVA Chemicals Ltd. (and are here designated with sample codes "S"). Molecular weight (from GPC), branch content (NMR and FTIR), and melt index (M.I.) characterizations of the samples are given in Table 2. LLDPE and LDPE samples were characterized by TREF (temperature rising elution fractionation), as shown in Figures 2 and 3 respectively. S226 (octene LLDPE), S227 (butene LLDPE), and S229 (butene LLDPE) were Ziegler-Natta (ZN) products. ZN-LLDPEs are known

for their intra- and intermolecular heterogeneity (Usami et al., 1986). The TREF profiles for LLDPE and LDPE (Figure 2) and clearly reveal the complexity and breadth of distribution of molecular structure of ZN LLDPEs.

It is relevant to note that the ZN TREF profiles clearly display two peaks, corresponding to the linear-chain components and the branched-chain components of the ZN products (which are revealed as being intrinsically blends themselves and potentially phase-separated even before being mixed with the other PE products used in this study). (This complication about ZN LLDPE products used in PE blend research seems to have escaped most investigators.) S216 and S231 in Figure 3 were LDPEs made by high-pressure free-radical gas polymerization and are characterized by TREF profiles that are basically unimodal (though a shoulder appears in the profile of S231, Figure 3b).

All polyethylene samples used were commercial resins and contained proper amounts of antioxidant (AO).

Normally, 0.1% (1000 ppm) or less of primary and secondary antioxidants are used commercially for polyolefins [Bair, (1997)]. Here, an additional 1000 ppm of AO mixture was added to the as-received resin(s) before melt conditioning in the blender. The mixture of extra antioxidants had the following composition: a 50/50 blend of Irganox 1010 {Phenol B, tetrakis[methylene 3-(3′,5′–di-t-butylphenol) propionate]methane, M_w=1178, the primary antioxidant} and the phosphorous-containing compound Irgafos 168 {P-1, tris[2,4-di-t-butylphenol] phosphite, M_w=646, the secondary antioxidant}. Both antioxidants are made by Ciba Specialty Chemicals.

B. Melt Conditioning in the Blender

The Haake Rheocord 90 is designed for use as a computer-controlled torque rheometer, which can also be operated as an extruder or as a mixer. The latter configuration, featuring a sample bowl containing 60 mL of melt, was used for conditioning (or blending) different polymers at constant temperature, rotor speed, and for a fixed time. The LDPE and LLDPE resins used in this study were conditioned in the melt blender at 50 rpm and 190°C for 10 minutes. Blends of S229 and S226 with S216 as well as 'pure' polymers were conditioned in the presence of 1000 ppm of additional antioxidant. A previous degradation study [Hussein et al. (2000a)] showed that this level of AO is adequate to prevent degradation of the Z-N LLDPEs during melt blending. The "conditioned" samples were then removed from the mixing bowl, and air-cooled.

C. Rheological Measurements

A Rheometrics Mechanical Spectrometer RMS 800 was employed for small-strain, ω-sweep measurements of dynamic properties, usually at 190°C. A shear strain amplitude (γ^{o}) of 10% was used, after a strain sweep showed that this γ^{o} was sufficiently small to produce sinusoidal torque responses and dynamic properties independent of γ^{o} (i.e., linear properties were obtained). The ω-sweep testing was performed at 190°C over the range $\omega=10^{-2}$ to 10^{2} rad/s except for the low-M_w PE blend which was tested over the range $\omega=1$ to 100 rad/s at 140°C. The ω-sweep tests were carried out using a cone-and-plate (CP) geometry of 25-mm diameter platens. The cone angle was 0.1 radian with a 53 μm truncated apex. The RMS testing was carried out on discs molded from the samples of the air-cooled mixer-conditioned resins. All measurements were conducted using nitrogen as the convection-heating medium to alleviate possible oxidative sample degradation during the sweep tests. The stability of the blends was established from time sweep

measurements, G'(t), at different temperatures and repeat measurements for the 10% and 90% S229 blends with S216 as given elsewhere (see Figures C1 to C3 of Hussein, 1999). Sample preparation and test procedure are explained elsewhere (Hussein and Williams, 1999a).

IV. Results and Discussion

A. Influence of the M_w

1. Blends of the Low-M_w Pair

The dynamic flow measurements were obtained at T_{test}=140°C for the low-M_w LLDPE S227, S231, and their blends. Lower T_{test} was selected for these low-viscosity components than for the high-M_w pair to enhance viscosity and thus assure that the torque signal was above the sensitivity level of the RMS. The blends were characterized primarily by the following rheological functions: η' (or G") and η'' (or G') as functions of composition, ϕ, and frequency, ω.

The ϕ-dependence of η' for the low-M_w pair (obtained at low ω) is shown in Figure 4. The $\eta'(\phi)$ data follow the linear additivity rule ($\eta=\sum_i \phi_i \eta_i$, indicated by a solid straight line), suggesting the miscibility of blends of the low-M_w pair as proposed in Figure 1.

2. Blends of the high-M_w Pair

In the following analysis, we aimed at presenting the rheological data in different formats to facilitate the assessment of the miscibility, and possibly help scrutinize the different methods. The dynamic shear data were examined as:

a. $G'(\phi)|_{\omega=const}$ as well as $\eta'(\phi)|_{\omega=const}$ obtained directly from the ω-sweep measurements (method widely used in the literature).

b. $\eta'(\phi)|_{\tau=const}$ obtained through curve fitting of stress-dependent data $\eta'(\tau)$ data (suggested by Van Oene, 1978, since the boundary conditions at the immiscible fluid-fluid interfaces require the continuity of the shear stress). At constant τ, the ϕ-

dependence of η' leads to $(\partial \eta'/\partial \phi)_\tau > (\partial \eta'/\partial \phi)_\omega$ since $\{(\partial \eta'/\partial \phi)_\tau = (\partial \eta'/\partial \phi)_\omega [1-\omega(\partial \eta'/\partial \tau)_\phi]\}$ and $(\partial \eta'/\partial \tau)_\phi$ is negative. Figure 5 gives $\eta'(\omega)$. From this and the definition $\tau = \eta^*(\omega)$, the function $\eta'(\tau)$ was obtained and is given elsewhere (Hussein, 1999).

c. Comparison of $\eta^*(\omega)$ and steady shear viscosity, $\eta(\dot{\gamma})$. Lack of superposition of $\eta^*(\omega)$ and $\eta(\dot{\gamma})$ (Cox-Merz behavior) indicates immiscibility (Utracki and Schlund, 1987).

d. Zero-shear viscosity, $\eta_o(\phi)$, extracted from fitting the $\eta'(\omega)$ data to a rheological model.

We now examine these points in detail:

(a) First, the $\eta'(\phi)_{\omega=const}$ data are presented in Figure 6 for intermediate ω (0.1 rad/s). There is a strong PDB from linear-additivity and log-additivity in the LDPE-rich blends and around $\phi=50\%$, with the blend η' exceeding (in some cases) the viscosity of the more viscous component as suggested in Figure 1 for emulsions. The $\eta'(\phi)_{\omega=const}$ for LLDPE-rich blends tended to converge to the linear-additivity rule (as in Figure 1). However, the semi-log plots of $\eta'(\phi)_{\omega=const}$ (used to check the applicability of the log-additivity rule) were generally showing much stronger PDB compared to the linear additivity rule. On the other hand, linear plots of $G'(\phi)_{\omega=const}$ were similar to their counterparts of $\eta'(\phi)$ with semi-log plots showing much stronger PDB in the low-ω range. The ϕ-dependency of η' and G' suggest the miscibility of LLDPE-rich blends (high ϕ) and the immiscibility of the LDPE-rich blends (low ϕ). More data on $\eta'(\phi)_{\omega=const}$ and $G'(\phi)_{\omega=const}$ are shown elsewhere (Figures C.6, C.7 and C.16 to C.19 of Hussein, 1999).

(b) Second, the $\eta'(\tau)$ data, where τ was calculated as equal to $|\eta^*| \times \omega$ (employed by Wissbrun and Griffin, 1982), followed a trend similar to that of $\eta'(\omega)$ [see Hussein and Williams, (1999c)]. However, the curves are distinctly separated from each other. This observation supports the suggestion of Van Oene (1978) that $(\partial \eta'/\partial \phi)_\tau > (\partial \eta'/\partial \phi)_\omega$.

Results for $\eta'(\phi)_{\tau=const}$ are similar to the previous plots of $\eta'(\phi)_{\omega=cont}$ (Figure 6) suggesting the immiscibility of the high-M_w pair in the 50/50 composition range as well as the LDPE-rich ($\phi<0.5$) blends. On the other hand, the LLDPE-rich ($\phi>0.8$) blends are likely to be miscible.

The different methods of presenting the dynamic shear data, discussed so far, suggest that the LDPE-rich blends are likely immiscible; and the LLDPE-rich blends are likely miscible. Hence, in a blend of high-M_w components S229 (LLDPE) and S216 (LDPE) a 10% S229 blend is likely to be immiscible while that of 90% S229 is likely miscible.

(c) To investigate further the miscibility at the two ends of the composition spectrum, steady shear measurements were performed. Utracki and Schlund (1987) suggested that $\eta'(\omega) \cong \eta(\dot{\gamma})$ for $\omega = \dot{\gamma}$ for miscible blends. The steady shear measurements were obtained in the CP geometry in the range $\dot{\gamma} = 0.01$ to 1.0 s^{-1}; 3 minutes of steady shearing were allowed after a $\dot{\gamma}$-change to achieve steady state followed by 30 seconds of data acquisition, or measurement time.

The steady and dynamic shear measurements for the 10% and 90% S229 blends are displayed in Figure 7 as $\eta^*(\omega)$ and $\eta(\dot{\gamma})$. The 90% blend (LLDPE-rich blend, suggested above to be miscible) showed a very good degree of superposition of $\eta^*(\omega)$ and $\eta(\dot{\gamma})$ over the whole range of shear confirming the previous interpretations. On the other side, the steady and dynamic shear results for the 10% S229 (LDPE-rich blend, suggested above to be immiscible) lacked superposition over the same shear range. This comparison of steady and dynamic shear

viscosities at selected compositions that represent the LLDPE-rich and LDPE-rich blends reinforce the findings of the previous methods of data treatment.

(d) Finally, $\eta_o(\phi)$, is another important parameter that we explored. However, it is often difficult to observe a low-ω Newtonian plateau for high-M_w materials with high polydispersity (PD). This was the case for several samples of the high-M_w pair. In these cases, it is appropriate to use rheological models that can be extrapolated to $\omega=0$ to obtain η_o.

Utracki (1987) proposed a simple generalization of the Carreau 'Model A' relation between viscosity and rate of deformation in steady shear [Carreau, (1972)]. Utracki and coworkers [Utracki and Schlund, (1987); Utracki, 1989a,b; Dumoulin et al., (1991)] used the following generalization of the $\eta(\dot{\gamma})$ model to describe their $\eta'(\omega)$ data:

$$\eta' = \frac{\eta_o}{\left[1 + (\omega\theta)^{m_1}\right]^{m_2}} \tag{5}$$

where η_o is one of the adjustable parameters, the other three being: θ, the mean relaxation time, and the two exponents, m_1 and m_2. It can be seen that for large dimensionless frequencies ($\omega\theta \gg 1$), a 'power law', $\eta' = \left(\frac{\eta_o}{\theta^{m_1 m_2}}\right) \omega^{-m_1 m_2}$ is recovered. In the context of a traditional powerlaw model, $\tau \propto \omega^n$ so $\eta' = \tau/\omega \propto \omega^{n-1}$.

The SigmaPlot nonlinear curve fitter was used to fit equation 5 to the $\eta'(\omega)$ data as described by Dumoulin et al. (1991). The parameters obtained from the regressions are listed in Table 3.

The mean relaxation time, $\theta(\phi)$, closely followed the log-additivity rule in the LLDPE-rich range ($\phi \geq 70\%$) [see Figure C.12 of Hussein, 1999]. However, the 50/50 and the LDPE-rich blends showed a strong PDB. The θ values were high and insensitive to changes in composition

in the range $\phi \leq 30\%$ LDPE suggesting the presence of a multiphase system [Scholz et al., (1989); Graebling et al., (1993)].

The computed $\eta_o(\phi)$, plotted in Figure 8, shows a large PDB. The shape of the curve of $\eta_o(\phi)$ is similar to those of $\eta'(\phi)_{\omega=const}$ and $\eta'(\phi)_{\tau=const}$ (e.g., Figure 6). The $\eta_o(\phi)$ values reinforce the previous observations of the dynamic and steady shear measurement.

At this stage, it is appropriate to offer a tentative explanation for the high $\eta_o(\phi)$ of the LDPE-rich blends. The likelihood of these blends being two-phase systems (already supported by various arguments above), will be analyzed in terms of emulsion models. In the low-ω limit, the Palierne model reduces to equation 1 (dilute Newtonian emulsion model). The line representing equation 1 for the dilute-S229 regime is shown in Figure 8. The model gives a reasonably good prediction of the zero-shear viscosity at low ϕ [e.g., $(\eta_{o,theor} - \eta_{o,\exp})/\eta_{o,\exp} \sim 0.07$ for 10% S229]. Further, this model predicts and explains the increase in the viscosity above that of the high-η_o fluid (LDPE) due to the addition of 10% of the low-η_o fluid (LLDPE).

In the high-ω non-Newtonian regime, both the Palierne and Bousmina-Kerner models require knowledge of the ratio α/R; yet, this is difficult to obtain for polyethylenes. One way of estimating α/R is to extract that ratio from the low-ω $G'(\omega)$ data using equation 2 and assume that it stays constant in the high-ω regime. According to equation 2 (a low-ω approximate model) a log-log plot of $G'(\omega)$ should be linear with a slope of 2. For the 10% S229, the plot was indeed linear ($r^2=0.997$); however, the slope was ~1 and a first estimate of α/R was obtained as 4.4×10^4 N/m^2. This value was decreased until model curve-fits were optimized for Figure 8. The best fitting of $G^*(\omega)$ data was obtained with $\alpha/R=3 \times 10^3$ N/m^2. However, deficiencies in the curve-fit were obvious.

Clearly, a better job of data-fitting could be expected from the viscoelastic emulsion models. This is demonstrated in Figure 9 for the G'(ϕ) data at ω=1.0 rad/s. Only the Palierne Model was used (Bousmina-Kerner does as well) and the theoretical curve is subject to the constraint that α/R does not change with ϕ. The curve-fit obtained yielded α/R=3×10^3 N/m^2. Several features in Figure 9 are worthy of discussion.

1. The "Rule of Mixtures" line emerges as a special case (α=0) which corresponds to having no interfaces at all (i.e., a miscible system). Thus, our prior use of this line as our reference condition (miscibility) is justified. (This α=0 limit is identical for the Bousmina model).

2. A very reasonable maximum emerges in the G'(ϕ) function near the high-G' side of the range when the low-G' component is added to the high-G' component. This can only happen if immiscibility prevails, as must be the case for α/R as large as 10^3 N/m^2 and above.

3. Even better predictions can be made by the model at specific ϕ if α/R is allowed to vary with ϕ. Such variation is reasonable, since the two phases on opposite sides of the interface need not maintain their own compositions as the system overall composition changes (thus, α/R can also be ϕ-dependent). Still, the variation of $\frac{\alpha}{R}(\phi)$ to secure exact agreement with the data points is not large. Values of α/R in the range (1 to 3)×10^3 N/m^2 suffice to fit all the data points in Figure 9 exactly.

Predictions of G' and G" over a wide range of frequency, using the Palierne and Bousmina-Kerner models are given in Figure 10. Model predictions for the 10% S229 blend are shown for α/R=3×10^3 N/m^2. The two models give almost the same predictions of G' and G" and show good

agreement with data (shown in Figure 10 as circles and squares) over the whole frequency range. The value of α/R used in Figure 10 (α/R=3×10^3 N/m^2) is comparable to that reported for known immiscible but compatibilized polymer blends (Brahimi et al., 1991). If the droplet phase has a size of R≅1 μm, then the order of magnitude of α is about 1 mN/m (1 dyne/cm) -very low, but consistent with an interface between two phases so chemically similar. At low ω, the Bousmina-Kerner model was found to be more sensitive to variations in the ratio α/R than was the Palierne model.

Thus, the different methods of data treatment suggest that the high-M$_w$ pair mixed at 190°C is likely *miscible* only in the LLDPE-rich blends ($\phi \geq$70% LLDPE); and likely *immiscible* in the 50/50 and LDPE-rich blends (ϕ<50% LLDPE). The immiscibility of the blends can be predicted by Palierne and Bousmina-Kerner models in the sense that they predict η*(ω) and η'(ϕ) and G'(ϕ) with good accuracy based on the assumption of 2-phase behavior and reasonable values of α/R.

The LLDPE (S229) and the LDPE (S216) used in this study have almost the same average M$_w$ and branch content (see Table 1), suggesting that the two components have equivalent molecular volumes. However, the above results show that adding a small amount of the structurally bimodal LLDPE (heterogeneous, with small size molecules that are highly branched) to the structurally unimodal LDPE is more likely to cause immiscibility than the addition of a small amount of LDPE to LLDPE (e.g., see Figures 7 and 8). These experimental findings are in agreement with theoretical predictions of Fredrickson et al. (1994). They showed that compositional asymmetry is present in polyolefin blends if the two components have equivalent overall molecular volumes. Hence, adding a small amount of a highly branched component to a

lightly branched melt is more likely to cause liquid-liquid phase separation than vice versa (Fredrickson et al., 1994).

The influence of high M_w (usually deemed the dominant factor for inducing <u>immiscibility</u>) must be re-examined in view of <u>partial</u> miscibility depicted by this study, despite the fact that the components of the blend (S229 and S216) have almost the same high M_w. Further, previous studies on similar systems (of even higher M_w than those covered in the present study, see Table 1) reported partial miscibility, too. The influence of M_w on the miscibility of high-M_w LLDPE/LDPE blends shown above (e.g., see Figures 7 and 8), suggests an unexpectedly strong influence of molecular structure, possibly more so than molecular weight, on the miscibility of polyethylenes. This seems consistent with theoretical findings [Fredrickson and Liu, (1995); Bates and Fredrickson, (1994)] that acknowledge the important influence of the *conformational* and *architectural* "mismatch" between components of polyolefin blends on the miscibility of polyolefins.

B. Influence of Comonomer Type

Here, the influence of the comonomer type (or branch length) on the miscibility of LLDPE/LDPE systems was studied. For this purpose, an octene-LLDPE (S226) of the same high M_w (see Table 2) and similar TREF profile (see Figure 2) as that of the butene-LLDPE (S229) was selected for blending with S216 (LDPE). The blends examined were 20, 50, and 80 % S226 (octene) in addition to the 'pure' polymers. Dynamic shear data was obtained and analyzed in the same fashion as described earlier.

The dynamic viscosities of the octene blends $\eta'(\omega)$, are shown in Figure 11. At low ω, the LDPE-rich blends (ϕ<50%) show viscosities that are approximately the same as that of LDPE (higher η_0 component). The $\eta'(\omega)$ of the 20% S226 (octene-LLDPE) blend was higher than that

of LDPE ($\eta_{o, \text{LDPE}} > \eta_{o, \text{LLDPE}}$) for over a decade of ω. PDB was observed over the whole composition range, and the behavior was more pronounced in the LDPE-rich blends. The parameters of the Carreau Model were determined by fitting the $\eta'(\omega)$ data to equation 5 as discussed earlier. The extracted $\eta_o(\phi)$ data shows PDB for the LDPE-rich (the 20% S226) and the 50/50 blends, while η_o follows linear-additivity for the LLDPE-rich (the 80% S226) blend.

Palierne's model was used to estimate η_o of the 20% S226 blend; however, this composition may be outside the range of the applicability of the model (not sufficiently dilute). For the octene LLDPE, the deviation of model predictions from data $[(\eta_{o,theor} - \eta_{o,\exp})/\eta_{o,\exp}]$ was higher (~17%) at $\phi=0.2$ than that obtained for the butene S229 blend (~7% at $\phi=0.1$). However, no conclusion could be drawn from this comparison since the composition was different. In general, the strong PDB (in the LDPE-rich range) of the *butene* LLDPE (S229) was not that great in the *octene* LLDPE blends. This is evident in plots like $\eta'(\phi)|_{\omega \text{ or } \tau=\text{const}}$, and $G'(\phi)|_{\omega \text{ or } \tau=\text{const}}$.

Similarly, different data treatment techniques (Hussein, 1999) supported the η_o results in suggesting the miscibility of the 80% S226 blend. For the 50/50 *octene* blend, η_o exhibited PDB from linear-additivity rule, but less severe than that of the *butene* system. This suggests that longer branching in LLDPE improves miscibility with LDPE.

C. Immiscibility of Polyethylenes: Tentative explanations

Earlier, we pointed out the importance of molecular structure on the miscibility of polyethylenes. Further, the details of the molecular structure are becoming more important in view of the reported immiscibility of LLDPE/LLDPE systems (Utracki, 1989b) and liquid-liquid phase separation in 'pure' LLDPE [Hill and Puig, (1997); Munstedt et al., (1998); Gabriel et al., (1998); Wardhaugh and Williams (1995)]. Here, we will try to give a tentative explanation for the immiscibility of polymethylenes in light of our investigation of 'pure' polymers.

Both rheology and thermal analyses have shown that HDPE, lightly branched LDPE and LLDPE possess molecular order in the liquid state; however, this is not the case for a highly branched LLDPE which is suggested to have amorphous conformation (Hussein and Williams, 1998; Hussein and Williams, 1999a-c). The molecular order is accompanied by high temperature (208°, 227°C) transitions. This suggests a correlation between molecular architecture and conformation. Furthermore, *conformational* "mismatch" is evident especially in ZN-LLDPE with components ranging from linear to highly branched molecules (see Figure 1). The recognition of the molecular order (or disorder) and the high-T transitions in molten polyethylenes can explain the immiscibility of LLDPE and its blends with other polyethylenes. The existence of these transitions also implies the importance of another parameter that is usually overlooked, i.e. T_{mix} (Hussein and Williams, 1999c).

D. ALTERNATIVE EXPLANATIONS

Although the rheological evidence presented here seems persuasive that LLDPE/LDPE blends in the melt state contain heterogeneities of an emulsion nature for sufficiently high molecular weights and over wide composition ranges, there remains a question as to whether a proper interpretation is that immiscibility (liquid-liquid phase separation) occurs in these systems or other explanations exist (inasmuch as conventional thermodynamics might argue that such similar hydrocarbon chains should be mutually soluble).

For example, one might suggest that the blending process was simply insufficient, perhaps because of cross-linking, which is common in polyethylenes at high temperatures in the presence of oxygen. If so, the particles created would not blend homogeneously. However, our parallel study of such behavior (Hussein et al., 2000a) showed that this did not occur when the AO was present at the level used here. Furthermore, such cross-linking would not exhibit the ϕ-

dependence observed here nor the molecular weight dependence. Moreover, if cross-linking occurred, the particles would not yield data that could be fitted by emulsion-based theories which presume liquid state deformability impossible for cross-linked particles.

Alternatively, the blender might be accused of inadequacies because of the difficulty in shearing (or "conditioning") components having high viscosity when M_w was high. However, when blends of the same species but different M_w were prepared, there was rheological and DSC evidence only of homogeneity.

V. Conclusions

Several data-treatment approaches were used in this study. First, plots of $\eta'(\omega)$, $\eta'(\phi)|_{\omega=const}$, $\eta'(\tau)$, $G'(\omega)$, $G'(\phi)|_{\omega=const}$ were shown to be beneficial; making it possible to identify the miscible and phase-separated regions in the high-M_w blends. Second, the comparison of $\eta'(\omega)$ and $\eta(\dot{\gamma})$ was found to be an important indicator of miscibility. Third, the four-parameter Carreau model was used to model $\eta'(\omega)$ data, allowing the assessment of miscibility through $\eta_o(\phi)$ and $n(\phi)$. Certain techniques, like $\eta'(\phi)|_{\omega\ or\ \tau=const}$, were found to be particularly useful. However, for ω-sweep measurements, plots of $\eta'(\phi)|_{\omega=const}$ are easy to generate.

In conclusion, the effects of molecular weight and branch type on the miscibility of LLDPE/LDPE blends were investigated. The following is a summary of the previous observations suggested by the different methods of data treatment:

a. Blends of low-M_w ZN-LLDPE (butene) and LDPE are likel*y miscible* over all ϕ.

b. Blends of high-M_w ZN-LLDPE (butene) and LDPE mixed at 190^oC are *partially* miscible. *Immiscibilty* is likely to occur around the 50/50 composition and in the LDPE-rich blends. Blends are likely *miscible* in the LLDPE-rich range.

c. The immiscibility of the blends leads to $\eta'(\phi)$ and $\eta'(\omega)$ that *can* be explained by *emulsion* models (e.g., dilute emulsion model; Palierne model; Bousmina-Kerner model).

d. The complex molecular mixture constituting ZN-LLDPE and the 'mismatch' in the molecular *conformation* of LLDPE and LDPE is likely responsible for their immiscibility. Further conclusions are contained in another investigation wherein metallocene LLDPE is involved (Hussein and Williams, 2003).

e. Increasing the branch length from butene to octene in LLDPE increases miscibility with LDPE.

VI. Acknowledgements

VII. References

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Table 1: Molecular Characteristics of LLDPE/LDPE blends used in Previous Studies

LLDPE*			LDPE			Blend Miscibility	Reference
M_w	ρ, g/cm^3 (solid, at 25°C)	BC**	M_w	ρ, g/cm^3	CH$_3$/1000C		
133K	N/A	N/A	64.2K	N/A	N/A	Immiscible	Utracki and Schlund
133K	0.9185	N/A	130K	0.9215	N/A	Partially Miscible	Datta and Birley
133K	N/A	N/A	152K	N/A	N/A	Partially Miscible	Utracki (1989b)
130K	N/A	N/A	110K	N/A	N/A	Partially Miscible	Mullar and Balsamo
134K	N/A	16	388K	N/A	32***	Partially Miscible	Lee and Denn

  *Ziegler-Natta resins
**Branch Content, CH$_3$/1000 C
***Total number of short and long branches

Table 2: Characterization of as-received polyethylenes

Sample Code	Density 25°C g/cm^3	Polymer Type	CH$_3$/1000 C	M$_n$	M$_w$	M$_w$/M$_n$=PD	M$_z$	M.I.
S227	0.924	LLDPE(butene)*	20.7	14.7 K	50.8K	3.46	115 K	20
S229	0.918	LLDPE(butene)*	22.1	29.5 K	105.3 K	3.57	268 K	1.0
S226	0.920	LLDPE(octene)*	14.7	17.0 K	106.0 K	6.2	343 K	1.0
S231	0.918	LDPE	23**	13.4 K	71.8K	5.37	183 K	7.0
S216	0.919	LDPE	22**	15.5 K	99.5K	6.45	281 K	0.75

* Ziegler-Natta resin
**Total number of short and long branches

Table 3: Blends of S229 and S216: Parameters for Equation 5

Composition	η_o (Pas), $x10^{-2}$	θ (s)	m_1	m_2
S216 (LDPE)	354	19.6	0.78	0.74
10% S229	373	21.3	0.75	0.74
30% S229	341	20.1	0.73	0.68
50% S229	316	9.8	0.50	1.0
70% S229	203	0.7	0.37	1.68
90% S229	120	0.16	0.40	1.61
100% S229 (LLDPE)	92	0.13	0.53	1.2

Legends for Figures:

Figure 1. Schematic behavior of $\eta(\phi)$ for soluble and immiscible (emulsion) blends.

Figure 2. TREF profiles for LLDPEs: (a) S227 (butene); (b) S229 (butene); (c) S226 (octene).

Figure 3. TREF profiles for LDPE: (a) S216 (b) S231.

Figure 4. $\eta'(\phi)$ for blends of S227 (butene LLDPE) and S231 (LDPE), (low-M_w pair, $T_{test}=140^oC$, $\gamma^o=10\%$, $\omega=1$ rad/s, $T_{mix}=190^oC$).

Figure 5. $\eta'(\omega)$ for high-M_w pair. $T_{test}=190^oC$, $T_{mix}=190^oC$ over range $\omega=0.01$ to 100 rad/s.

Figure 6. $\eta'(\phi)$ for blends of S229 (butene LLDPE) and S216 (LDPE), (high-M_w pair, $T_{test}=190^oC$, $\gamma^o=10\%$, $\omega=0.1$ rad/s, $T_{mix}=190^oC$).

Figure 7. Comparison of $\eta(\dot\gamma)$ and $\eta^*(\omega)$ for blends of S229 (butene LLDPE) and S216 (LDPE), (high-M_w pair, $T_{test}=190^oC$, $\gamma^o=10\%$, $\dot\gamma=0.01$-1 s^{-1}, $T_{mix}=190^oC$).

Figure 8. $\eta_o(\phi)$ obtained with Carreau model from $\eta'(\omega)$ data in Figure 5 for blends of S229 (butene LLDPE) and S216 (LDPE), (high-M_w pair, $T_{test}=190^oC$, $\gamma^o=10\%$, $T_{mix}=190^oC$).

Figure 9. Predictions of Palierne model for G'(ϕ) when ($\alpha/R=3\times10^3$ N/m^2 for all ϕ, as compared with data for blends of S229 (LLDPE) and S216 (LDPE) at $T_{test}=190^oC$.

Figure 10. Palierne and Bousmina Model Predictions of G' and G" for the 10% S229 (butene LLDPE) blend with LDPE ($\alpha/R=3\times10^3$ N/m^2, $T_{test}=190^oC$, $\gamma^o=10\%$, $T_{mix}=190^oC$).

Figure 11. $\eta'(\tau)$ for blends of S226 (octene LLDPE) and S216 (LDPE), ($T_{test}=190^oC$, $\gamma^o=10\%$, $\omega=0.1$-100 rad/s, $T_{mix}=190^oC$).

Fig. 1

η_B

η_o

η_A

Emulsion Viscosity

"Rule of Mixtures"

0

1

ϕ, volume fraction A

Fig 2a

Co/Ho 90°C = 8.0
Co/Ho 82°C = 2.2

Integrated Area
25-60°C – 15.8%
60-75°C – 34.2%
75-90°C – 38.9%
90-105°C – 11.1%

74.6°C

85.3°C

Fig 2b

Co/Ho = 3.5

Integrated Area
25-60°C – 16.2%
60-75°C – 22.1%
75-90°C – 39.8%
90-105°C – 22%

54.8°C

Fig 2c

Co/Ho 90°C = 2.7
Co/Ho 91.5°C = 3.1

Integrated Area
25-60°C – 6.1%
60-75°C – 27.1%
75-90°C – 40.1%
90-105°C – 26.7%

95.7°C

Fig 3a

Co/Ho = N/A

Integrated Areas
25-60°C – 11.2%
60-75°C – 49.0%
75-90°C – 39.7%
90-105°C – 0.0%

7601°C

Fig 3b

Co/Ho = N/A

Integrated Areas
25-60ºC – 22.0%
60-75ºC – 67.1%
75-90ºC – 10.9%
90-105ºC – 0.0%

72.7ºC

Fig. 4

Fig. 5

η', Pas

- ● S216 (LDPE)
- ⬡ 10% S229
- △ 30% S229
- ▽ 50% S229
- ▲ 70% S229
- ☐ 90% S229
- ◯ S229 (LLDPE)

high-M_w pair

105/100k

Powerlaw Regime, $\eta' \propto \omega^{n-1}$

ϕ

Frequency, ω, rad/s

Fig. 6

Fig. 7

Fig. 8

Fig. 9

Fig. 10

Fig. 11