

Rheological Study of the Influence of Branch Content on the Miscibility of Octene m-LLDPE and ZN-LLDPE in LDPE

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The influences of branch content on the miscibility of octene LLDPE made by metallocene catalyst (m-LLDPE) and by Ziegler-Natta LLDPE (ZN-LLDPE) in LDPE were investigated with rheological methods. Dynamic and steady shear measurements were carried out in a Rheometrics Mechanical Spectrometer 800. Here, m-LLDPEs were used to isolate interaction of molecular parameters. Blends of octene m-LLDPE and ZN-LLDPE with LDPE were mixed at 190°C in the presence of an adequate amount of antioxidant. The miscibilities of blends were revealed by the dependence of their measured η_0 , η' and G' on blend composition as well as on agreement with predictions of different emulsion models. Blends of m-LLDPE with LDPE were found to be almost miscible in the LLDPE branching range 10–30 branches/1000 C. However, immiscibility was found to develop at lower LLDPE branch contents. For ZN-LLDPE/LDPE systems, branch content plays a significant role especially at low branch contents. The comparison of m-LLDPE and ZN-LLDPE systems suggest the strong influence of branch distribution (uniform and random, respectively). Palierno, Bousmina, and Scholz models fitted the loss and storage moduli data well with a value of α/R in the range 10^3 – 10^4 N/m². *Polym. Eng. Sci.* 44:660–672, 2004.

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INTRODUCTION

The miscibility of blends of polyethylenes has received a great deal of attention during the past decade, due to its significance to the understanding of processing and final properties of blends containing different types of polyethylenes (PEs). Although substantial efforts have been made with the subject, an agreement has not yet been achieved concerning the melt miscibility of blends of different kinds of PEs. For blends composed of high-density polyethylene (HDPE) and LDPE as well as HDPE and LLDPE, Hill and co-workers proposed liquid-liquid phase separation (1–3), while Alamo and co-workers suggested complete homogeneity (4, 5). The first group used TEM,

while the second group used SANS. Recently, Stori's group (6, 7) used TEM, AFM and DSC to study the miscibility of blends of linear and branched PEs. Also, other techniques like thermal fractionation and molecular simulation techniques have recently been introduced (8, 9). For blends of HDPE/LLDPE systems, researchers have shown that the branch content (BC) of LLDPE is the major molecular factor that controls miscibility (5–7, 9–11).

Blends of LLDPE and LDPE have been reported miscible, immiscible or partially miscible (9, 12–18). However, most of these studies have used LLDPE from multi-site Ziegler-Natta catalysis (ZN-LLDPE). 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 (19). Previous work on blends of HDPE and branched polyethylenes showed that the phase separation in melt state is governed by molecular parameters like M_w , MWD, BC and branch

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distribution along the backbone (2, 4, 9, 20). Hence, the previous studies that used ZN-LLDPE do not give a definite answer on miscibility because of the interaction of many molecular parameters. In fact, some researchers have suspected that "pure" (unblended) ZN-LLDPE could be intrinsically multiphase (21–24). With the development of metallocene catalysts, now it is possible to obtain m-LLDPEs with very narrow MWD and almost uniform branch distribution. It should be noted that the effect of these molecular parameters of m-LLDPE on its miscibility with LDPE have not been studied, except in the recent work of Xu *et al.* and Hussein *et al.* that investigated the effect of composition distribution for butene and hexene m-LLDPE/LDPE blends respectively (25, 26).

In this study, the effect of branch content of octene m-LLDPE on its miscibility in LDPE was studied. In addition, ZN-LLDPEs of almost the same average molecular characteristics (M_w ; BC) were examined for miscibility in the same LDPE to provide insight on the effect of composition distribution relative to the BC variable. Here, rheology was the tool of investigation.

Generally, phase separation causes the storage and loss moduli G' and G'' to exceed values for the matrix phase, owing to the presence of droplets of the dispersed phase. This increase is a result of "emulsion morphology" present in phase separated systems. Even in a mixture of two Newtonian liquids, the emulsion morphology gives rise to a non-zero G' . That is, their emulsion exhibits elastic behavior due to interfacial tension between the phases, in addition to the viscous nature (27, 28).

Scholz *et al.* (29) derived a constitutive equation for dilute emulsions of noninteracting, spherical and monodisperse droplets of Newtonian liquids. The two liquids were assumed incompressible, and totally immiscible. For the linear viscoelastic range of deformation, the emulsion was shown to have dynamic moduli given by:

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

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

where,

η_m = the viscosity (Newtonian) of the matrix liquid.

η_d = the viscosity (Newtonian) of the dispersed droplets

$$k = \frac{\eta_d}{\eta_m}$$

R = radius of the dispersed domains

α = surface tension between the two liquids

ϕ = volume fraction of the dispersed phase.

In the Newtonian limit η' reduces to η_0 and Eq 1 reduces to Taylor's expression (27). The storage modulus $G'(\omega)$ obtained experimentally at low ω for immiscible polymer blends, other than PE/PE systems, was reported to be higher than those of the components (29–33). Earlier work of the Williams group

showed similar increase in $\eta'(\phi)$ and $\eta(\dot{\gamma})$ for an immiscible HDPE/PMMA system (34). Their rheological measurements were supported by SEM micrographs. The low-shear data showed excellent agreement with the predictions of $\eta_0(\phi)$ by the dilute emulsion model (25, 26). For more detailed literature review on rheology of multiphase systems, the reader is referred to the authors' recent publications and references therein (16, 17).

Here, rheology was employed to investigate the effect of branch content on the miscibility of m-LLDPE and ZN-LLDPE in LDPE and experimental results were compared with predictions of different emulsion models.

EXPERIMENTAL

Materials

The polyethylenes used in this study were produced by NOVA Chemicals Corp. of Calgary, Canada. The metallocene LLDPEs were experimental resins. Two pairs of LLDPE and LDPE were selected to study the effect of BC. The details of the molecular parameters are given in Table 1, which provides information about density at room temperature, melt index (MI) at 190°C, number-average and weight-average molecular weights as well as polydispersity (PD) obtained by GPC in our laboratory and branch content (NMR and FTIR) reported as number of branches/1000 backbone carbon atoms. The label 1 denotes the LLDPE with low BC and 2 is for the LLDPE resin with high BC. The same LDPE was used in all of these blends. The effect of the branch content of LLDPE was investigated by testing blends of LLDPE1 with LDPE and comparing results to those of LLDPE2 with LDPE. ZN-LLDPEs and m-LLDPEs were paired to study one variable at a time. As can be seen from Table 1, comparison of results for LLDPE1 and LLDPE2 will reveal the effect of BC on the miscibility of LLDPE in LDPE for both ZN and m-LLDPE blends. Also, since the m-LLDPEs and ZN-LLDPEs do have about the same average BC then the comparison of m-LLDPE1 vs ZN-LLDPE1 and m-LLDPE2 vs. ZN-LLDPE2 will provide a close look at the effect of composition distribution on the miscibility of m-LLDPE with LDPE.

Melt Blending and Sample Preparation

Octene m-LLDPE and ZN-LLDPE were mixed with LDPE in a Haake Rheocord 90 melt blender at 190°C, 50 rpm for 10 minutes in the presence of 1000 ppm of extra antioxidant (AO). The AO consisted of two AO components both made by Ciba Specialty Chemicals.

Table 1. Characterization of Resins.

Resin	Density	MI	M_n	M_w	PD	BC
m-LLDPE1	0.9218	2.6	38,700	77,400	2.0	11.4
m-LLDPE2	0.9023	3.2	25,700	69,390	2.7	30.4
ZN-LLDPE1	0.9233	1.02	20,500	102,500	5.0	12.9
ZN-LLDPE2	0.9021	1.02	17,300	105,530	6.1	35.0
LDPE*	0.919	0.75	15,458	99,464	6.45	*

*Total number of short branches = 22.

One was Irganox 1010 (Phenol B, tetrakis[methylene 3-(3',5'-di-*t*-butylphenol) propionate]methane, $M_w = 1178$, the primary AO) and the other a phosphorous-containing compound Irgafos 168 (P-1, tris[2,4-di-*t*-butylphenol] phosphite, $M_w = 646$, the secondary antioxidant). Here, an adequate amount of extra AO mixture was added to the as-received resin(s) before melt conditioning in the blender. Details on the determination of the adequate amount needed to avoid degradation are discussed elsewhere (35). Pure resins as well as blends of 10, 30, 50, and 80 wt% LLDPE were conditioned in the melt blender. The maximum difference between the densities of the resins is within 2%; hence weight and volume fractions can be interchanged. The "conditioned" samples were then removed from the mixing bowl, and air-cooled.

Specimens for rheological testing were prepared from melt-blended resin(s) by molding discs, about 2 mm thick and 25-mm diameter, designed to match the platen diameters employed in the rheometer; this molding process was operated in a Carver hydraulic press.

Rheological Experiments

A Rheometrics Mechanical Spectrometer (RMS 800) was used in various automated modes to study both linear and nonlinear rheological properties as functions of steady shear rate $\dot{\gamma}$ (nonlinear properties), strain amplitude γ° , and sinusoidal frequency ω (linear properties). To show the reproducibility of the RMS 800 measurements, results for the same as-received LDPE tested at the same conditions in RMS 800 (in Canada) and in a Rheometrics ARES (in Saudi Arabia) are shown in Fig. 1a. The stability of the blends was established from the one-hour sweep measurements, $G'(t)$.

As suggested in the previous degradation study (35), the rheology of as-received and conditioned pure resins should be the same. To confirm that degradation did not take place during melt blending, the rheology of as-received and conditioned ZN-LLDPE1 is shown in Fig. 1b as an example. This test was always performed on pure resins before we proceeded with melt blending. All rheological measurements were performed at 190°C and under nitrogen environment using a cone-and-plate geometry of 25-mm-diameter platens. The cone angle was 0.1 radian with a 53 μm truncated apex. The dynamic ω -sweep tests were carried out in the range 0.01–100 rad/s at strain amplitude (γ°) of 15%, confirmed by a strain sweep test to be in the linear viscoelastic range. The steady shear measurements were performed in the range 0.01–5 s^{-1} ; higher shear rates were avoided to stay away from the known elastic instabilities.

RESULTS AND DISCUSSION

Effect of Branch Content on the Miscibility of m-LLDPEs in LDPE

For blends of m-LLDPE1 (BC = 11.4 $\text{CH}_3/1000$ C) and LDPE (BC = 22 $\text{CH}_3/1000$ C) dynamic shear data

were obtained. Results for $\eta'(\omega)$ and $G'(\omega)$ for blends involving m-LLDPE1 are given in Figs. 2a and 2b respectively. Results are shown for the 10%, 30%, 50%, and 80% m-LLDPE1 blends as well as for the pure resins. Similarly, plots of $\eta'(\omega)$ and $G'(\omega)$ for blends m-LLDPE2 (BC = 30.4 $\text{CH}_3/1000$ C) are shown in Figs. 3a and 3b. Data for $\eta'(\phi)$ at low ω near-Newtonian regime ($\omega = 0.5$ rad/s) were extracted from Figs. 2a and 3a and plotted in Fig. 4a. Results show that $\eta'(\phi)$ for blends of m-LLDPE2 (high BC) with LDPE followed linear additivity rule. Hence, these blends are likely to be miscible in the whole composition range. For the low BC pair (m-LLDPE1), weak positive deviation behavior (PDB) of $\eta'(\phi)$ from linear additivity rule ($\eta = \sum \phi \eta_i$, indicated by a solid straight line) was observed in the 30% and 50% m-LLDPE1 blends suggesting partial miscibility even at these compositions. This is also evident in the wide differences between the predictions of Scholz *et al.* (29) dilute emulsion model (see Fig. 4a) and the experimental data as presented in Fig. 4a. Experimental data and model predictions suggest a weak influence for branch content of m-LLDPE on its miscibility with LDPE. However, it should be noted that partial immiscibility might develop at low branch contents as observed in the results of the m-LLDPE1 pair. Also, these results are limited to m-LLDPE blends with branch content in the range of 11–30 branches/1000 C. Plots of $\eta'(\phi)|_{\tau = \text{const}}$ obtained through curve fitting of $\eta'(\tau)$ data [suggested by Van Oene (36)] produced similar results.

Further, ARES Orchestrator software was used to fit the $\eta'(\omega)$ data for blends of m-LLDPE1 and m-LLDPE2 with LDPE to the Carreau model. Zero shear viscosity, η_0 , was obtained from the fitting and results for both pairs were displayed in Fig. 4b. Plots of $\eta_0(\phi)$ support the previous finding from $\eta'(\phi)$ data. Again, the PDB is weak and the high BC pair is close to being completely miscible in the whole composition range, while the low BC pair is showing weak PDB immiscibility. This weakness can easily be observed in the significant difference between the η_0 obtained for the 10% m-LLDPE1 from rheological data and the predictions of the Einstein suspension model [$\eta_b = \eta_m(1 + 2.5\phi)$] derived for dilute Newtonian fluids which represents an upper bound for the systems discussed in this study. Here, $\eta_0(\phi)$ data support the weak effect of BC (11–30 $\text{CH}_3/1000$ C) on the miscibility of m-LLDPE with LDPE.

Furthermore, steady shear measurements were performed on the 10% blend of m-LLDPE1 and m-LLDPE2 with LDPE for the comparison of $\eta^*(\omega)$ and $\eta(\dot{\gamma})$. The steady shear measurements were obtained in the cone-and-plate geometry in the range $\dot{\gamma} = 0.01 - 1$ s^{-1} ; 1 minute of steady shearing before measurements was followed by 30 seconds of measurement time. Lack of superposition of $\eta^*(\omega)$ and $\eta(\dot{\gamma})$ [Cox-Merz behavior (37)] indicates immiscibility as suggested by Utracki and Schlund (38). The results given in Fig. 4c do not show any significant differences between the low BC and the high BC m-LLDPE blends that support the above findings. The Cox-Merz rule test is not sensitive enough to

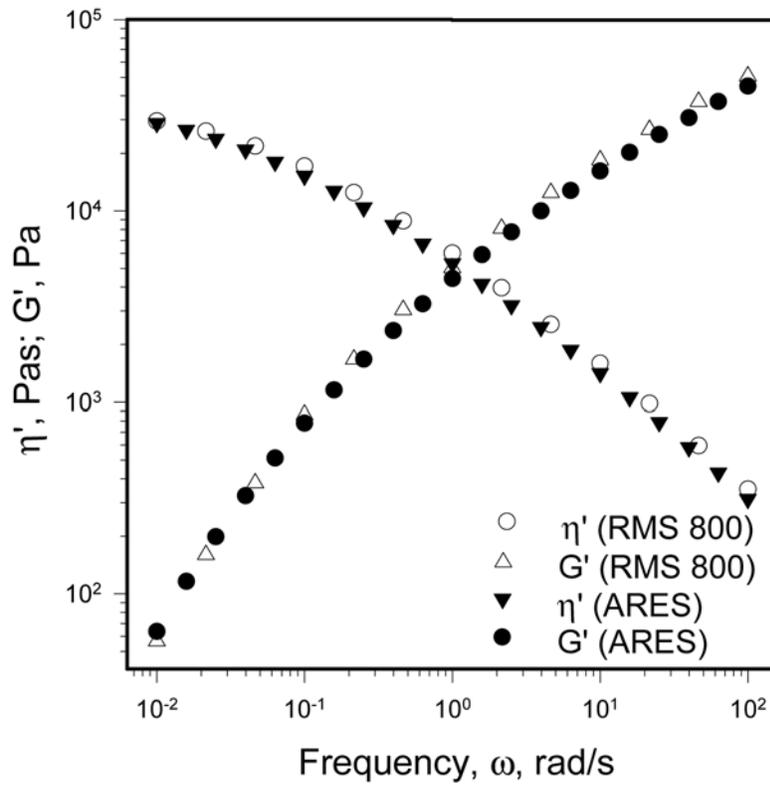


Fig. 1a. Dynamic frequency sweep for as-received LDPE obtained in RMS and ARES ($T_{test} = 190^{\circ}\text{C}$, $\gamma^{\circ} = 15\%$).

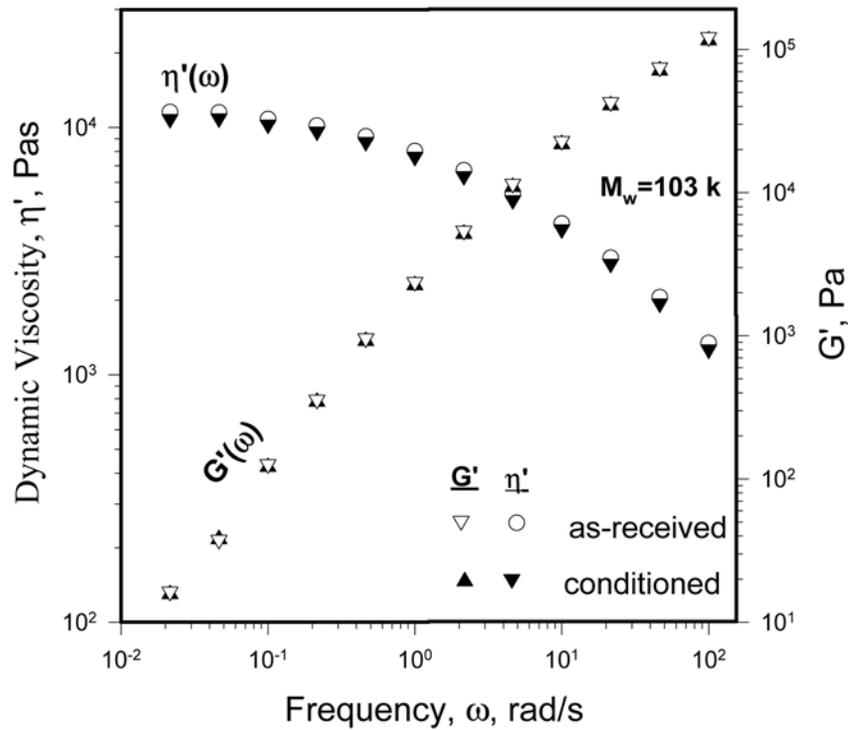


Fig. 1b. Comparison of the rheology of as-received and conditioned (with extra 1000 ppm AO) ZN-LLDPE1 ($T_{cond} = 190^{\circ}\text{C}$, $T_{test} = 190^{\circ}\text{C}$, $\gamma^{\circ} = 15\%$).

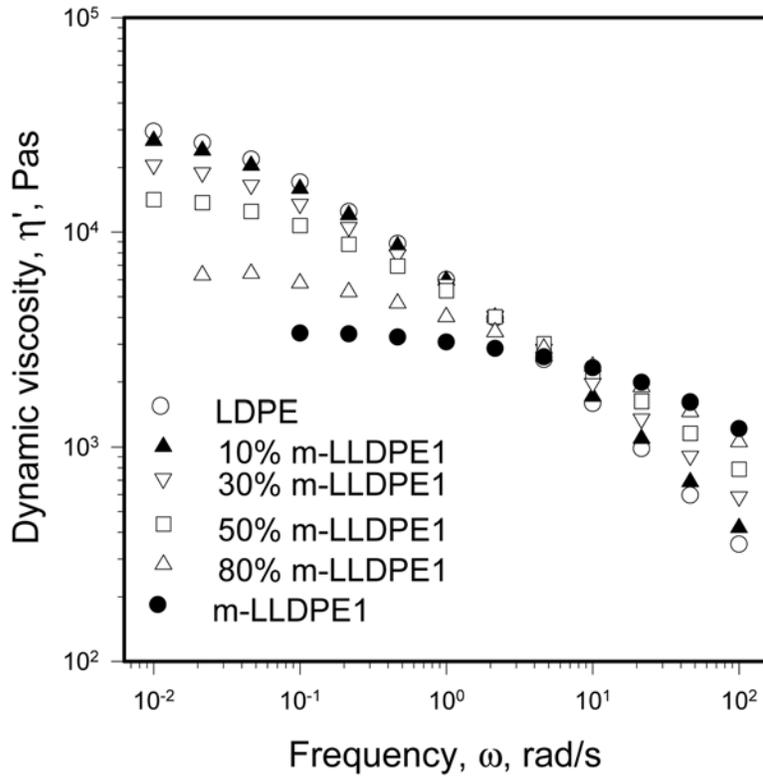


Fig. 2a. $\eta'(\omega)$ for blends of *m*-LLDPE1 ($BC = 11.4 \text{ CH}_3/1000 \text{ C}$) and LDPE ($T_{\text{cond}} = 190^\circ\text{C}$, $T_{\text{test}} = 190^\circ\text{C}$, $\gamma^\circ = 15\%$).

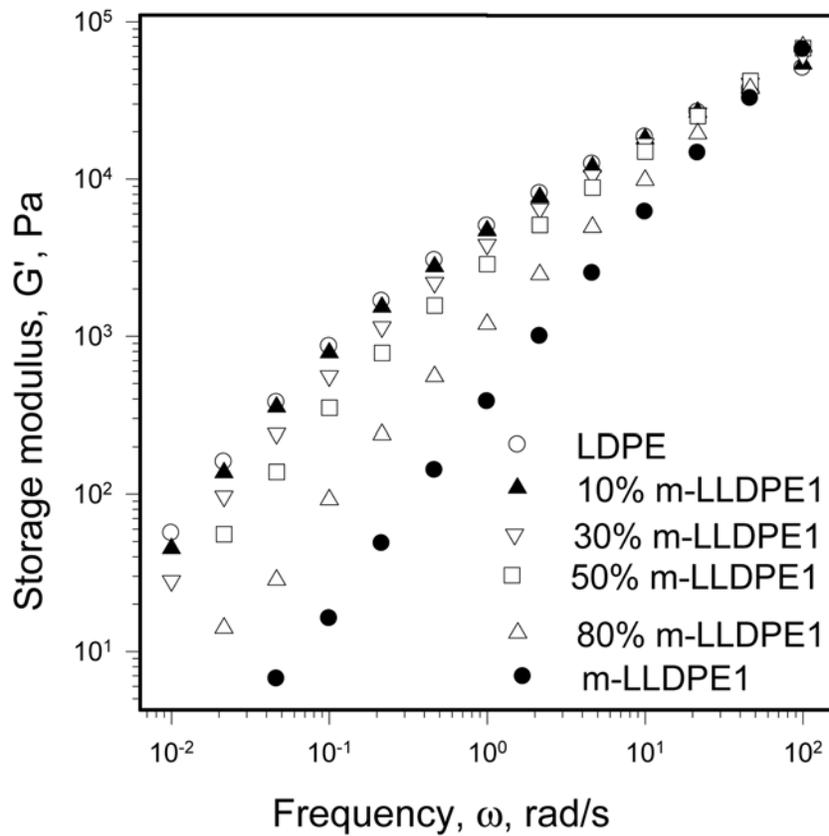


Fig. 2b. $G'(\omega)$ for blends of *m*-LLDPE1 ($BC = 11.4 \text{ CH}_3/1000 \text{ C}$) and LDPE ($T_{\text{cond}} = 190^\circ\text{C}$, $T_{\text{test}} = 190^\circ\text{C}$, $\gamma^\circ = 15\%$).

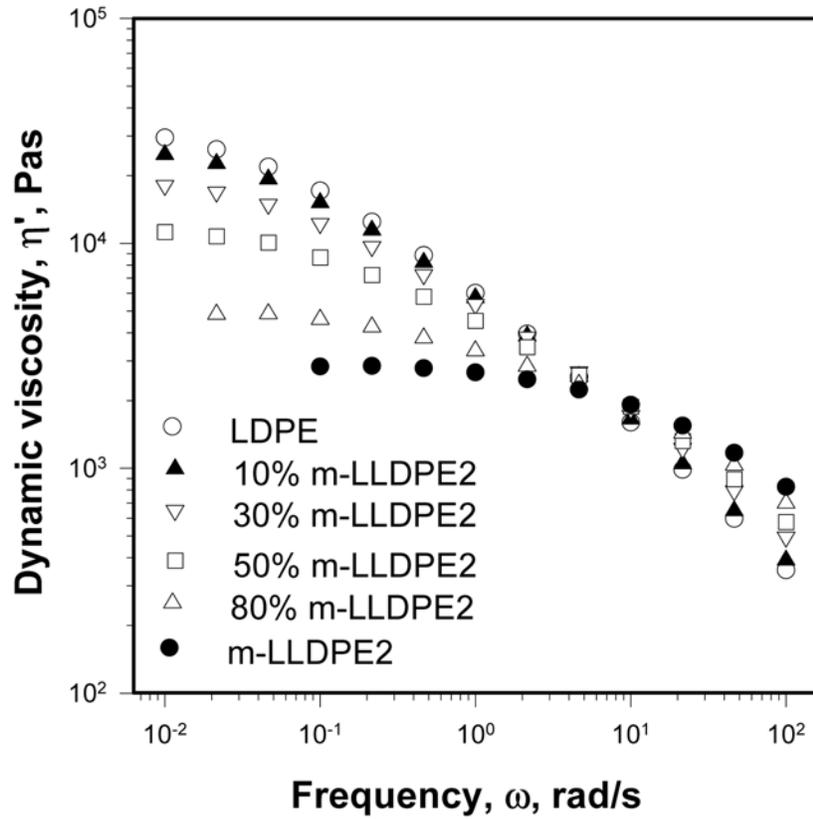


Fig. 3a. $\eta'(\omega)$ for blends of m-LLDPE2 ($BC = 30.4 \text{ CH}_3/1000 \text{ C}$) and LDPE ($T_{\text{cond}} = 190^\circ\text{C}$, $T_{\text{test}} = 190^\circ\text{C}$, $\gamma^\circ = 15\%$).

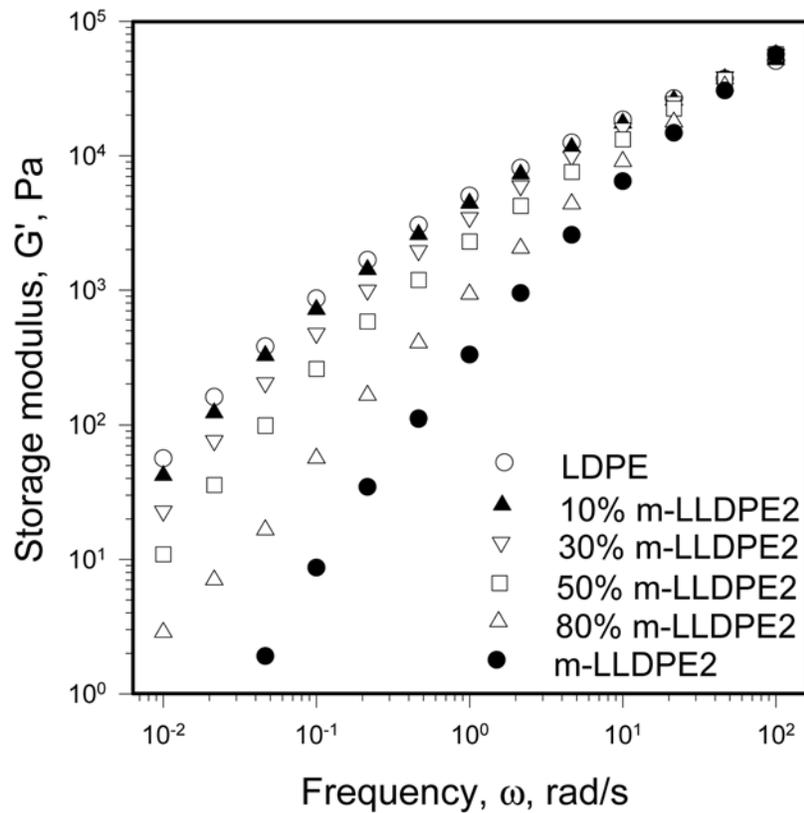


Fig. 3b. $G'(\omega)$ for blends of m-LLDPE2 ($BC = 30.4 \text{ CH}_3/1000 \text{ C}$) and LDPE ($T_{\text{cond}} = 190^\circ\text{C}$, $T_{\text{test}} = 190^\circ\text{C}$, $\gamma^\circ = 15\%$).

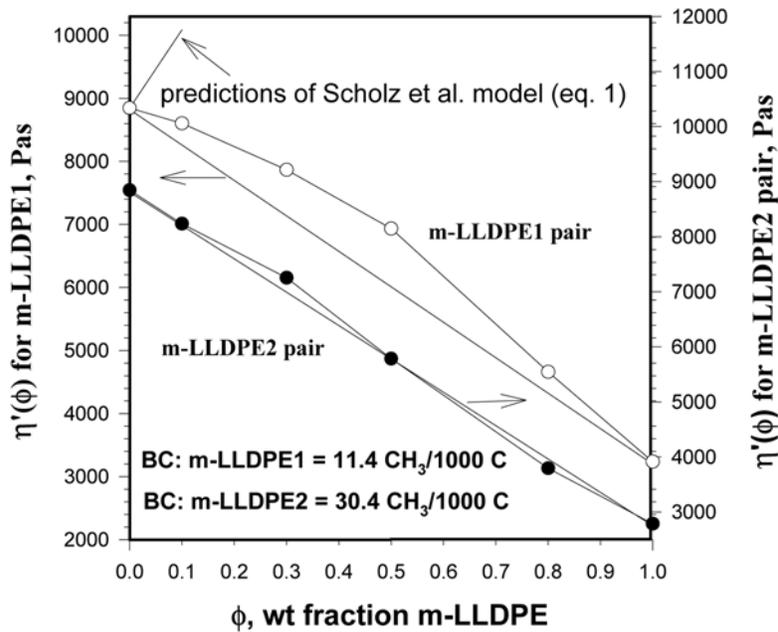


Fig. 4a. $\eta'(\phi)$ for blends of m-LLDPE1 and m-LLDPE2 with LDPE ($T_{cond} = 190^\circ\text{C}$, $T_{test} = 190^\circ\text{C}$, $\gamma^\circ = 15\%$, $\omega = 0.5 \text{ rad/s}$).

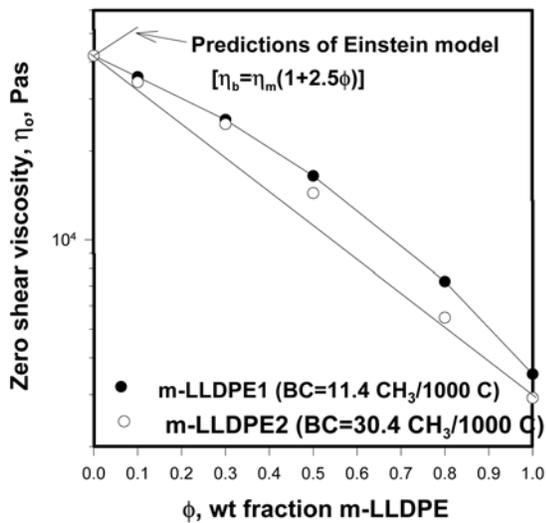


Fig. 4b. $\eta_0(\phi)$ for blends of m-LLDPE1 and m-LLDPE2 with LDPE ($T_{cond} = 190^\circ\text{C}$, $T_{test} = 190^\circ\text{C}$, $\gamma^\circ = 15\%$).

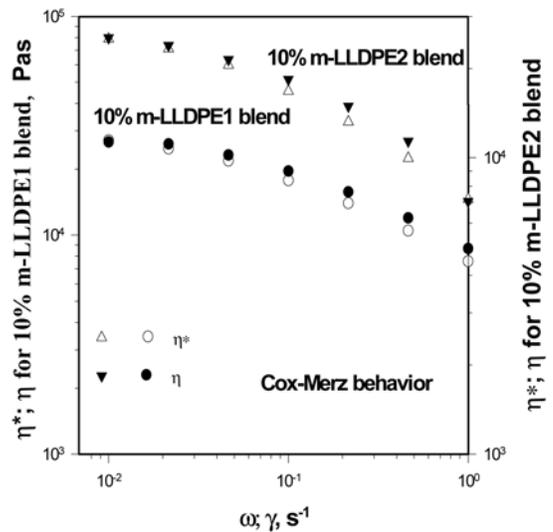


Fig. 4c. $\eta^*(\omega)$ and $\eta(\dot{\gamma})$ for 10% m-LLDPE blends with LDPE. ($T_{cond} = 190^\circ\text{C}$, $T_{test} = 190^\circ\text{C}$).

show differences between the low and the high-BC pair as observed in other methods of data analysis.

Effect of Branch Content on Miscibility of ZN-LLDPEs in LDPE

On the other hand, dynamic shear data were obtained for blends of ZN-LLDPE1 and ZN-LLDPE2 with LDPE. The same LDPE resin was used in blends of both ZN-LLDPE and m-LLDPEs. The ZN-LLDPE1 (BC = 12.9 CH₃/1000 C) and ZN-LLDPE2 (BC = 35.0 CH₃/1000 C) were of about the same M_w and MWD (see Table 1). Data for $\eta'(\omega)$ and $G'(\omega)$ for blends of ZN-LLDPE1 (low-BC pair) with LDPE are shown in Figs. 5a and 5b respectively. Also, plots of $\eta'(\omega)$ and $G'(\omega)$

for blends of ZN-LLDPE2 (high-BC pair) are given in Figs. 6a and 6b respectively.

The $\eta'(\phi)$ data for blends of ZN-LLDPE1 (low-BC pair) and ZN-LLDPE2 (high-BC pair) with LDPE were shown in Fig. 7. The results of $\eta'(\phi)$ at low ω ($\omega = 0.05 \text{ rad/s}$) are in agreement with the previous $\eta_0(\phi)$ data. Here, the low-BC pair is showing stronger PDB in comparison to the high-BC pair for LDPE-rich blends. A comparison of the rheology of the 10% ZN-LLDPE1 blend to predictions of Scholz *et al.* (29) suggests partial miscibility of the LDPE-rich blends. Computed $\eta_0(\phi)$ are plotted in Fig. 8 for ZN-LLDPE1 and ZN-LLDPE2 blends with LDPE at all compositions. Results of $\eta_0(\phi)$ followed the same trend of plots of $\eta'(\phi)$ at low ω .

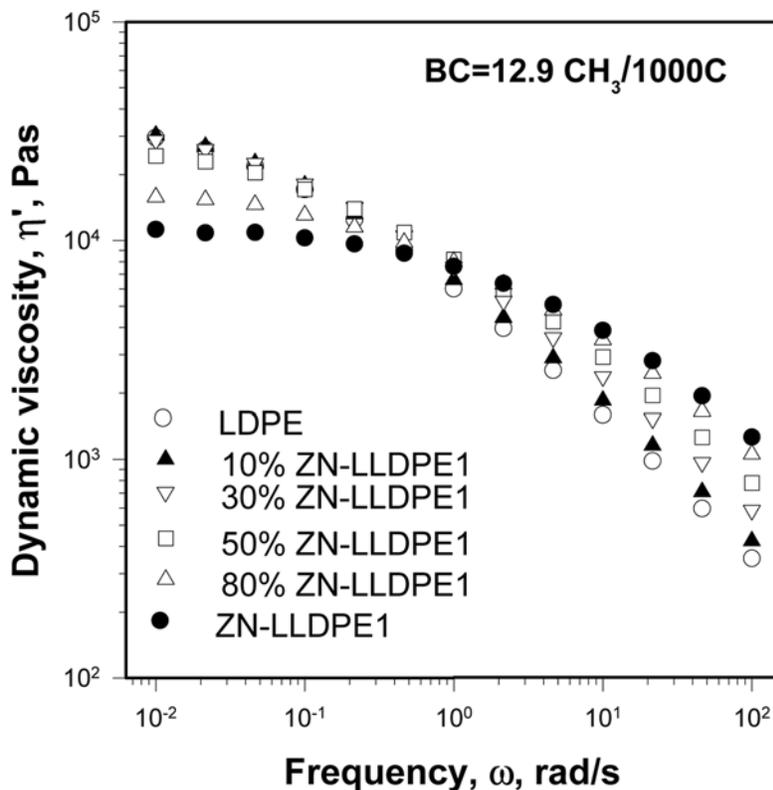


Fig. 5a. $\eta^*(\omega)$ for blends of ZN-LLDPE1 and LDPE ($T_{cond} = 190^\circ\text{C}$, $T_{test} = 190^\circ\text{C}$, $\gamma^\circ = 15\%$).

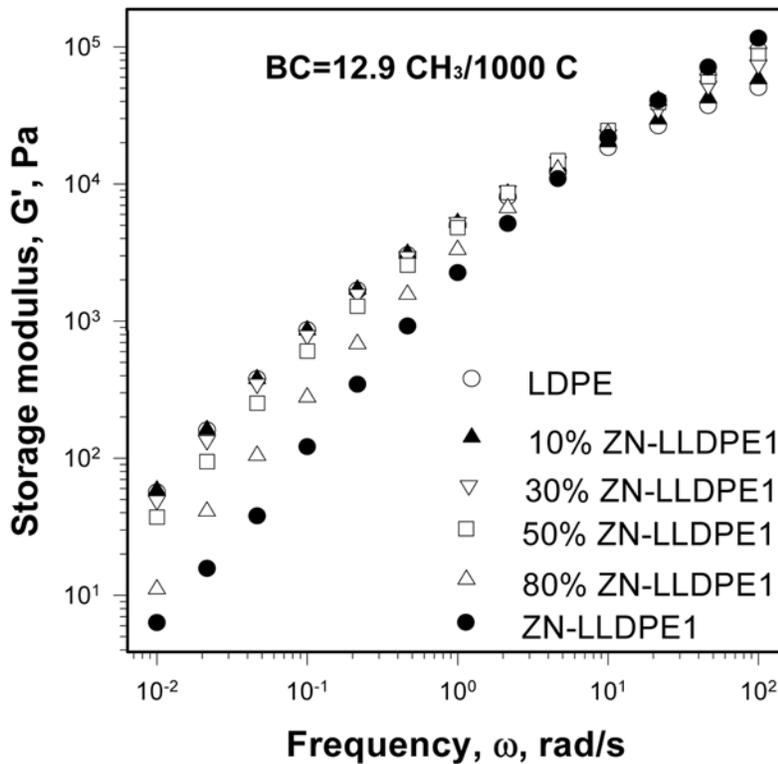


Fig. 5b. $G'(\omega)$ for blends of ZN-LLDPE1 and LDPE ($T_{cond} = 190^\circ\text{C}$, $T_{test} = 190^\circ\text{C}$, $\gamma^\circ = 15\%$).

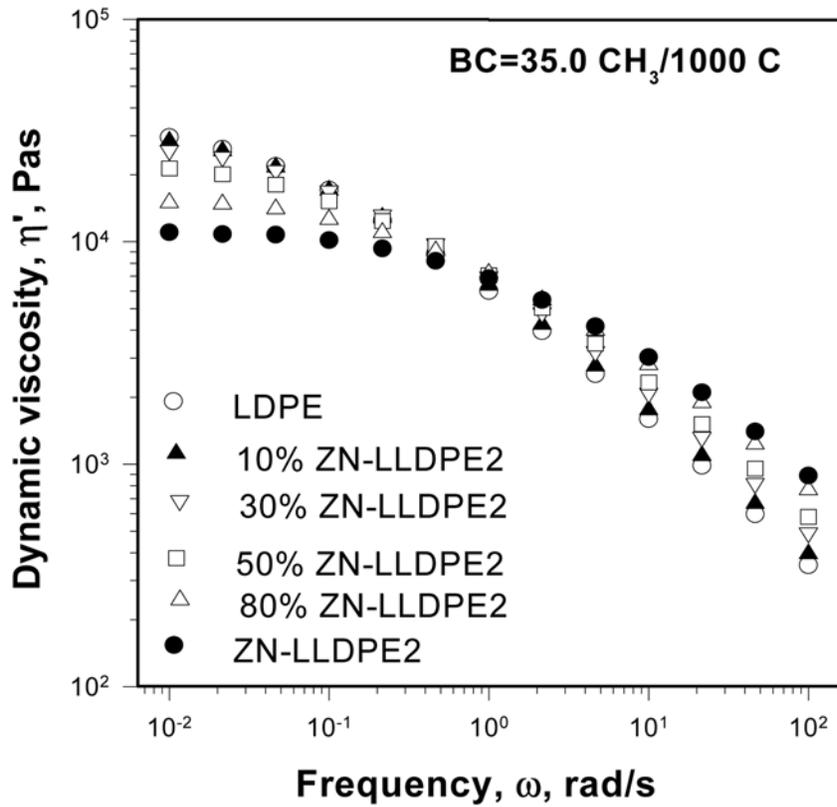


Fig. 6a. $\eta'(\omega)$ for blends of ZN-LLDPE2 and LDPE ($T_{cond} = 190^\circ\text{C}$, $T_{test} = 190^\circ\text{C}$, $\gamma^\circ = 15\%$).

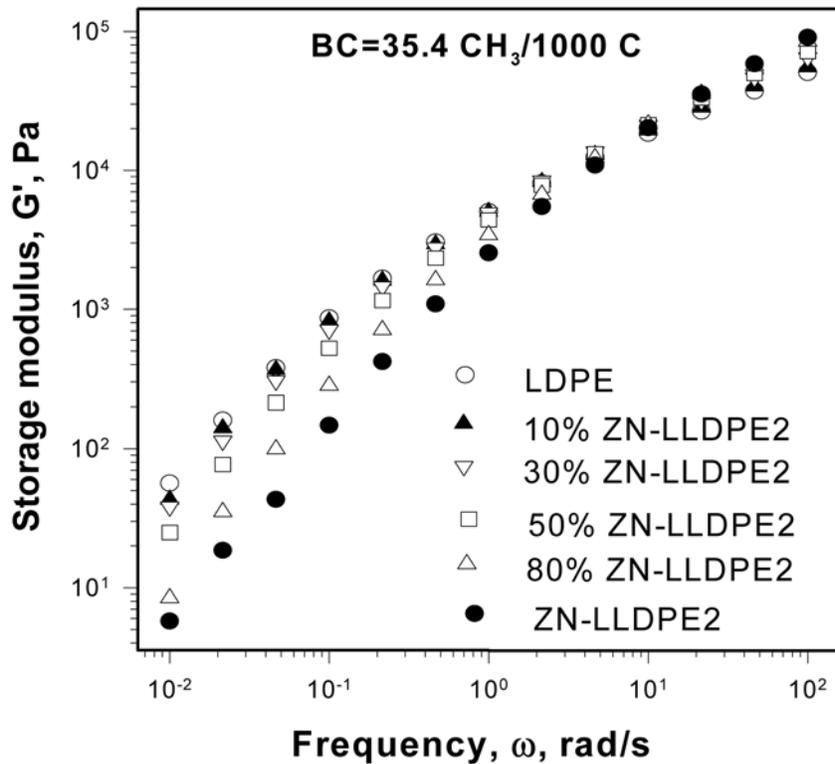


Fig. 6b. $G'(\omega)$ for blends of ZN-LLDPE2 and LDPE ($T_{cond} = 190^\circ\text{C}$, $T_{test} = 190^\circ\text{C}$, $\gamma^\circ = 15\%$).

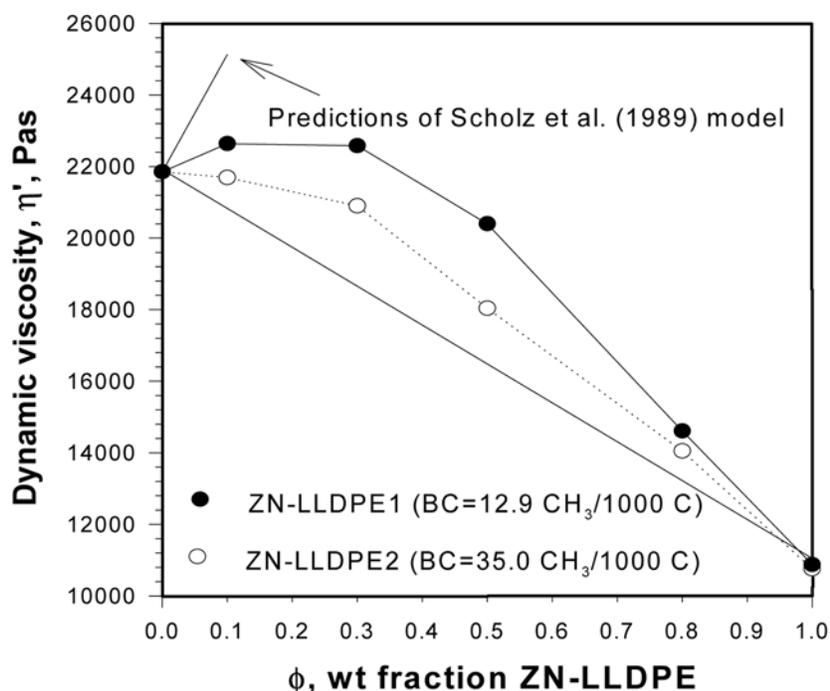


Fig. 7. $\eta'(\phi)$ for blends of ZN-LLDPE1 and ZN-LLDPE2 in LDPE ($T_{\text{cond}} = 190^\circ\text{C}$, $T_{\text{test}} = 190^\circ\text{C}$, $\gamma^\circ = 15\%$, $\omega = 0.05 \text{ rad/s}$).

Here, both systems show immiscibility in the LDPE-rich region. Immiscibility is pronounced in the ZN-LLDPE1/LDPE system (low BC) a trend that is similar to that observed for m-LLDPE1 blends with LDPE. These results indicate immiscibility of LLDPE in LDPE-rich blends. However, this miscibility is still partial immiscibility as observed by the differences between the experimental data and the predictions of the Einstein model shown in Fig. 8. Again, the high-BC blends of LLDPE (metallocene or Ziegler-Natta) showed improved miscibility with LDPE. However, the low-BC blends of ZN-LLDPE showed stronger immiscibility compared to weak immiscibility in the case of m-LLDPE blends. This suggests that when the LLDPE chain has longer linear segments (low branch content), immiscibility with LDPE is likely to evolve.

On the other hand, LLDPE with high branch content is expected to produce more random coil-like chains (39), similar to that of LDPE, and hence improve the conformational match and miscibility of LLDPE/LDPE blends (40, 41). The results on ZN-LLDPEs show the importance of the composition distribution, which seems to be more significant than branch content especially at low BC. However, for ZN-LLDPE these results can be generalized since ZN-LLDPEs tend to have higher degrees of short chain branching in the lower M_w components (42). This may explain the conflicting reports (as discussed earlier) about miscibility of ZN-LLDPEs in LDPE because each ZN-LLDPE is a unique "soup" of molecular structures. The significance of composition distribution over BC has also been acknowledged in a recent study of crystallization of ZN-LLDPE and m-LLDPE (43). However, one of the authors has recently reported the significance

of BC over composition distribution for blends of butene m-LLDPE and HDPE (44).

A comparison of the blend rheology of ZN-LLDPE1 and m-LLDPE1 systems is likely to reveal the effect of composition distribution. Results shown in Fig. 4b for blends of m-LLDPE1 and those given in Fig. 7 for blends of ZN-LLDPE1 suggest an increase in the degree of immiscibility in the ZN-LLDPE blends. Hence, the increase in the degree of immiscibility of the ZN-LLDPE pair is likely to be attributed to the effect of composition distribution in the ZN-LLDPE rather than to its branch content.

Once more in Fig. 9, a comparison was made between $G'(\phi)$ for ZN-LLDPE1 and m-LLDPE1 blends with LDPE. Both LLDPEs have about the same number of octene branches. The ZN-LLDPE1 pair showed a strong PDB in comparison with the m-LLDPE1 pair that follow linear additivity rule. These results reinforce the previous findings from other rheological tests. The $G'(\phi)$ data support our contention that composition distribution is of much stronger effect on miscibility than is branch content.

Moreover, $G'(\omega)$ and $G''(\omega)$ for the 10% ZN-LLDPE1 with LDPE are plotted in Fig. 10 as an example of the immiscible system. Experimental data are compared to the predictions of the model of Palierne and Bousmina (46) for emulsions of viscoelastic multiphase systems under small-amplitude dynamic shear (45, 46). For the Palierne model, the complex modulus of a blend, $G_b^*(\omega)$, is given by:

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

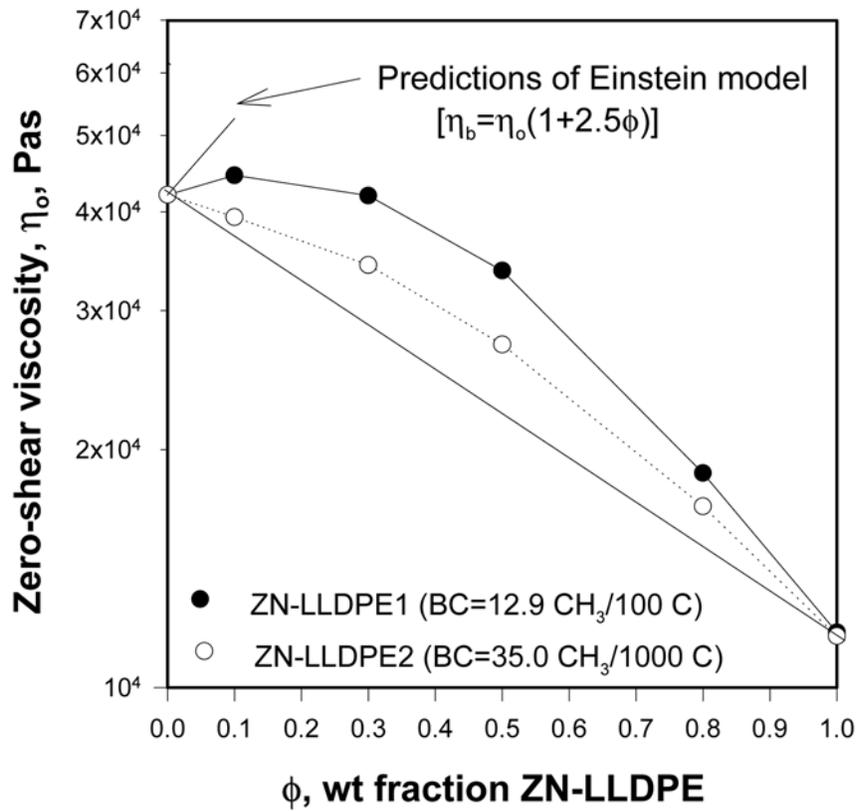


Fig. 8. $\eta_0(\phi)$ for blends of ZN-LLDPE1 and ZN-LLDPE2 with LDPE ($T_{cond} = 190^\circ\text{C}$, $T_{test} = 190^\circ\text{C}$, $\gamma^\circ = 15\%$).

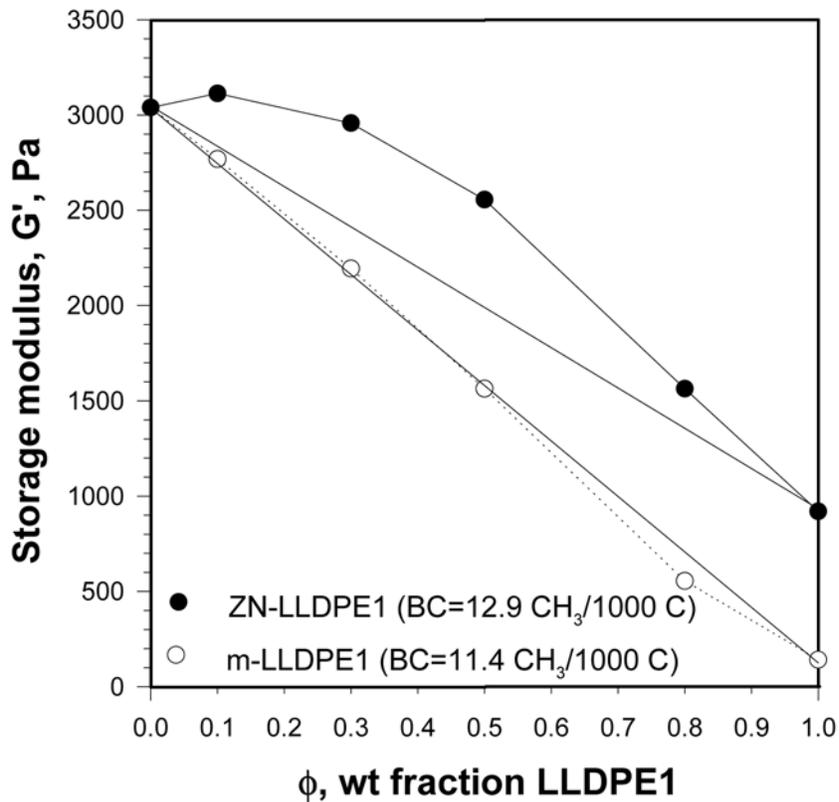


Fig. 9. $G'(\phi)$ for blends of m-LLDPE1 and ZN-LLDPE1 with LDPE ($T_{cond} = 190^\circ\text{C}$, $T_{test} = 190^\circ\text{C}$, $\gamma^\circ = 15\%$, $\omega = 0.5 \text{ rad/s}$).

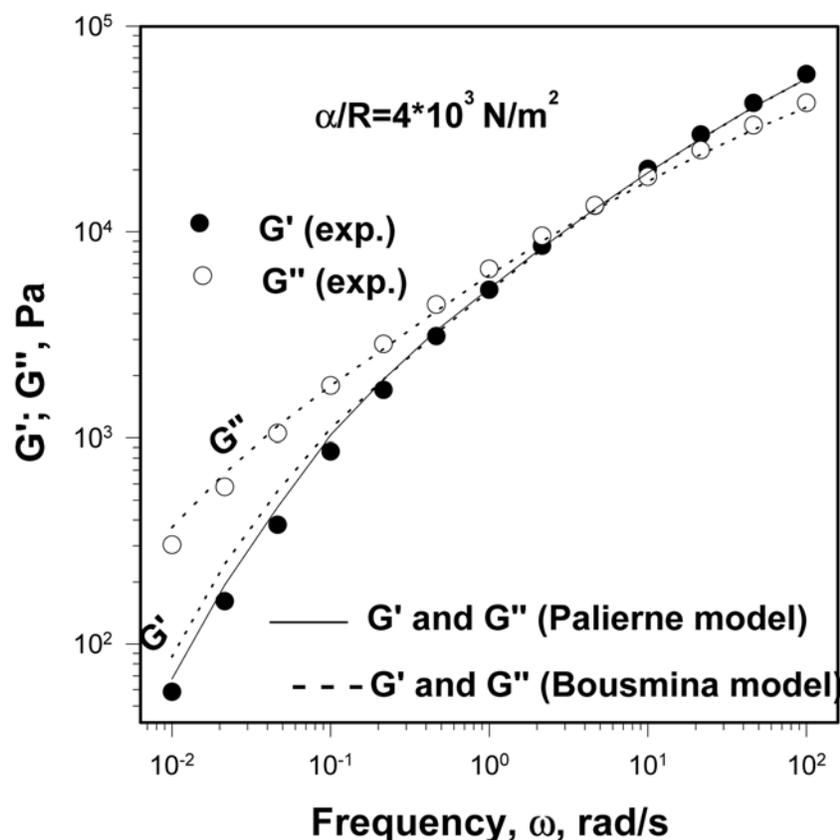


Fig. 10. Predictions of Palierne and Bousmina models for $G'(\omega)$ and $G''(\omega)$ as compared with experimental data for 10% ZN-LLDPE1 blend with LDPE ($\alpha/R = 4 \times 10^3 \text{ N/m}^2$) ($T_{\text{cond}} = 190^\circ\text{C}$, $T_{\text{test}} = 190^\circ\text{C}$, $\gamma^\circ = 15\%$).

where,

$$H(\omega) = \frac{4(\alpha/R)[2G_m^*(\omega) + 5G_d^*(\omega)] - [G_m^*(\omega) - G_d^*(\omega)] \times [16G_m^*(\omega) + 19G_d^*(\omega)]}{40(\alpha/R)[G_m^*(\omega) + G_d^*(\omega)] + [3G_m^*(\omega) + 2G_d^*(\omega)] \times [16G_m^*(\omega) + 19G_d^*(\omega)]} \quad (4)$$

Expressions for G' and G'' are given elsewhere (47). On the other hand, the expression for $G_b^*(\omega)$ for the Bousmina-Kerner model is given by:

$$G_b^* = G_m^* \frac{2(G_d^* + \alpha/R) + 3G_m^* + 3\phi(G_d^* + \alpha/R - G_m^*)}{2(G_d^* + \alpha/R) + 3G_m^* - 2\phi(G_d^* + \alpha/R - G_m^*)} \quad (5)$$

Expressions for G' and G'' are given elsewhere (16). Both models have given almost the same predictions for $G'(\omega)$ and $G''(\omega)$ as shown in Fig. 10. The best fit was obtained with $\alpha/R = 4 \times 10^3 \text{ N/m}^2$ which is comparable to that reported for known immiscible but compatibilized polymer blends (48). Similarly, Scholz *et al.* (Eq 2 above) predicted a value of α/R , at $\omega = 0.5 \text{ rad/s}$, for blends of the 10% ZN-LLDPE1 blend with LDPE that is higher than that of the 10% ZN-LLDPE2. However, at this stage no TEM scans are available for LLDPE/LDPE systems and we do not know whether the droplets are spherical, and hence it is very difficult to make any conclusions about the physical meaning of the above value of α/R .

All these results support our argument that the use of ZN-LLDPE in previous miscibility studies was not conclusive because of the heterogeneity of the structure of the ZN-LLDPE, which was found in this study to play a significant role. However, it should be noted that partial immiscibility might develop at low branch contents especially for ZN-LLDPE blends. This conclusion can be drawn from results shown in Fig. 9 where weak positive deviation behavior is observed in the LDPE-rich blends. At high BC, the m-LLDPE molecule becomes more similar to LDPE and this can lead to miscibility. However, at low BC the LLDPE molecule becomes more linear and hence more dissimilar.

CONCLUSIONS

In this study, the effect of branch content and distribution on the miscibility of octene m-LLDPE and ZN-LLDPE in LDPE was studied. It was found that blends of octene m-LLDPEs with LDPE were likely to be miscible for m-LLDPE systems with 10–30 branches/1000 C. Partial immiscibility is expected to develop at

low BC. For octene ZN-LLDPE, branch content has a significant role especially for low branch content LLDPE systems. Here, the low-BC blends of octene ZN-LLDPE showed stronger immiscibility with LDPE compared to weak immiscibility in the case of m-LLDPE blends. Different emulsion models (Einstein, Scholz *et al.*, Palierne and Bousmina) support the presence of a multiphase system in LDPE-rich blends of ZN-LLDPE with LDPE.

The dissimilarities in molecular structure are likely to be the reason behind the partial immiscibility. High branching in LLDPE chains is expected to produce conformations similar to that of the highly branched LDPE and hence improve the conformational match and miscibility of LLDPE/LDPE blends (40, 41). Comparison of the ZN and m-LLDPE blends with LDPE suggests that branch distribution has a more significant role to play in the miscibility of LLDPE/LDPE systems than branch content.

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