Influence of Branching Characteristics on Thermal and Mechanical Properties of Ziegler–Natta and Metallocene Hexene Linear Low-Density Polyethylene Blends with Low-Density Polyethylene

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ABSTRACT: The effect of the branch content (BC) and composition distribution (CD) of linear low-density polyethylene (LLDPE) on the thermal and mechanical properties of its blends with LDPE were studied. All blends and pure resins were conditioned in a Haake PolyDrive blender at 190°C and in the presence of adequate amounts of antioxidant. Two metallocene LLDPEs (m-LLDPE) and one Ziegler–Natta (ZN) hexene LLDPE were melt blended with the same LDPE. The effect of the BC was investigated by blending two hexene m-LLDPEs of similar weight-average molecular weights and molecular weight distributions but different BCs with the same LDPE. The effect of the CD was studied by using a ZN and an m-LLDPE with similar weight-average molecular weights, BCs, and comonomer type. Low-BC m-LLDPE blends showed separate crystallization whereas cocrystallization was observed in the high-BC m-LLDPE-rich blends. However, ZN-LLDPE/LDPE blends showed separate crystallization together with a third population of cocrystals. The influence of the crystallization behavior was reflected in the mechanical properties. The BC influenced the modulus, ultimate tensile strength, and toughness. The addition of a small amount of LDPE to a low-BC m-LLDPE resulted in a major improvement in the toughness, whereas the results for the high-BC pair followed the additivity rule. ZN-LLDPE blends with LDPE blends were found to be more compatible and exhibited superior mechanical properties compared to m-LLDPE counterparts with the same weight-average molecular weight and BC. All mechanical properties of ZN-LLDPE blends follow the linear rule of mixtures. However, the CD had a stronger influence on the mechanical properties in comparison to the BC.

Key words: linear low-density polyethylene/low-density polyethylene blends; mechanical properties; differential scanning calorimetry; branch content; composition distribution

INTRODUCTION

Linear low-density polyethylene (LLDPE) is a copolymer of an α-olefin such as 1-butene, 1-hexene, or 1-octene and ethylene produced by Ziegler–Natta (ZN) or more recently by metallocene catalysis. LLDPEs were reported to have superior mechanical properties like high tensile strength, high elongation at break, and better tear and impact strength. However, they show poor processability (sharkskin effects and melt fracture at high rates). Conversely, LDPE is characterized by good toughness and flexibility. Moreover, LDPE exhibits excellent processability because of the presence of long chain branching. LLDPE is usually blended with LDPE to combine the superior mechanical properties of the former with the ease of processing of the latter. Further, blending LDPE into LLDPE gives excellent optical properties and better bubble stability in blow molding applications because of the increase in melt strength. Blends of LLDPE and LDPE are used in applications in the film and blow molding industries.

However, the improvement in the properties of the melt or solid state is determined by the compatibility of the blend. Blends of LLDPE and LDPE were reported to phase separate in the melt. Conversely, complete melt homogeneity of these blends was reported. However, LLDPE/LDPE blends are reported to be immiscible (incompatible) in the solid state. This phase separation is usually dictated by molecular parameters such as the weight-average molecular weight ($M_w$), molecular weight distribution (MWD), branch content (BC), composition distribution (CD), and structural heterogeneity, and blend composition. Whereas the melt...
miscibility/immiscibility is governed by the mismatch of the conformations of blend components,\textsuperscript{10,15,21,22} the solid-state behavior is controlled by separate or cocrystallization. Muller et al.\textsuperscript{7} observed separate crystal populations in ZN-LLDPE/LDPE blends with some degree of cocrystallization in the LLDPE-rich blends. However, it was concluded that there was good interaction between the phases because the tensile properties indicated that the blends were mechanically compatible. Kyu et al.\textsuperscript{23} used differential scanning calorimetry (DSC) and light scattering to study slowly cooled blends of ZN-LLDPE/LDPE blends. They observed that ZN-LLDPE crystallized first, forming skeletal spherulites within which LDPE had crystallized. Separate crystallization in LLDPE/LDPE blends was also reported by other researchers.\textsuperscript{1,14,16} However, ZN-LLDPE is known for its structural heterogeneity, mainly inter- and intramolecular heterogeneities,\textsuperscript{24–26} which makes isolation of molecular parameters very difficult, if not impossible.

Recently, blends of metallocene LLDPE (m-LLDPE) and LDPE were investigated. Chen et al.'s\textsuperscript{12} thermal fractionation measurements suggested cocrystallization at all compositions of m-LLDPE/LDPE blends, whereas the DSC data of Yamaguchi and Abe\textsuperscript{11} suggested separate crystallization. The effect of BC was reported to be critical on the crystallization behavior of blends of linear and branched PEs.\textsuperscript{18,19,20,24,25,27} The critical BC for separate crystallization was reported to be much less in the m-LLDPE/HDPE blends compared to ZN-LLDPE/HDPE blends.\textsuperscript{20,28} However, no such investigation was carried out for LLDPE/LDPE blends. Moreover, the CD is an important parameter that determines the crystallization behavior of PE blends. Recently, Xu et al.\textsuperscript{13} reported higher degrees of cocrystallization in ZN-LLDPE/LDPE blends compared to m-LLDPE/LDPE blends for the same BC and comonomer type. However, other researchers suggested no effect for the CD\textsuperscript{25,27} (usually referred to in these publications as branch distribution).

Many studies have appeared on the mechanical characteristics of polyolefin blends.\textsuperscript{2,5–7,20–34} La Mantia and coworkers\textsuperscript{3,34} investigated the effect of comonomer type and $M_w$ on the rheology and mechanical characteristics of ZN-LLDPE/LDPE blends. The comonomer type was found to influence the mechanical properties only slightly. On the contrary, the mechanical properties were a strong function of the $M_w$. Cho et al.\textsuperscript{6} observed that ZN-LLDPE/LDPE blends show synergistic effects on the yield strength and elongation at break whereas the strength at break varies linearly with the composition. The mechanical properties of blends of different LLDPE/LLDPE resins of uniform branch distribution were found to be a function of the total crystallinity rather than the type of crystallinity.\textsuperscript{33} Recently, Hussein et al. showed that both the BC and CD of LLDPE influence its melt miscibility with LDPE.\textsuperscript{22} Here, the investigation is extended to the solid state and the influence of the BC and CD of LLDPE on the thermal and mechanical properties of LLDPE/LDPE blends is studied.

### Experimental

**Materials and sample preparation**

Two commercial samples of m-LLDPE, one with high BC (BC = 32.2 CH$_3$/1000 C) and another one with low BC (BC = 14.4 CH$_3$/1000 C), and an LDPE were used. The three resins were ExxonMobil products. ZN-LLDPE was provided by SABIC (ExxonMobil technology). All LLDPEs were hexene-based copolymers. The BC of LLDPE was obtained from $^{13}$C-NMR. Table I provides characterization data such as the density at room temperature and the melt index as provided by the manufacturer. The number-average molecular weight, $M_{\text{na}}$, and polydispersity were obtained by a Waters 2000 gel permeation chromatography instrument. Trichlorobenzene was used as a solvent (135°C) and standard polystyrene samples were utilized for calibration. The label 1 denotes an m-LLDPE with low BC as a metallocene ethylene–hexene copolymer (m-EH1) and the resin with high BC was labeled m-EH2. The ZN-LLDPE is labeled as ZN-EH. The same LDPE was used in all of these blends. The effect of the BC of LLDPE was investigated by studying blends of m-EH1 and LDPE and results were compared to those obtained by blending m-EH2 and LDPE. Samples m-EH1 and m-EH2 were chosen in a way that the BC would be the only primary molecular parameter in this comparison. As shown in Table I,

<table>
<thead>
<tr>
<th>Resin</th>
<th>Density (g/cm$^3$)</th>
<th>MI (g/10 min)</th>
<th>$M_w$ (kg/mol)</th>
<th>PD = $M_w/M_n$</th>
<th>Branch content CH$_3$/1000 C</th>
</tr>
</thead>
<tbody>
<tr>
<td>m-EH1</td>
<td>0.912</td>
<td>1.2</td>
<td>102</td>
<td>2.14</td>
<td>14.4</td>
</tr>
<tr>
<td>m-EH2</td>
<td>0.883</td>
<td>2.20</td>
<td>97</td>
<td>2.02</td>
<td>32.2</td>
</tr>
<tr>
<td>ZN-EH</td>
<td>0.917</td>
<td>2.80</td>
<td>107</td>
<td>4.01</td>
<td>16.7</td>
</tr>
<tr>
<td>LDPE</td>
<td>0.923</td>
<td>1.2</td>
<td>100</td>
<td>4.14</td>
<td>11*a</td>
</tr>
</tbody>
</table>

*a Total number of short and long branches.*
m-EH1 and m-EH2 were the same branch type (hexene) and had similar $M_w$ and MWD, and both LLDPEs were metallocene resins. Hence, a comparison of m-EH1 and m-EH2 blends with LDPE is expected to reveal the effect of the BC on the thermal and mechanical characteristics of m-LLDPE/LDPE systems. Similarly, the comparison of m-EH1 and ZN-EH blends with LDPE is likely to show the influence of CD, because the BC and $M_w$ were similar.

The LDPE and LLDPE resins used in this study were conditioned (or blended) in a Haake PolyDrive melt blender. The conditions and details of the melt blending and sample preparation of the dogbone-shaped samples for thermal and mechanical analyses were discussed in a previous publication that studied the melt miscibility of these samples.\(^{15}\)

**DSC analysis**

Thermal analysis was performed with a TA Instruments DSC 2910 equipped with Thermal Analyst 2200 software, and a nitrogen gas flow was used as a blanket. Samples (5–10 mg) were sliced and then compressed into aluminum pans for testing. The samples were heated from 25 to 200 °C at 10 °C/min to remove the thermal history, held at 200°C for 1 min, and then cooled to 25 °C at the same rate. All samples were subjected to a second identical heating cycle. Crystallinity calculations were based on a heat of fusion of 290 J g\(^{-1}\) for the PE crystal.\(^{35}\)

**Mechanical testing**

Dogbone-shaped samples were prepared according to ASTM D 638 (type V). The tensile tests were performed on an Instron 5567 tensile testing machine at 25°C. The gauge length was kept at 25 mm with a crosshead speed of 125 mm/s. All samples ruptured within 0.5–5 min of testing time. All the reported mechanical parameters are based on an average of a minimum of five samples.

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**Figure 1** DSC (a) heating scans and (b) cooling scans for m-EH1/LDPE blends.
RESULTS AND DISCUSSION

Thermal analysis

DSC melting endotherms for the low-BC m-LLDPE (m-EH1) blends with LDPE together with pure resins are given in Figure 1(a). The second heating curves were used for comparison to avoid the effects of ambient cooling. LDPE showed the highest melting temperature ($T_m$), which shifts to a lower value as the amount of m-EH1 increases in the blend. Further, all LDPE-rich blends showed a single sharp melting peak. However, the m-EH1 and 90% m-EH1/LDPE blends displayed two distinct melting peaks. The double peak in the pure m-EH1 signifies the bimodal nature of this resin and is a clear indication of different crystal populations. In addition, the peaks of m-EH1-rich blends are relatively broader than that of LDPE-rich blends. In an attempt to obtain further information on the crystallization mechanism, DSC cooling-run measurements were also performed. Figure 1(b) shows the DSC crystallization thermograms obtained at a cooling rate of 10 °C/min. In contrast to the heating curves, only single peaks were observed. The LDPE showed the highest crystallization temperature ($T_c$) that decreased systematically as the m-EH1 component increased in the blends. The influence of blending was further examined by comparing the observed crystallinities to those obtained by adding the component crystallinities in the same proportion in which they appear in the blend. The DSC crystallinities of each polymer will be an additive in the blend if blends crystallize in the same manner as in pure polymers. However, a low or high crystallinity of the blend compared to the pure components was taken as an argument in favor of separate or cocrystallization. It can be very clearly seen from Figure 2(a) that all blends follow the linear additivity rule. Hence, it could be easily concluded that these blends form separate crystals. These results are in agreement with previous observations that Yamaguchi and Abe made for m-LLDPE/LDPE blends. The percentage of crystallinity for all blends is given in Figure 2 for ease of comparison.
of comparison and is discussed in the following sections.

Figure 3(a) shows the melting endotherms for the blends of m-EH2 with LDPE. Once again LDPE showed the highest \( T_m \) whereas m-EH2 had the lowest, which is due to the large number of short chain branches in m-EH2. The depression in the \( T_m \) for increasing comonomer incorporation is explained by the occurrence of shorter ethylene sequences between short chain branches in the sample containing high amounts of comonomer.\(^{20}\) The LDPE-rich blends show sharp peaks whereas the m-EH2-rich blends melt over a broad range. The crystallization peaks are shown in Figure 3(b). The shift in the \( T_c \) is broad compared to that seen in the m-EH1 blends. Again, the observed crystallinities were compared with those calculated from the additivity rule [Fig. 2(b)]. For blends with \( \phi \geq 30\% \), the observed crystallinities are less than those calculated by the additivity rule. As discussed before, this observation suggests cocrystallization. Although high BC is expected to hinder cocrystallization, the opposite is observed. This is likely to be attributable to structural heterogeneities of m-LLDPEs.\(^{20,25}\) In addition, it was found that the comonomer distribution is more homogeneous in samples containing low BC compared to samples containing higher BC.\(^{20}\) Hence, the cocrystallization is suggested to take place between the less branched segments of m-EH1 and similar fractions of the LDPE. In fact, temperature rising elution fractionation analysis of blends of LLDPE and LDPE suggested that fractions containing similar branches were more likely to cocrystallize than fractions with different BCs.\(^{12,37}\) The leftover highly branched fractions were suggested to form separate crystal populations.

DSC melting peaks for ZN-LLDPE (ZN-EH) are shown in Figure 4(a). LDPE and ZN-EH exhibit sharp melting peaks whereas all blends display multiple peaks over a broad range of temperatures. The presence of multiple peaks in ZN-EH/LDPE blends is interesting because no such peaks were observed in the m-LLDPE blends. Take for instance the 30/70 blend in Figure 4(a). The peak at 109.5°C most probably represents the LDPE or more precisely the LDPE-rich phase whereas the peak at 124.6°C exhibits the presence of ZN-EH-rich crystals. Thus, what does the third peak at 120.56°C represent? It is likely for cocrystals of ZN-LLDPE and LDPE. In fact, similar multiple peaks were observed by other researchers for the ZN-LLDPE/LDPE blends.\(^{7,12,36}\) Xu et al.\(^{13}\) worked with ZN-LLDPE and LDPE blends and reported similar melting peaks in the 50/50 blend. It was suggested that these peaks represent three different crystal populations in the blend, namely, LDPE or more accurately LDPE-rich crystals, segregated cocrystals, and ZN-LLDPE-rich crystals. Compared to the low-BC LLDPE (m-EH1), which has almost the same BC, ZN-EH displays a higher melting temperature, even higher than LDPE. The linear fractions of ZN-EH can really form thicker lamellas, melting at high temperatures (see fig. 59 of Wunderlich).\(^{35}\) The DSC cooling curves for the ZN-EH blends are shown in Figure 4(b). To assess the degree of cocrystallization, the crystallinities were compared to those calculated by assuming completely separate crystallizations [Fig. 3(c)]. A very symmetric trend is observed around the 50% composition, which shows crystallinity less than that calculated by the additive rule. For all other compositions, the observed crystallinity is higher than that calculated, assuming separate crystallizations. The increase in crystallinity could be explained as the summation of separate crystals composed of LDPE-rich and ZN-EH-rich blends are equal to the crystallinity predicted by additivity rule whereas the separately existing cocrystals population contributes an additional value to the observed crystallinity.

Hence, in summary, the BC and distribution of LLDPE were found to influence the solid-state morphology of LLDPE/LDPE blends. Blends containing high-BC m-LLDPE showed some cocrystallization in the LLDPE-rich blends, that is, improved compatibility. However, in the case of low-BC m-LLDPE blends with LDPE, only separate crystallization was observed. This is contrary to the behavior reported for linear and branched PEs in which higher branching leads to sep-
arate crystallization.\textsuperscript{18–20,24} However, the ZN-LLDPE blends behaved quite differently. Multiple peaks suggesting three different populations of crystals existed at all compositions. These observations indicate that ZN-LLDPE/LDPE blends were more compatible than m-LLDPE/LDPE blends. The heterogeneity of ZN-EH, especially the presence of linear PE, may have helped in the cocrystallization with the long chain branches present in LDPE.

Mechanical properties

The tensile modulus values as a function of composition for m-EH1/LDPE are shown in Figure 5(a). The error bars show standard deviations of the results for at least five specimens. The modulus for LDPE is 145.9 MPa whereas that of m-EH1 is 78.65 MPa. Moduli for the blends were lower than that calculated by the linear rule of mixtures. The moduli for the m-EH1-rich blends were even less than that of pure constituents. The modulus for m-EH2 is 23.68 MPa. This is due to the high comonomer content and the resulting low crystallinity. The moduli for m-EH2-rich blends were very close to those predicted by the rule of mixtures. This is attributable to the cocrystallization observed in these blends in contrast to separate crystallization in m-EH1/LDPE blends [see Fig. 2(a,b)]. However, LDPE-rich blends show negative deviation from the linear rule of mixtures, although single melting peaks were observed for these blends [Fig. 3(a)]. Figure 5(c) shows the moduli for ZN-EH blends. The modulus for ZN-EH is 119.73 MPa, which is almost twice the value of the more homogeneous m-EH1 polymer with similar BC. All moduli for ZN-EH/LDPE blends show linear variation with composition. Again, cocrystallization is suggested as the reason for the compatibility of these blends. A comparison of Figure 5(a,c) suggests that CD influences the modulus, especially m-LLDPE-rich blends. Hence, both BC and CD influenced the modulus; however, the effect of CD is stronger for LDPE-rich blends.

The strength at yield for the three blend systems under investigation is shown in Figure 6. Blends of
m-EH2 with LDPE follow a behavior similar to that of the modulus. For blends of m-EH1 with LDPE, only the LDPE-rich blends showed similar behavior to the modulus. Figure 6(a,b) shows the effect of BC on yield strength. For LDPE-rich blends, the strength at yield displayed weak negative deviations from the linear rule of mixtures, whereas LLDPE-rich blends followed the rule. Moreover, the strength at yield approximately followed the rule of mixture, regardless of the BC. The strength at yield of ZN-EH/LDPE blends again exhibits a linear relationship with respect to composition [Fig. 6(c)] similar to the modulus. The strength at yield of ZN-EH is comparable to that of m-EH1 with similar BC. Hence, both the BC and CD have little influence on the strength at yield.

The ultimate tensile strength for the above blends is displayed in Figure 7. In all cases the strength at break for LLDPE is higher than that of LDPE with the same $M_{w}$, which is consistent with previous reports. The ultimate tensile strength of m-EH1/LDPE blends increases linearly with the addition of m-EH1 [Fig. 7(a)]. The strength at break for m-EH1 was 30.88 MPa and that for m-EH2 was 23.26 MPa. This shows that increasing the BC has a negative effect on the ultimate tensile strength. Further, the ultimate tensile strength values of the m-EH2/LDPE blends show a synergistic effect [Fig. 7(b)]. The 30 and 50% m-EH2 blends with LDPE show values comparable to the strength at break of pure m-EH2 whereas those of the m-EH2-rich blends are even higher. In contrast, ZN-EH/LDPE followed a linear trend with respect to the composition [Fig. 7(c)]. Similar behavior for ZN-LLDPE/LDPE blends was reported by Cho et al. A comparison of Figure 7(a,b) shows the strong effect of the BC on the ultimate tensile modulus. In addition, Figure 7(a,c) suggests the influence of the CD on the ultimate strength with ZN-LLDPE closely following linear additivity. Here, the effect of the BC on the ultimate strength is stronger than that of the CD, especially for m-LLDPE-rich blends.

The elongation at break for different blend systems is given in Figure 8. Similar to the strength at break
values, the elongation at break for LLDPEs was found to be higher than LDPE, irrespective of the BC or synthesis type. As seen in Figure 8(a,b), the low-BC and high-BC m-EH blends with LDPE display similar trends, although m-EH2 shows a higher elongation at break. The elongation at break for the blends was always higher than the predictions of the rule of mixtures. However, the ZN-EH/LDPE blends show a linear increase in the elongation at break as the ZN-EH fraction increases in the blend [Fig. 8(c)]. In addition, ZN-EH shows an elongation at break that is twice that of m-EH1 with similar BC and $M_w$ which is likely due to the presence of the linear fractions in ZN-LLDPE. Hence, for the elongation at break the influence of the CD is stronger than that of the BC and synergistic effects were obtained in all m-EH blends.

Finally, the area under the stress–strain curve that is proportional to the toughness of the material is given in Figure 9. Two regions were detected for m-EH1/LDPE and m-EH2/LDPE blends: LDPE rich ($\phi < 0.5$) and LLDPE rich ($\phi > 0.5$). A similar trend is observed in the LDPE-rich blends ($\phi < 0.5$) with the 30% LLDPE blend showing maximum toughness. However, in the LLDPE-rich blends ($\phi > 0.5$), there is tremendous enhancement in the toughness for m-EH1/LDPE blends whereas the m-EH2 blends exhibit toughness close to the estimations from additivity. The ZN-EH is almost twice as tough as m-EH1. The toughness of ZN-EH blends varies linearly with the addition of the tougher component (ZN-EH). In contrast, the addition of a small amount of LDPE to m-EH1 resulted in major improvement of the toughness. Again, the effect of the CD of m-LLDPE on the toughness of m-LLDPE/LDPE blends was observed to be stronger than the influence of the BC.

The above discussion can be summarized as follows:
1. With the same $M_w$ values the three LLDPEs (m-EH1, m-EH2, and ZN-EH) exhibited different mechanical properties. In the linear elastic range, ZN-EH showed the maximum modulus whereas the strength at yield was comparable for ZN-EH and m-EH1. The high-BC m-EH2 displayed the lowest properties. Moreover, the properties were associated with the degree and type of crystallization in these polymers. At large deformations, m-EH2 displayed the highest ultimate tensile strength whereas ZN-EH exhibited maximum elongation at break and toughness.

2. The influence of the BC on blends was observed in the modulus, ultimate tensile strength, and toughness. m-EH2/LDPE blends displayed synergistic effects in the ultimate tensile strength whereas m-EH1-rich blends with LDPE were tougher than m-EH2 rich blends. The BC had little or no significant influence on the elongation at break and strength at yield. The influence of the BC on the ultimate strength is stronger than that of the CD.

3. In general, the effect of the CD on the mechanical properties prevailed over that of the BC.

CONCLUSION

Blends of three different LLDPEs (two metallocene based and one ZN based) with similar $M_w$ values were melt blended with the same LDPE. The LLDPEs were selected to study the effect of BC and CD, one variable at a time. The effects of both the BC and the CD on the thermal and mechanical properties of LLDPE/LDPE were investigated. Low-BC m-LLDPE blends with LDPE showed separate crystallization whereas cocrystallization was observed in the high-BC-rich blends of m-LLDPE with LDPE. However, ZN-LLDPE/LDPE blends showed separate crystallization together with a third population of cocrysrals. The influence of the crystallization behavior was reflected in the mechanical properties. The BC and CD of LLDPE influenced the mechanical properties of LLDPE/LDPE blends. In general, the influence of the CD was enormous. Addition of a small amount of LDPE to m-LLDPE resulted in major improvement of both the toughness.
The ultimate tensile strength as a function of the composition.

The elongation at break as a function of the composition.

The tensile modulus as a function of the composition.

The strength at yield as a function of the composition.

The elongation at break as a function of the composition.
for low-BC m-LLDPE/LDPE blends and the ultimate tensile strength of low- and high-BC blends. Further, ZN-LLDPE/LDPE blends were found to be the most compatible and exhibited superior mechanical properties compared to their metallocene counterparts. All the mechanical properties of ZN-LLDPE/LDPE blends can be predicted by the simple rule of mixtures.

The authors acknowledge King Fahd University of Petroleum and Minerals for the financial support of this work. We thank Prof. M. C. Williams and Dr. Jiang Bai of the University of Alberta, Canada, for their help with the DSC analysis; Mr. Aleem Rizvi of the Research Institute, King Fahd University of Petroleum and Minerals, for his help with the mechanical testing; and Mr. M. Arab of the Chemistry Department, King Fahd University of Petroleum and Minerals, for his help with the NMR analysis. The second author (T.H.) thanks King Fahd University of Petroleum and Minerals for a MS research assistantship.

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