

# Implications of melt compatibility/ incompatibility on thermal and mechanical properties of metallocene and ziegler–Natta linear low density polyethylene (LLDPE) blends with high density polyethylene (HDPE): influence of composition distribution and branch content of LLDPE

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**Abstract:** In this paper, the implications of melt compatibility on thermal and solid-state properties of linear low density polyethylene/high density polyethylene (LLDPE/HDPE) blends were assessed with respect to the effect of composition distribution (CD) and branch content (BC). The effect of CD was studied by melt blending a metallocene (m-LLDPE) and a Ziegler–Natta (ZN) LLDPE with the same HDPE at 190 °C. Similarly, the effect of BC was examined. In both cases, resins were paired to study one molecular variable at a time. Thermal and solid-state properties were measured in a differential scanning calorimeter and in an Instron mechanical testing instrument, respectively. The low-BC m-LLDPE (BC = 14.5 CH<sub>3</sub>/1000 C) blends with HDPE were compatible at all compositions: rheological, thermal and some mechanical properties followed additivity rules. For incompatible high-BC (42.0 CH<sub>3</sub>/1000 C) m-LLDPE-rich blends, elongation at break and work of rupture showed synergistic effects, while modulus was lower than predictions of linear additivity. The CD of LLDPE showed no significant effect on thermal properties, elongation at break or work of rupture; however, it resulted in low moduli for ZN-LLDPE blends with HDPE. For miscible blends, no effect for BC or CD of LLDPE was observed. The BC of LLDPE has, in general, a stronger influence on melt and solid-state properties of blends than the CD.

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**Keywords:** LLDPE; HDPE; mechanical properties; DSC; branch content; composition distribution

## INTRODUCTION

High density polyethylene (HDPE) is used for applications that require stiff products and linear low density polyethylene (LLDPE) is usually blended to improve flexibility<sup>1</sup> or to reduce extruder backpressure and increase output.<sup>2</sup> The compatibility (the word miscibility is usually used rather than compatibility) of LLDPE and HDPE blends has received wide attention in the literature.<sup>3–10</sup> LLDPE is produced either by Ziegler–Natta (ZN-LLDPE) or more recently by metallocene catalysis (m-LLDPE). Most of the previous studies used ZN-LLDPE, which is known for its inter- and intra-molecular heterogeneity.<sup>11–13</sup> The multi-site nature of ZN catalyst results in a product with a diverse composition distribution (CD):

weight-average molecular weight ( $M_w$ ), molecular weight distribution (MWD) and branch content (BC). These molecular parameters have a strong influence on the compatibility of PE/PE blends.<sup>3–7,14–17</sup> This explains the suspected or suggested phase separation in ‘pure’ ZN-LLDPE,<sup>18–22</sup> which is in fact a blend of high- $M_w$  mostly linear molecules with low- $M_w$  highly branched molecules.<sup>11</sup>

The crystallization behavior of blends of linear and branched PE was reported to be a critical function of BC.<sup>7,23–27</sup> The critical BC for separate crystallization in m-LLDPE/HDPE blends was observed to be lower than that of ZN-LLDPE/HDPE systems.<sup>11,24</sup> Also, CD is another important parameter that determines the crystallization behavior of PE blends. Recently,

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1 ZN-LLDPE/LDPE blends were suggested to have  
2 a higher degree of co-crystallization when compared  
3 to m-LLDPE/LDPE blends for the same BC and  
4 comonomer type.<sup>28</sup> However, other researchers have  
5 suggested no effect for CD (usually referred to in  
6 these publications as branch distribution).<sup>25,27,29</sup> The  
7 effect of the CD of LLDPE on the crystallization of  
8 LLDPE/HDPE blends is yet to be studied.

9 Mechanical properties of polyolefin blends have  
10 received wide attention in the literature.<sup>30–39</sup>  
11 Acierno and co-workers<sup>31,32</sup> investigated the effect of  
12 comonomer type and  $M_w$  on the rheology and mechan-  
13 ical characteristics of ZN-LLDPE/LDPE blends.  
14 Comonomer type was found to influence the mechan-  
15 ical properties only slightly. In contrast, mechanical  
16 properties were a strong function of  $M_w$ . Cho *et al.*<sup>33</sup>  
17 observed that ZN-LLDPE/LDPE blends show syner-  
18 gistic effects on the yield strength and elongation at  
19 break while the strength at break varies linearly with  
20 composition. The mechanical properties of blends of  
21 different LLDPE/LLDPE resins of uniform branch  
22 distribution were found to be a function of total crys-  
23 tallinity rather than of the type of crystallinity.<sup>39</sup>

24 The polymers used in this study were paired in order  
25 to study one molecular variable at a time. To study the  
26 effect of CD, two butene LLDPE resins of comparable  
27 BC and  $M_w$  were selected and blended with the same  
28 HDPE. The CD was the only molecular parameter  
29 that was varied. The effect of BC was studied by  
30 using two butene m-LLDPEs of the same  $M_w$  and  
31 MWD but of different densities (BC). All LLDPEs  
32 were blended with the same HDPE. This approach of  
33 isolating the effect of other molecular parameters was  
34 not followed in most of the previous studies. In recent  
35 studies, the author and co-workers showed that both  
36 BC and CD of LLDPE influence its melt compatibility  
37 with HDPE<sup>3</sup> and LDPE.<sup>17,40</sup> Here, the implications  
38 of melt compatibility (or incompatibility) on thermal  
39 and mechanical properties of LLDPE/HDPE blends  
40 were examined on the same blend systems.<sup>3</sup>

## 43 EXPERIMENTAL

### 44 Materials and sample preparation

45 Three commercial samples of butene LLDPE and  
46 one linear HDPE were used in this study. Two  
47 of the LLDPE ethylene-butene copolymers were  
48 metallocene resins (m-EB1 and m-EB2) of different  
49 BC and the third was an ethylene-butene ZN-LLDPE  
50 copolymer (ZN-EB). All samples were ExxonMobil  
51 products. Table 1 provides characterization data such  
52

53 **Table 1.** Characterization of resins

54 Resin	55 Density (g cm <sup>-3</sup> )	56 MI (g/10 min)	57 $M_w$ (kg mol <sup>-1</sup> )	58 $M_w/M_n$	59 BC (CH <sub>3</sub> / 1000 C)
57 ZN-EB	0.918	1.0	118	3.1	13.2
58 m-EB1	0.9100	1.2	108	2.0	14.5
59 m-EB2	0.8800	0.8	125	1.8	42.0
60 HDPE	0.9610	0.7	102	6.7	0

61 as density at room temperature and melt index  
62 (MI) at 190 °C as provided by ExxonMobil. In  
63 addition, information about  $M_w$  and BC as revealed  
64 by gel permeation chromatography (GPC) and <sup>13</sup>C  
65 NMR is included. Details about the GPC and  
66 NMR characterizations were given in a previous  
67 publication.<sup>3</sup> The rheology of all the LLDPEs does  
68 not suggest the presence of any long chain branches.  
69 The resins with low and high BC were labeled as  
70 m-EB1 and m-EB2, respectively. The effect of BC of  
71 LLDPE was investigated by examining m-EB1/HDPE  
72 and m-EB2/HDPE blend systems. Resins m-EB1 and  
73 m-EB2 were selected so that BC would be the only  
74 primary molecular variable in this comparison (see  
75 Table 1).

76 Similarly, to study the effect of CD, ZN-EB was  
77 chosen to have about the same  $M_w$  and BC as  
78 m-EB1. The HDPE used in all of these blends  
79 has a density higher than 0.960 g cm<sup>-3</sup> and hence  
80 should have no branches,<sup>41</sup> which is confirmed by  
81 our own <sup>13</sup>C NMR measurements. The HDPE and  
82 LLDPE resins used in this study were conditioned  
83 (or melt blended) in a Haake PolyDrive melt blender  
84 at 190 °C for 10 minutes at 50 rpm in the presence  
85 of an adequate amount of antioxidant as discussed in  
86 previous publications.<sup>3,40,42</sup> Sample preparation in a  
87 Carver press for thermal and mechanical testing was  
88 the same as that discussed earlier in the rheological  
89 study.<sup>3</sup>

### 91 Differential scanning calorimetry (DSC)

92 Thermal analysis was performed with a TA Instru-  
93 ments DSC 2910 equipped with Thermal Analyst  
94 2200 software, and nitrogen gas flow was main-  
95 tained from a liquid nitrogen vessel. The samples  
96 obtained from the Carver press were used in the  
97 DSC analysis. Samples of 5–10 mg were sliced and  
98 then compressed into aluminium pans for testing. The  
99 samples were heated from 25 to 200 °C at a heating  
100 rate of 10 °C min<sup>-1</sup> to eliminate the thermal history,  
101 held at 200 °C for 1 min and then cooled to 25 °C at  
102 10 °C min<sup>-1</sup>. All samples were subjected to a second  
103 heating cycle identical to the first one. Calculations of  
104 crystallinity were based on a heat of fusion of 290 J g<sup>-1</sup>  
105 for polyethylene crystal.<sup>43</sup>

### 107 Mechanical testing

108 Samples obtained from the Carver press were cut  
109 according to ASTM D638 (type V). The tensile tests  
110 were performed on the Instron 5567 tensile testing  
111 machine at room temperature. The gauge length was  
112 kept at 25 mm with a crosshead speed of 100 mm s<sup>-1</sup>.  
113 The results reported in this study are based on an  
114 average of a minimum of five samples.

## 118 RESULTS AND DISCUSSION

119 A previous rheological study<sup>3</sup> on the melt compatibility  
120 of these blends suggested the following conclusions:

- 1 (1) Blends of m-EB1 and HDPE are miscible at all  
 2 compositions.  
 3 (2) Blends of ZN-EB and HDPE are miscible at  
 4 all compositions and ZN-EB blends are more  
 5 miscible than their m-EB counterparts.  
 6 (3) Blends of the high-BC m-EB2 and HDPE  
 7 showed that HDPE-rich blends are miscible  
 8 while m-EB2-rich blends are immiscible. The  
 9 rheology of miscible systems followed additivity  
 10 rules while immiscible blends displayed negative  
 11 deviation from additivity. Layered morphology  
 12 was proposed as an explanation for the observed  
 13 rheology.  
 14  
 15

16 In the following sections, the implications of this  
 17 compatibility/incompatibility on the thermal and  
 18 mechanical properties are discussed.  
 19  
 20

### 21 Thermal analysis

22 DSC melting and crystallization thermograms for m-  
 23 EB1 (the low-BC component) blends with HDPE  
 24 together with pure resins are given in Fig 1. The  
 25 values of the melting ( $T_m$ ) and crystallization ( $T_c$ )  
 26 peaks are shown on all DSC thermograms. In all  
 27 endotherms, the second heating curves were used to  
 28 remove previous history.<sup>21,35,40</sup> Similarly, in Fig 2 the  
 29 DSC results for m-EB2 (the high-BC component)  
 30 blends with HDPE are displayed. In all DSC curves,  
 31 HDPE showed the highest  $T_m$  (or  $T_c$ ), which shifts  
 32 to a lower value as the amount of LLDPE increases  
 33 in the blend. Also, m-EB2 showed the lowest  $T_m$ ,  
 34 followed by m-EB1. These observations are due to  
 35 the occurrence of shorter ethylene sequences between  
 36 short chain branches in the high-BC m-LLDPE.<sup>13,19,24</sup>  
 37 The depression in the melting point for the three blend  
 38 systems is given in Table 2.

39 Both HDPE and m-EB1 showed a single peak;  
 40 however, the m-EB1 peak is very broad. Further  
 41 more, all HDPE-rich blends with either m-EB1 or  
 42 m-EB2 showed a single sharp melting peak. This  
 43 suggests the existence of one type of crystal population,  
 44 hence, the complete homogeneity of these blends  
 45 in the solid state. However, the m-EB1-rich blends  
 46 had at least two melting peaks. The 90 % m-  
 47 EB1 blend showed three melting peaks, with two  
 48 major peaks representing the pure components and a  
 49 third one that is probably due to co-crystallization.<sup>24</sup>  
 50 In m-EB1-rich blends, the sharpness of the lower  
 51 melting peak decreases as the fraction of the linear  
 52 component is increased, which further supports co-  
 53 crystallization.

54 The crystallization mechanism of m-EB1 blends  
 55 with HDPE was examined, and results are displayed  
 56 in Fig 1(b). Here, only single peaks were observed  
 57 for HDPE-rich blends and a maximum of two  
 58 peaks were obtained for m-EB1-rich blends. The  
 59 90 % m-EB1 blend showed two distinct peaks that  
 60 are located between the two peaks representing the

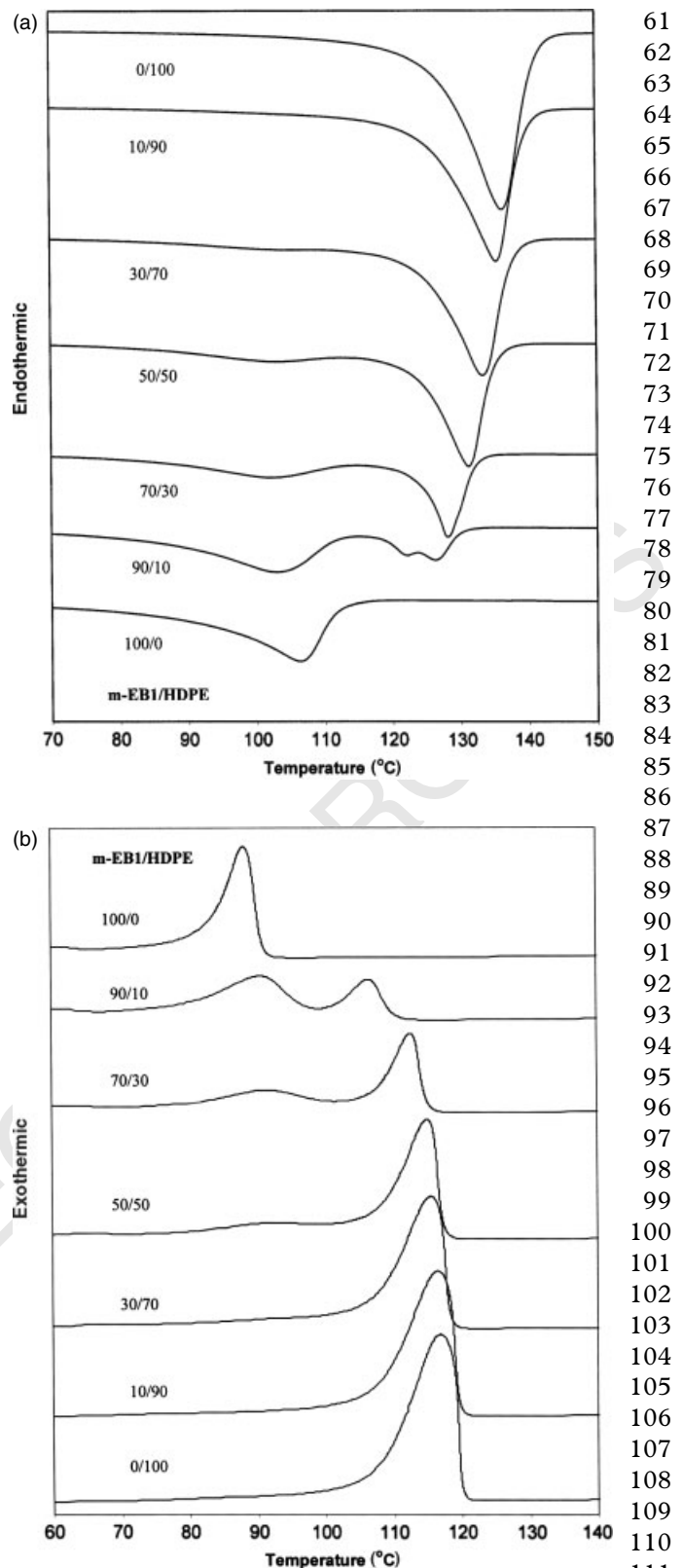


Figure 1. DSC scans for m-EB1/HDPE blends: (a) heating;  
 (b) cooling.

pure components. This shift in  $T_c$  supports co-  
 crystallization and partial compatibility of the  
 m-EB1-rich blends. Again, the sharpness of the m-  
 EB1 peak decreased as the fraction of the linear  
 component was increased. So, for low-BC pair,  
 blends of m-LLDPE and HDPE are compatible

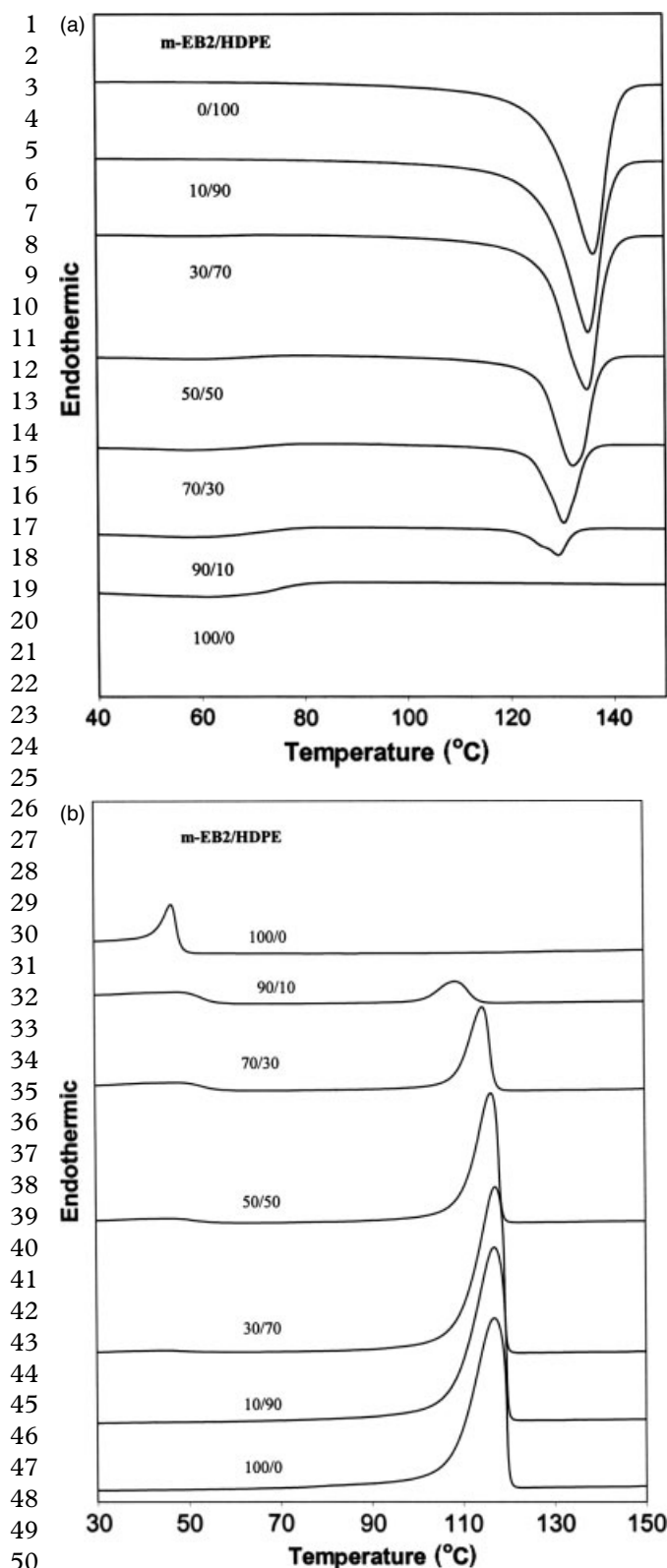


Figure 2. DSC scans for m-EB2/HDPE blends: (a) heating; (b) cooling.

Table 2. Melting point depression, in °C, for blends of different LLDPEs with HDPE

Composition	ZN-EB blends	m-EB1 blends	m-EB2 blends
0 (HDPE)	—	—	—
0.1	0.80	0.84	1.05
0.3	2.39	2.92	1.32
0.5	3.77	5.04	4.13
0.7	6.81	8.12	6.17
0.9	9.74	9.53	7.00
1.0 (LLDPE)	12.47	29.88	73.67

the same trend. Plots of  $\Delta T_m(\phi)$  showed strong depression in m-EB1-rich blends (results not shown here).

For blends of m-EB2 with HDPE, the results of heating and cooling are shown in Fig 2. The highly branched m-EB2 shows a very broad and weak transition in the range 60–80 °C. The depression in  $T_m$  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.<sup>24</sup> Addition of HDPE to m-EB2 resulted in a peak at  $\approx 130$  °C, which represents the HDPE crystals. The sharpness of the peak increases with the increase of the HDPE fraction in the blend. For HDPE-rich blends, the major melting peak of HDPE shifts with the increase of m-EB2 fraction and single peaks were observed, suggesting solid-state compatibility in this composition range. However, for m-EB2-rich blends, a shoulder was observed in the 90 % m-EB2 blend and a weak and broad melting point representing the m-EB2 was detected. This observation suggests the existence of separate crystals of the pure components. The third crystal population in the 90 % blend is probably due to the formation of co-crystals of HDPE with the linear part of the highly branched m-EB2. Highly branched m-LLDPEs were recently suggested to have intramolecular heterogeneity.<sup>24</sup> Also, temperature rising elution fractionation analysis on blends of LLDPE and LDPE suggested that fractions containing similar branches were more likely to co-crystallize than fractions with different BCs.<sup>44,45</sup> A previous rheological study<sup>3</sup> suggested the existence of a layered morphology for m-EB2-rich blends in the melt state, which was supported by molecular dynamics investigation.<sup>46</sup> The layered morphology is likely to promote co-crystallization and explain the observed third crystal population in the 90 % m-EB2 blend. These results are in agreement with previous reports that suggest separate crystallization with some amount of co-crystals in blends of high-BC m-LLDPE and HDPE.<sup>47</sup>

The crystallization of m-EB2 blends with HDPE is given in Fig 2(b). The results are similar to those of the low-BC pair. Again, only single peaks were observed for HDPE-rich blends and a maximum of two peaks were observed for m-EB2-rich blends. The 70 % and the 90 % m-EB1 blends with HDPE showed

in the solid state in the HDPE-rich range, and partially compatible in the m-LLDPE-rich range. In addition, single crystals in HDPE-rich blends and multi-crystals in the m-LLDPE-rich blends were also observed. The depression in the peak melting temperature,  $\Delta T_m$ , for m-EB1 blends followed

1 two peaks that are located between the two peaks  
 2 representing the pure components. This shift in  $T_c$   
 3 supports the co-crystallization and compatibility of  
 4 the m-EB2-rich blends. In addition, the sharpness  
 5 of the m-EB2 peak decreased as the fraction of  
 6 the linear component was increased. However, the  
 7 broad and shallow melting peak of pure m-EB2  
 8 shown in Fig 2(a) has turned into a sharp peak in  
 9 crystallization. So, for high-BC blends of m-LLDPE  
 10 and HDPE, solid-state compatibility is suggested by  
 11 DSC at all compositions; however, a multi-crystal  
 12 population is likely to develop in m-EB2-rich blends.  
 13 The comparison of the melting and crystallization  
 14 of low- and high-BC pairs suggests that BC has  
 15 little or no influence on melting and crystallization  
 16 of HDPE-rich blends, with blends showing single  
 17 peaks. However, m-LLDPE-rich blends are likely to  
 18 be partially compatible with multi types of crystals.  
 19 Hence, the melting and crystallization of low- and  
 20 high-BC m-LLDPE/HDPE blends are similar, but  
 21 composition-dependent.

22 DSC melting and crystallization peaks for ZN-EB  
 23 blends with HDPE are shown in Fig 3. HDPE and  
 24 ZN-EB as well as all blends exhibit sharp melting and  
 25 crystallization peaks over the range of temperature  
 26 examined. Both  $T_m$  and  $T_c$  increased with the increase  
 27 in the fraction of the linear component. The results  
 28 are thus similar to those of m-EB1 blends shown in  
 29 Fig 1. No multiple peaks were observed. Comparison  
 30 of m-EB1 and ZN-EB (with almost the same BC)  
 31 shows that ZN-EB has higher  $T_m$  and  $T_c$ , which is  
 32 mainly due to the presence of a linear fraction in  
 33 ZN-LLDPE.<sup>11,12</sup> The linear fractions of ZN-EB can  
 34 form thicker lamellae, melting at higher temperature.  
 35 Comparison of ZN-EB and m-EB1 blends with  
 36 the same HDPE reveals that all ZN-EB blends  
 37 showed a single peak that shifts with composition,  
 38 which suggests the complete compatibility of ZN-EB  
 39 blends. Hence, ZN-EB is compatible with HDPE  
 40 over the whole composition range, with blends  
 41 showing single melting and crystallization peaks.  
 42 These observations are in agreement with previous  
 43 DSC and X-ray measurements that suggest the  
 44 formation of perfect co-crystallites between ZN-  
 45 LLDPE and HDPE<sup>48–51</sup> when the BC of ZN-LLDPE  
 46 is lower than 42 CH<sub>3</sub>/1000 C (8.2 mol %). However,  
 47 the thermal compatibility and melt compatibility of  
 48 ZN-EB blends with HDPE may not lead to mechanical  
 49 compatibility, as will be discussed in the next section.

50 HDPE-rich blends with m-EB1 are suggested to be  
 51 compatible; however, m-EB1-rich blends are likely to  
 52 be partially compatible in the solid state. Hence, the  
 53 influence of CD (ZN-EB versus m-EB1) on thermal  
 54 properties of LLDPE/HDPE blends is evident and  
 55 ZN-LLDPE is more compatible with HDPE than m-  
 56 LLDPE with the same average BC and  $M_w$ . It is worth  
 57 noting that the rheological study resulted in the same  
 58 suggestion with regard to melt compatibility.<sup>3</sup>

59 The crystallinity of m-EB1, m-EB2 and ZN-  
 60 EB blends with HDPE were calculated from

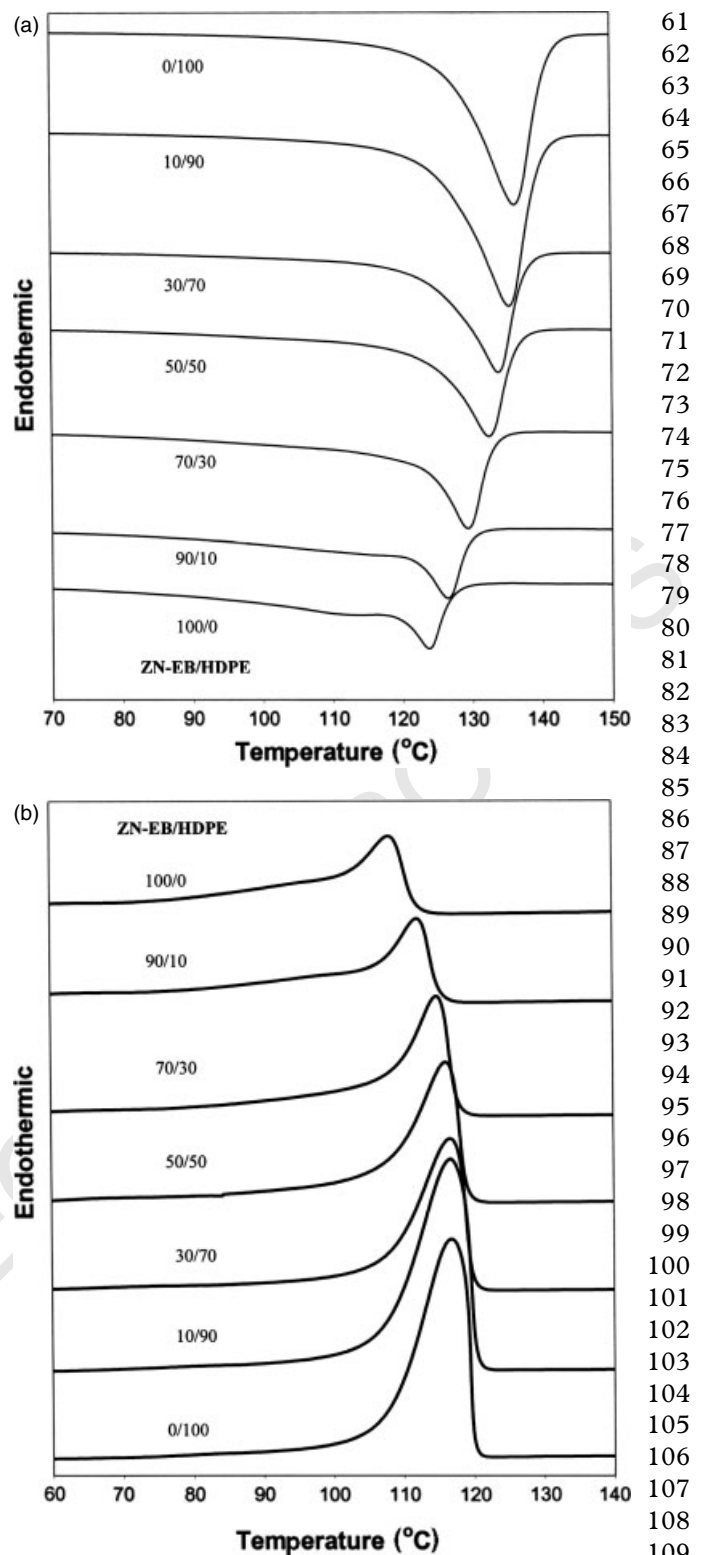


Figure 3. DSC scans for ZN-EB/HDPE blends: (a) heating;  
 (b) cooling.

Figs 1(a), 2(a) and 3(a), respectively, and the results  
 are given in Fig 4. • DSC cooling curves for ZN-EB  
 blends are shown in Fig 4(b) as a function of compo-  
 sition. The lines represent the calculated crystallinity  
 obtained by assuming linear additivity. A comparison  
 of Figs 4(a), 4(b) and 4(c) suggests that neither BC  
 nor CD influenced the total crystallinity. For ZN-EB

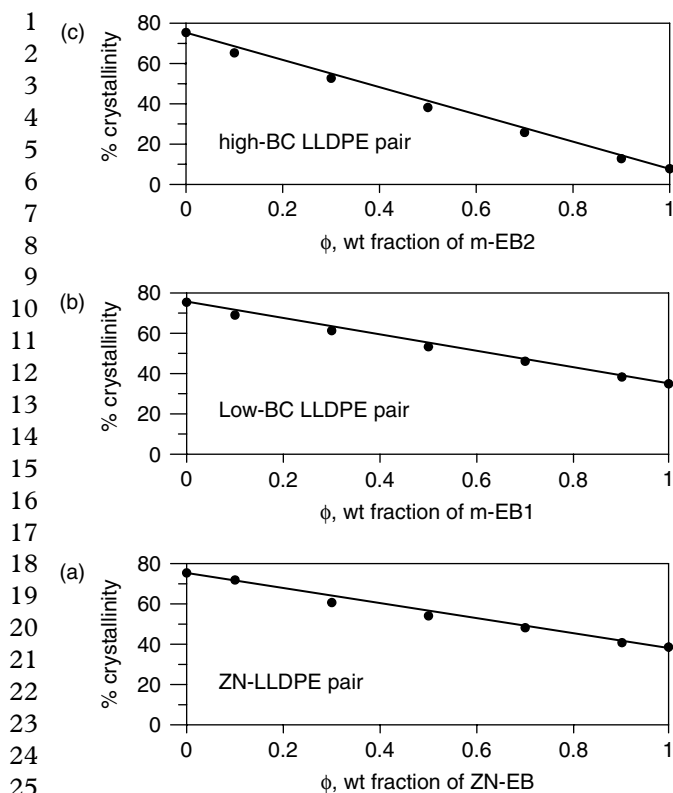


Figure 4. Percent crystallinity as a function of composition.

blends, the results shown in Fig 4(a) are consistent with those given in Fig 3(a). Also, for HDPE-rich blends with either m-EB1 or EB2, the results are in agreement with the DSC observations shown in Figs 1 and 2. However, for m-LLDPE (both m-EB1 and m-EB2) rich blends, co-crystallization was suggested, yet the total crystallinity followed a linear additivity rule. This observation requires further X-ray investigation on the effect of blending on lamella thickness of m-LLDPE/HDPE blends.

In summary, both BC and CD of m-LLDPE were found to influence the melting and crystallization of LLDPE/HDPE blends. HDPE-rich blends with either low-BC or high-BC pairs showed single melting and crystallization peaks. However, the ZN-LLDPE blends behaved quite differently with single melting and crystallization peaks at all compositions. The heterogeneity of ZN-LLDPE, especially the presence of linear PE, has probably helped in the co-crystallization with the linear HDPE. On the other hand, m-LLDPE-rich blends (regardless of their BC) showed multiple peaks. Total crystallinity is only composition dependent, with no influence of BC or CD.

### Mechanical properties

The tensile moduli as a function of composition for blends of m-EB1, m-EB2 and ZN-EB with HDPE are shown in Fig 5. In figures the displayed mechanical properties represent the average of at least five measurements. The error bars indicate the range of these results.

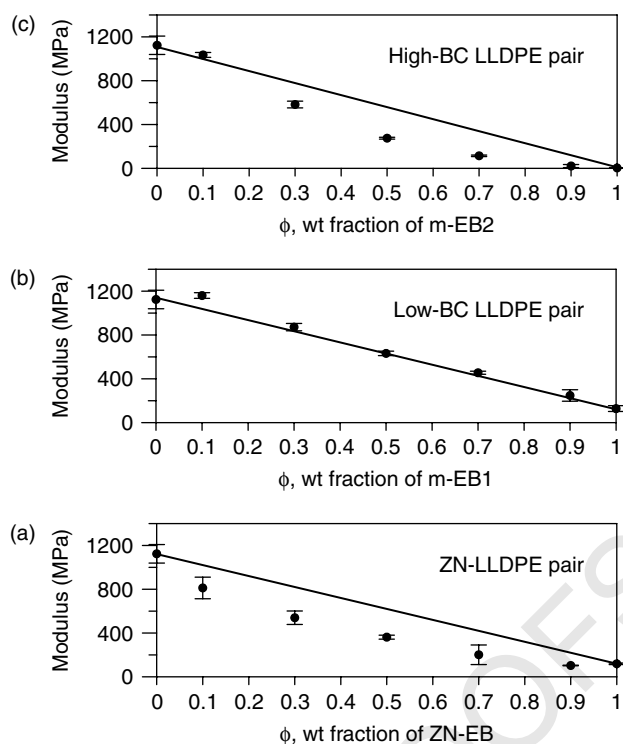


Figure 5. Tensile modulus as a function of composition.

In Fig 5(b), the modulus for HDPE is  $\approx 1100$  MPa, while that of m-EB1 is  $\approx 200$  MPa. In general, the moduli for the blends follow the linear rule of mixtures. However, the moduli for blends of ZN-EB and HDPE, as shown in Fig 5(a), are lower than the predictions of the linear rule of mixtures. Comparison of Figs 5(a) and 5(b) suggests that the CD of ZN-EB has influenced the moduli of its blends with HDPE at all compositions. However, the moduli for blends of m-EB1 (characterized by more uniformly distributed short chain branches) and HDPE are predicted by the simple rule of mixtures.

For the effect of BC on tensile modulus, Figs 5(b) and 5(c) are compared. The moduli for all m-EB2 blends, except the 10 % m-EB2, are lower than the simple rule of mixtures. The m-EB2-rich blends show the stronger deviations. The addition of 10 % m-EB2 to HDPE produced a proportional decrease in the modulus. On the other hand, addition of up to 30 % HDPE (the component with the highest modulus) to the highly branched m-EB2 did not result in any significant improvement in the tensile modulus. It is interesting to note that similar composition dependency of the melt dynamic viscosity and elastic modulus were observed for m-EB2-rich blends showing negative deviation behavior.<sup>3</sup> The proposed interlayer morphology<sup>3,43</sup> could explain the current observations. These results suggest that BC has a strong influence on the tensile modulus, especially for m-LLDPE-rich blends.

The effect of BC and CD on the strength at yield is shown in Fig 6. Again, comparison of Figs 6(a) and 6(b) is expected to show the effect of CD, while that of Figs 6(b) and 6(c) will indicate the effect of BC.

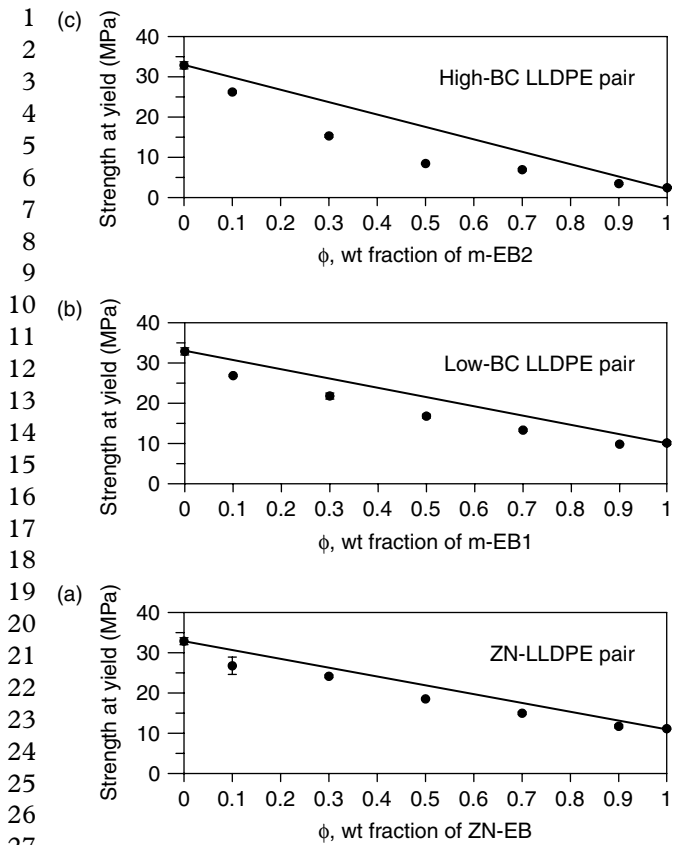


Figure 6. Strength at yield as a function of composition.

The strength at yield, for ZN-EB blends with HDPE, is in agreement with previous measurements of Cho *et al.*<sup>33</sup> HDPE showed the highest yield strength. It is clear that CD has little or no influence on strength at yield. Hence, the behavior of yield strength for ZN-LLDPE/HDPE blends is different from that of ZN-LLDPE/LDPE blends.<sup>33</sup> For the effect of BC, the results of the yield strength are similar to those of the tensile modulus. Negative deviations from linear additivity were observed. So, strength at yield is strongly influenced by BC, but not by CD.

The influence of CD and BC on the ultimate tensile strength is shown in Fig 7. The current findings for strength at break for the ZN-EB blends are similar to previous reports of Cho *et al.*<sup>33</sup> In general, the ultimate tensile strength for blends of m-EB1 and ZN-EB with HDPE is lower than the predictions of linear additivity. Nonetheless, CD showed little or no influence on ultimate tensile strength. It should be noted that the ultimate tensile strength (or strength at break) for ZN-LLDPE/HDPE blends showed a behavior that is contrary to that reported for ZN-LLDPE/LDPE systems. In Fig 7(c) the results for the high-BC pair are given. Both negative (HDPE-rich blends) and positive deviations (m-EB2-rich blends) are observed. The behavior of HDPE-rich blends is similar for both m-EB1 and m-EB2 blends. The effect of BC is observed in m-LLDPE-rich blends only. So, CD has little or no influence on ultimate tensile strength, and BC influences m-LLDPE-rich blends only.

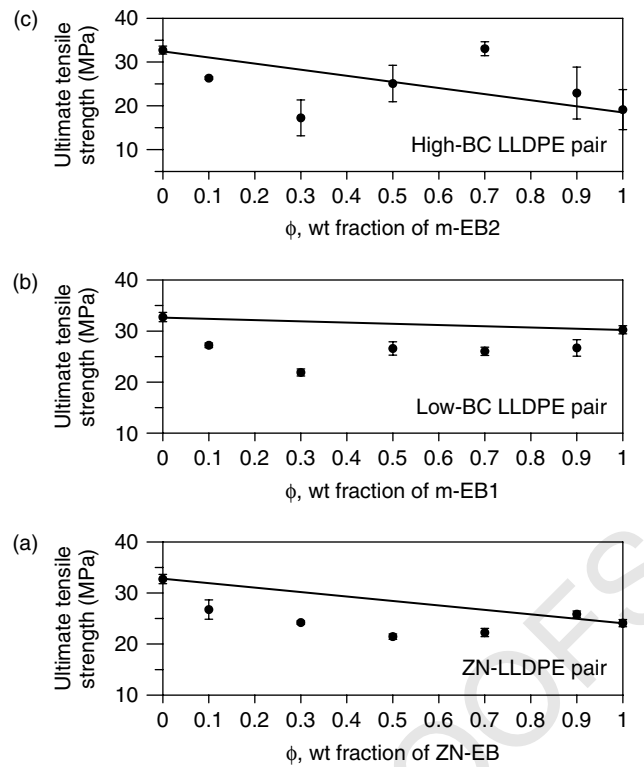


Figure 7. Ultimate tensile strength as a function of composition.

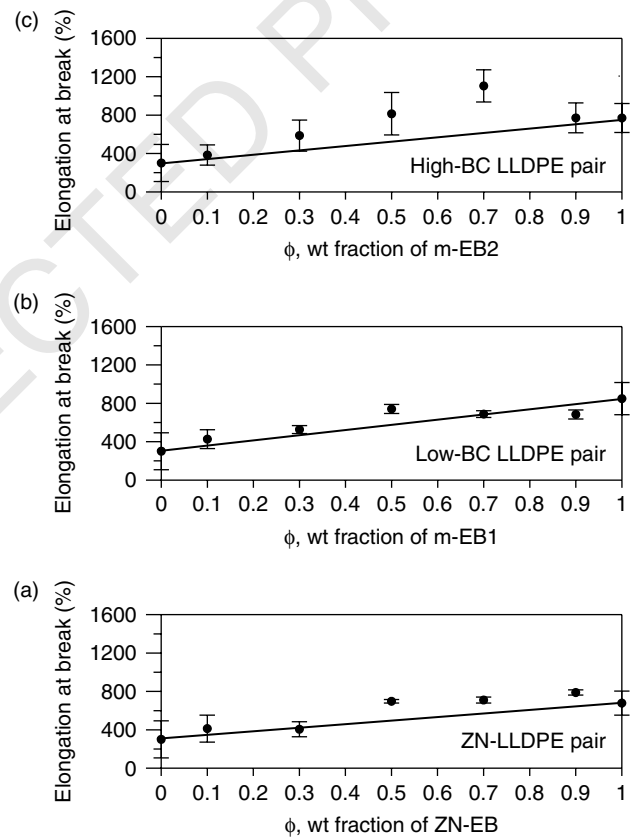


Figure 8. Elongation at break as a function of composition.

The elongation at break for the different blend systems is shown in Fig 8. The elongation at break for all LLDPEs was found to be higher than that of HDPE, irrespective of BC or synthesis mechanism.

1 The elongation at break of m-EB1 is higher than that of  
 2 ZN-EB, and this is mainly due to the absence of linear  
 3 molecules in m-EB1. As seen in Figs 8(a) and 8(b),  
 4 ZN-EB and m-EB1 blends with HDPE display similar  
 5 trends, which suggests no influence for CD. For  
 6 Figs 8(b) and 8(c), the behavior of HDPE-rich blends  
 7 is similar, but m-EB2-rich blends show synergistic  
 8 effects. The elongation at break obtained for the 50 %  
 9 and 70 % m-EB2 blends with HDPE was much higher  
 10 than that of m-EB1. This suggests that adding up  
 11 to 30 % HDPE to highly branched m-LLDPE will  
 12 improve the elongation at break. Hence, CD has no  
 13 effect on elongation at break, and BC influence is  
 14 observed for m-LLDPE-rich blends only. The area  
 15 under the stress–strain curve, which is proportional to  
 16 the toughness of material, is given in Fig 9. The effects  
 17 of BC and CD on the work of rupture are similar to  
 18 those of elongation at break.

19 In summary, for the same  $M_w$ , the three LLDPEs,  
 20 m-EB1, m-EB2 and ZN-EB, exhibited different  
 21 mechanical properties as shown in Figs 5 to 9. In  
 22 the linear elastic range, the solid-state tensile modulus  
 23 and yield strength for the low- and high-BC pairs are  
 24 mirror images of the melt state. However, ZN-LLDPE  
 25 was suggested to be more miscible with HDPE than  
 26 m-LLDPE, but it showed poorer moduli and yield  
 27 strength. This is contrary to what was expected. This  
 28 suggests that ZN-LLDPE/HDPE crystals are likely  
 29 to have smaller thickness in comparison to those of  
 30 m-LLDPE/HDPE. This observation requires further  
 31 exploration by X-ray. The incompatibility of the high-  
 32 BC pair resulted in poor tensile modulus and strength.  
 33 Also, CD was observed to influence both the moduli  
 34 and the tensile strength of blends at all compositions,  
 35

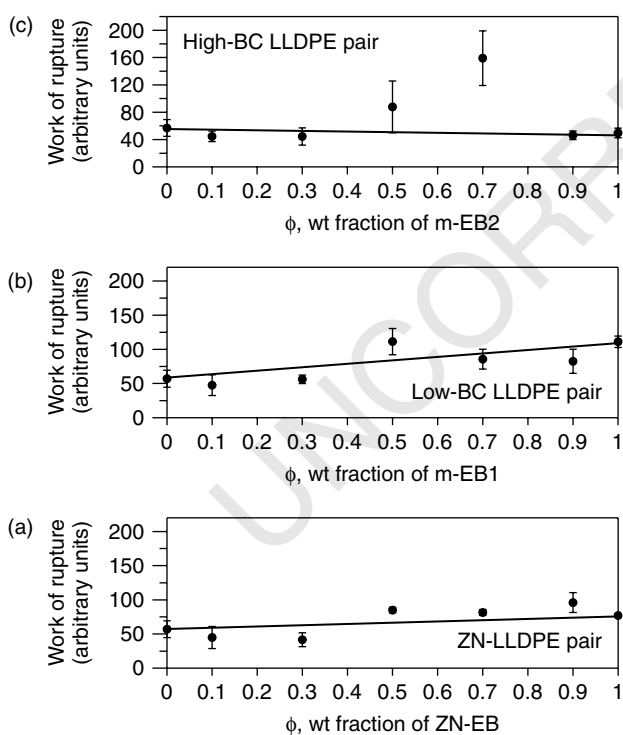


Figure 9. Work of rupture as a function of composition.

with ZN-LLDPE blends showing poorer properties.  
 For the ultimate tensile strength, elongation at break  
 and work of rupture, CD has little or no influence, and  
 BC influences m-LLDPE-rich blends only. In general,  
 BC has a stronger influence on mechanical properties  
 than CD.

## CONCLUSIONS

Blends of three different butene LLDPEs (two  
 metallocene-based and one Ziegler–Natta-based) with  
 similar  $M_w$  were melt blended with the same HDPE.  
 The LLDPEs were selected in order to study the  
 effect of branch content and composition distribution  
 of LLDPE on thermal and solid-state properties of  
 LLDPE/HDPE blends. Resins were paired to study  
 one molecular parameter at a time while keeping  
 other parameters very close to each other. The total  
 crystallinity of all blends studied was found to follow  
 a linear additivity rule and no effect for BC or CD was  
 observed. A correlation between melt compatibility  
 (or incompatibility) and mechanical properties of the  
 low- and high-BC m-LLDPE blends with HDPE was  
 observed. Miscible blends showed rheological<sup>3</sup> and  
 many mechanical properties that can be estimated  
 from additivity rules. High branch content of m-  
 LLDPE was observed to influence the rheological  
 and mechanical properties of its blends with HDPE.  
 The effect is pronounced in the m-LLDPE-rich  
 range. Elongation at break and work of rupture  
 showed synergistic effects, while modulus was lower  
 than predictions by linear additivity. Composition  
 distribution showed no significant effect on thermal  
 properties or on the work of rupture; however, it  
 did result in low moduli for ZN-LLDPE blends  
 with HDPE. Mechanical properties of LLDPE/HDPE  
 blends are not a function of total crystallinity like  
 LLDPE/LDPE blends<sup>39</sup>. It seems that the type and  
 thickness of crystals formed in each case are different  
 but this requires confirmation by scattering methods.  
 Comparison of the DSC results and mechanical testing  
 suggests that thermal analysis is inconclusive with  
 regard to the compatibility of blends. In addition, total  
 crystallinity does not correlate to melt or solid-state  
 properties of LLDPE/HDPE blends. In conclusion, a  
 direct correlation exists between melt compatibility  
 (or incompatibility) and thermal and mechanical  
 properties of LLDPE blends with HDPE, and branch  
 content, in general, has a stronger influence on these  
 properties than composition distribution.

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### Queries from the Copyeditor:

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