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## Influence of branch content on the microstructure of blends of linear and octene-branched polyethylene: a MD simulation study

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### Abstract

Microstructure of linear low-density polyethylene (LLDPE) with linear high-density polyethylene (HDPE) is investigated by molecular dynamics (MD) simulation. The branch content of LLDPE was varied from 10 to 60 branches/1000 C. An equimolar mixture of each of the two polymers is simulated in the NVT ensemble at 500 K and at average experimental densities of the two polymer melts. Initially, chains of LLDPE and HDPE were completely mixed and evolution of conformations with time was monitored. The blends were found to microphase separate when the branch content of LLDPE exceeded 30 branches/1000 C. At 40 branches/1000 C, the two polymers displayed partial microphase separation and complete microphase separation was observed at 60 branches/1000 C. Substantial short-range order and mismatch of molecular conformations is observed in the microphase-separated systems.

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*Keywords:* Polyethylene; Branch content; MD simulation; Self assembly; Microstructure; Blends

### 1. Introduction

Commercial linear low-density polyethylene (LLDPE) produced by Ziegler–Natta (ZN) catalysis is available in a range of densities from 0.900 to approximately 0.935 g/cm<sup>3</sup> depending on the amount of comonomer (1-butene, 1-hexene, or 1-octene) incorporated. LLDPE is usually blended in small amounts with high-density polyethylene (HDPE) to improve flexibility and reduce extruder backpressure [1,2]. The phase behavior of PE/PE blends has attracted considerable interest both by the research community and industry [3–9]. As a result, a better understanding of the microstructure of polyethylene blends is important for polymer processing and final product properties.

In the literature, different views have been expressed about the phase behavior of LLDPE/HDPE systems ranging from liquid–liquid phase segregation [9–13] to complete homogeneity in the melt [3–5]. It is known that the miscibility of PE/PE blends is influenced by different molecular parameters. These parameters are molecular weight ( $M_w$ ), branch type, branch content (BC), and branch distribution [14,15]. Unfortunately, most of the previous studies of LLDPE/HDPE blend miscibility used ZN-LLDPE [16–20]. It is known that conventional ZN-LLDPE contains considerable structure heterogeneity, with substantial amounts of the polymer having either low or high degree of comonomer incorporated [21]. There is evidence that the chain-to-chain heterogeneity of conventional ZN-LLDPE is broad enough to produce thermodynamically driven microphase separation in the melt of ‘pure’ ZN-LLDPE [13,22–25]. The introduction of single-site catalyst (i.e. metallocene) has made it possible to produce LLDPE with more molecular regularity and more homogeneous distribution of

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short chain branching (SCB) [26]. Few studies have made use of m-LLDPE in blend miscibility [27,28].

In the past, significant research work was conducted to study the miscibility of LLDPE and HDPE blends. A great deal of information was obtained from transmission electron microscopy (TEM) work of Hill's group [6–14,17–19] and small angle neutron scattering (SANS) of Alamo, Graessley, and Wignall groups [3–5,25,29,30].

Recently, SANS experiments showed that for heterogeneous LLDPEs with wide range of BC, a fraction of the highly branched chains, e.g.,  $>80$   $\text{CH}_3/1000$  C (80 branches per one thousand backbone carbon atoms) could phase separate from lightly branched majority, even when the average BC is low (e.g., 10–20  $\text{CH}_3/1000$  C) [25]. However, it was reported that there would be miscibility between linear and branched molecules when the branch level is low and immiscibility when the BC is high as suggested by TEM experiments [27]. Similarly, mixtures of HDPE and LLDPE were suggested to be homogeneous in the melt, when the BC is low (i.e.,  $<40$   $\text{CH}_3/1000$  C). However, when the BC is high ( $>80$   $\text{CH}_3/1000$  C), the blend phase separates [5]. However, different researchers reported different values for the cut-off BC of LLDPE that would lead to phase separation in LLDPE/HDPE blends [5,17,20,27].

Most of the above studies have used either SANS, differential scanning calorimetry (DSC), wide-angle X-ray diffraction (WAXD), or TEM techniques except the recent work of Choi and Fan et al. that used MD simulation [20,31]. In their study, HDPE and LLDPE molecules were constructed with a total of 500 C atoms each and random distribution of branches in the LLDPE chain. Each of the LLDPE and HDPE molecules were evaporated separately and cohesive energy density,  $E_{\text{CED}}$ , and Flory–Huggins interaction parameter,  $\chi$ , were then calculated [32]. Miscibility was then predicted from  $\chi$  values.

In this study, we investigate the microstructure of HDPE/LLDPE blends using molecular dynamics simulation. Initially, we mix molecules of LLDPE and HDPE to form a well mixed structure with random distribution of the two polymers. We then equilibrate the structure for 8–10 ns and monitor the microstructure of the system. The branch content of the LLDPE is varied from 10 to 60  $\text{CH}_3/1000$  C. This approach provides visual images of the microstructure of the LLDPE/HDPE blends (for the first time as far as we know). In addition, the radial distribution function and order parameter are used to quantify the structural differences and the level of microphase separation in the blend. Although results of this investigation cannot be directly used to judge the miscibility/immiscibility of PE/PE blends because of the small sizes of the systems investigated, the study of microstructure of polyethylenes with different branch

contents can pave the way to designing nano-structured materials from low cost thermoplastics.

## 2. Model and simulation method

Four chains of LLDPE composed of 125 backbone  $\text{CH}_2$  units each with various levels of octene incorporation and four chains of linear HDPE composed of 125 backbone segments were initially constructed. A limited number of simulations were conducted with two chains of PE composed of 250 backbone  $\text{CH}_2$  segments each and two chains of HDPE composed of 250  $\text{CH}_2$  segments each to investigate the influence of molecular size and chain ends on microstructure. The branch content (BC) of the m-LLDPE was 10, 30, 40 and 60 branches/1000 backbone carbons. The branches were randomly distributed along the chain to simulate the structure of m-LLDPE [26]. The branches were composed of five methylene units and an end methyl unit simulating the copolymerization of ethylene with 1-octene. Initially, chains with random torsion angle distribution were constructed. The chains of the two polymers were initially well mixed at the beginning of the simulation. Carbon and hydrogen atoms were explicitly considered in the simulation. The chains were subsequently placed in a low-density box with periodic boundary conditions at 600 K. After simulation for 0.5 ns at the elevated temperature of 600 K, the temperature was reduced to 500 K. The system was simulated for 1 ns while the volume was decreased to yield the average experimental density of the two polymers. The density was fixed and the pressure and energy were monitored for 8–10 ns to ensure equilibration. The system was then simulated in the canonical (NVT) ensemble using the Nose–Hoover method at densities averaged over the experimental bulk densities of both polymers [33]. Density at room temperature of different ExxonMobil metallocene octane LLDPEs was correlated to BC. The BC was measured by  $^{13}\text{C}$  NMR as  $\text{CH}_3/1000$  C. The density ( $\rho$ ) in  $\text{g}/\text{cm}^3$  was obtained as  $\rho = 0.92 - 0.012 \text{ BC}$ . A thermal expansion coefficient of  $2 \times 10^{-4} \text{ cm}^3/\text{g}/\text{K}$  was used [34] to estimate melt densities at 500 K. The estimated densities used in the simulation are shown in Table 1 for the different branch contents. The simulations were carried out using Materials Studio molecular modeling code (version 2.1, Accelrys Inc.). Periodic boundary condi-

Table 1  
Average density data used in the simulations at 500 K

BC $\text{CH}_3/1000$ C	Melt density, $\text{g}/\text{cm}^3$
10	0.88
30	0.86
40	0.84
60	0.82

152 tions were applied. The simulation temperature was  
153 limited to 500 K to simulate melt conditions and accel-  
154 erate equilibration of the polymers. An integration time  
155 step of 0.001 ps was used. A relaxation constant of 0.1  
156 for the relaxation heat variable bath was applied  
157 throughout the simulations. The compass force field  
158 potential was employed in the simulation [35]. The  
159 geometric and energetic parameters were as described by  
160 Sun [35]. The potential was validated for polyethylene  
161 and was found to reproduce the crystalline structure and  
162 experimental densities of HDPE [35]. Non-bonded  
163 interactions were modeled using a Lennard-Jones po-  
164 tential with a cut-off distance of 10 Å. Standard tail  
165 corrections were applied.

### 166 3. Results and discussion

167 Fig. 1a–d shows images of the final equilibrated  
168 conformations of the blends after 10 ns of simulation. It  
169 can be seen in Fig. 1a and b that the blends of HDPE  
170 and LLDPE containing 10 and 30 branches/1000 C are  
171 compatible and well mixed in the simulation box. The  
172 HDPE chains are shown in black while the m-LLDPE  
173 chains are shown in gray. No microphase separation was

174 displayed by these two systems. However, increasing the  
175 branch content to 40 causes the two polymers to mi-  
176 crophase separate as shown in Fig. 1c. The microphase  
177 separation becomes more evident at a branch content of  
178 60/1000 C when chains occupy distinct domains in the  
179 simulation box as shown in Fig. 1d. The snapshots  
180 shown are representative of the structure of the melt.  
181 The systems containing LLDPE with 40 and 60 bran-  
182 ches/1000 C were observed to display microphase separa-  
183 tion after 2 ns of simulation and remain phase  
184 segregated for the remaining equilibration period. The  
185 level of self assembly increased as the branch content  
186 increased from 40 to 60/1000 C. For example, some  
187 overlap is observed between the two polymers in the case  
188 of 40/1000 C (Fig. 1c) while the polymers occupy totally  
189 distinct domains in the 60/1000 C case (Fig. 1d). In  
190 addition, a layered morphology is observed in the mi-  
191 crophase separated blends (Fig. 1c and d).

192 In order to investigate the microstructure of the  
193 blend and the level of miscibility, we determined the  
194 unlike C–C radial distribution function (RDF) for  
195 backbone carbons belonging to HDPE and m-LLDPE.  
196 A comparison of the intermolecular RDF of the carbon  
197 atoms in the blend is shown in Fig. 2. It can be observed  
198 that unlike RDF (for carbons belonging to different

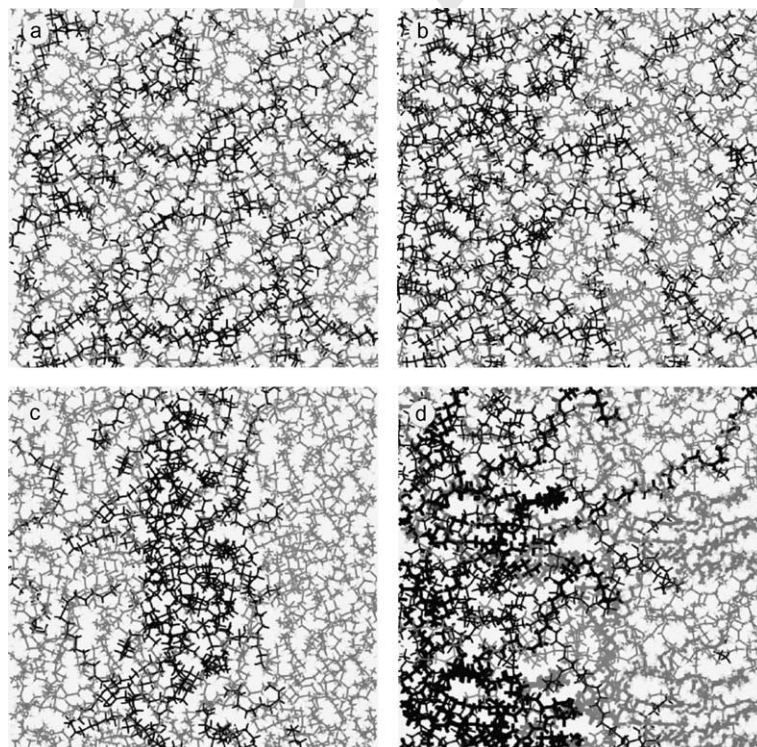


Fig. 1. (a) Configuration of the blend of HDPE with m-LLDPE containing 10 branches/1000 C. (b) Configuration of the blend of HDPE with m-LLDPE containing 30 branches/1000 C. (c) Configuration of the blend of HDPE with m-LLDPE containing 40 branches/1000 C. (d) Configuration of the blend of HDPE with m-LLDPE containing 60 branches/1000 C.

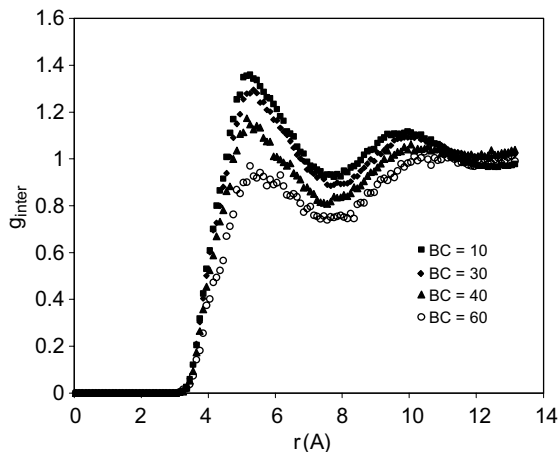


Fig. 2. Intermolecular RDF of CH<sub>2</sub> segments belonging to different type chains.

199 types of PE) decreases with increasing branch content  
200 from 10 to 60. The level of intermolecular correlation is  
201 maximum for the blend with BC=10 and decreases  
202 gradually as the branch content increases to 60. This  
203 increase in intermolecular correlation with increasing  
204 branch content indicates that methylene segments

205 belonging to the HDPE do not like to be in the neigh-  
206 borhood of LLDPE methylenes and prefer an environ-  
207 ment of segments belonging to the same type HDPE.  
208 This tendency increases with increasing branch content.  
209 For the miscible systems (BC = 10–30), the intermolec-  
210 ular RDF's are very similar. However, a large decrease  
211 in intermolecular RDF is observed for the microphase  
212 separated systems (BC = 40 and 60).

213 It is also observed that the two chain types assume  
214 different conformations in the melt in the immiscible  
215 systems. Fig. 3a–d show the intramolecular RDF for the  
216 C atoms in the blend for both the HDPE and m-  
217 LLDPE. It can be observed that at the low BC of 10,  
218 both the HDPE and LLDPE have very similar struc-  
219 tures in the melt. However, as the branch content in-  
220 creases, the height of the first peak becomes smaller for  
221 the m-LLDPE than that for the HDPE. This indicates  
222 that the HDPE molecules maintain a denser and more  
223 ordered structure in the blend than the LLDPE molec-  
224 ules. This also indicates that structural heterogeneity  
225 increases with increasing branch content in the blend.  
226 Fig. 4 shows a comparison of the order parameters (Eq.  
227 (1)) determined from the simulation for the HDPE and  
228 the m-LLDPE with BC = 30 in the melt blend. The order  
229 parameter is a quantity that provides an indication of

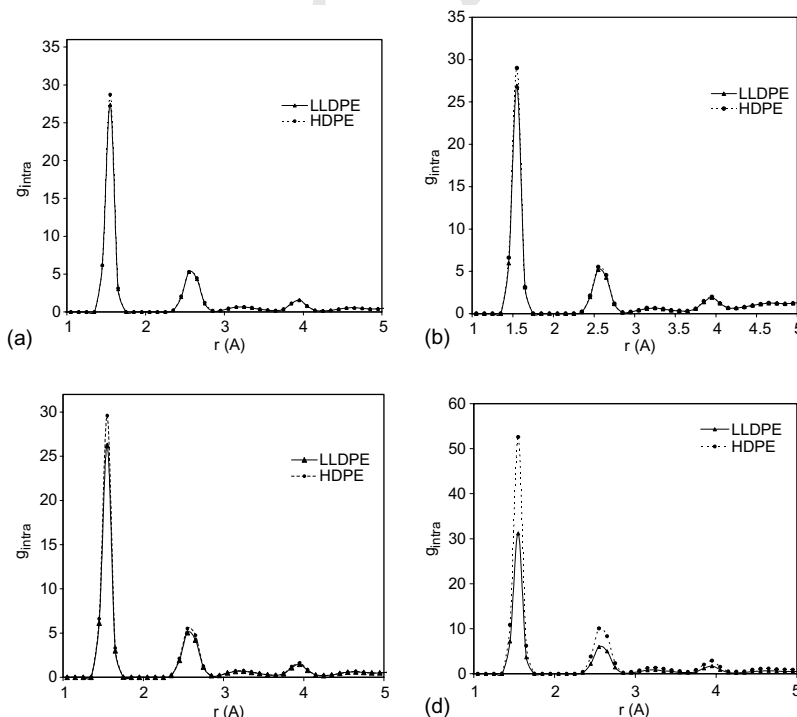


Fig. 3. (a) Intramolecular RDF of CH<sub>2</sub> segments belonging to the HDPE and m-LLDPE chains with BC = 10. (b) Intramolecular RDF of CH<sub>2</sub> segments belonging to the HDPE and m-LLDPE chains with BC = 30. (c) Intramolecular RDF of CH<sub>2</sub> segments belonging to the HDPE and m-LLDPE chains with BC = 40. (d) Intramolecular RDF of CH<sub>2</sub> segments belonging to the HDPE and m-LLDPE chains with BC = 60.

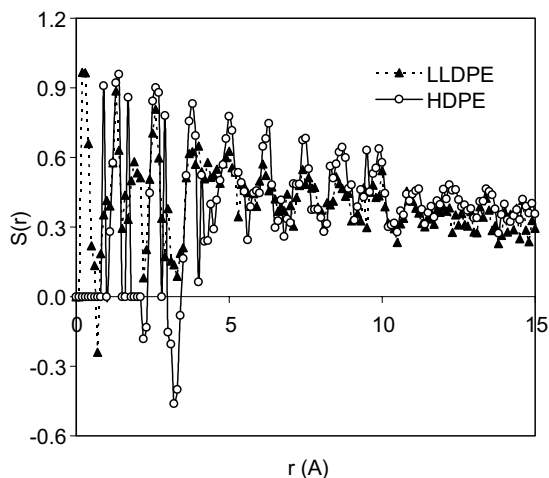


Fig. 4. Bond order correlation function for the two components of the blend (LLDPE with 30 branches/1000 C).

230 the structural source of incompatibility of the two  
231 polymers. The order parameter,  $S(r)$ , is defined by

$$S(r) = \frac{3\langle \cos^2 \theta \rangle - 1}{2} \quad (1)$$

233 where  $\theta$  is the angle between structural unit vector taken  
234 here as the vector connecting carbons separated by 10  
235 bonds and the reference direction. It can be observed  
236 that at the branch content of 30, the HDPE and m-  
237 LLDPE chains have similar levels of order in the blend.  
238 However, as the branch content increases to 60, Fig. 5  
239 shows that the level of order for the HDPE (open  
240 symbols) is much higher than that for m-LLDPE. These  
241 results suggest that the origin of the observed segrega-

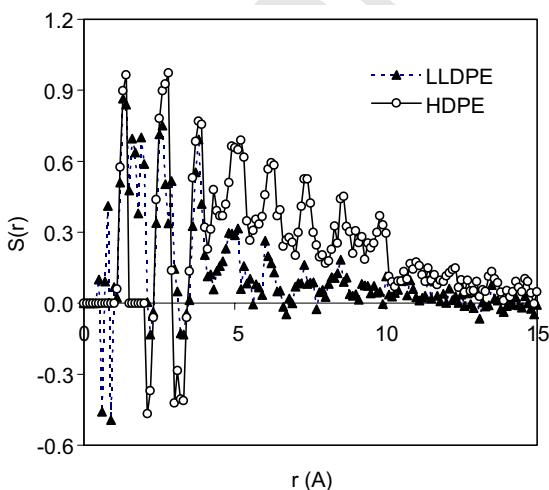


Fig. 5. Bond order correlation function for the two components of the blend (LLDPE with 60 branches/1000 C).

242 tion in these simulations is the difference in the local  
243 structures of the two polymers in the blend at high  
244 branch content. In particular, the HDPE and the  
245 LLDPE with low branch content are capable of forming  
246 locally ordered structures in the fluid state in which a  
247 lower energy state is formed when  $\text{CH}_2$  segments  
248 belonging to the same chain are neighbors to each other  
249 [36]. However, as the branch content exceeds 40, the low  
250 energy conformation of the HDPE is realized when  $\text{CH}_2$   
251 segments belonging to the same chain are neighbors.

252 The phase behavior of polymer mixtures has been  
253 traditionally described by extensions of the Flory-  
254 Huggins theory. In these extensions, the interaction  
255 parameter ( $\chi$ ) has been generally decomposed by many  
256 researchers into two components that correspond to the  
257 enthalpic contribution and entropic contribution to the  
258 excess Gibbs energy of mixing [37-40]. This work shows  
259 that the local structure of the pure polymers and the  
260 mismatch of the conformations of blend components are  
261 the likely causes of microphase separation in polyethy-  
262 lene blends [15]. Although results of this work cannot  
263 be used to explain the miscibility/immiscibility behavior  
264 of PE/PE blends, the layered morphology observed the  
265 self-assembled blends can provide insight into some  
266 rheological observations which suggest interlayer slip  
267 during flow. Fig. 6 shows a plot of the experimental  
268 dynamic viscosity  $\eta'(\phi)$  of a HDPE/m-LLDPE with high  
269 branch content. The experimental dynamic viscosity  
270 (open circles) exhibits negative deviation behavior  
271 (NDB) from log-additivity rule (straight line). The details  
272 of the rheological measurements are discussed  
273 elsewhere [43]. NDB rheology is believed by many

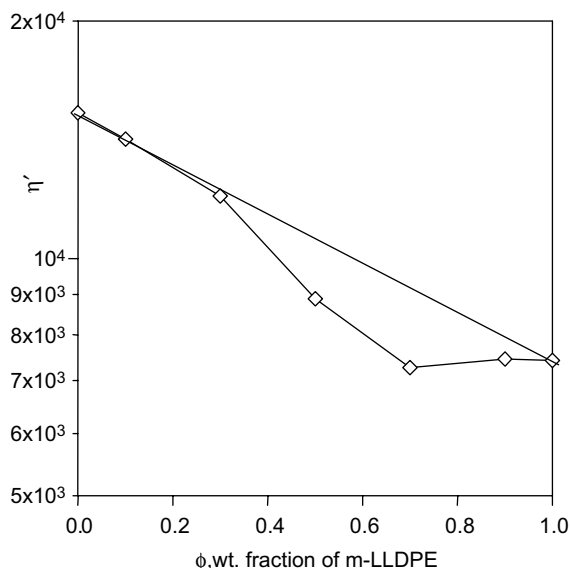


Fig. 6.  $\eta'(\phi)$  for blends of m-LLDPE with HDPE ( $T_{\text{mix}} = 190$  °C,  $T_{\text{test}} = 190$  °C,  $\gamma^\circ = 15\%$ ).

investigators to be a result of interlayer slip [41–43]. The microstructures of the blends shown in this work show that HDPE/LLDPE blends can self assemble in lamellar structures when the branch content of the LLDPE is sufficiently high. The lamella might be capable of slipping past each other, thus explaining the observed rheological behavior. A dynamic simulation of the polymers in a flow field can provide better evidence for this hypothesis. It is interesting to note that our group has recently reported emulsion rheology for LLDPE/LDPE blends [15]; however, layered morphology was obtained for LLDPE/HDPE systems studied in this paper.

Increasing the molecular weight of the polymers was not observed to change the final microstructures of the blends. However, it was observed that the time taken by the systems to display microphase separation was longer in case of the larger molecular weight polymers (4–5 ns). However, eventually the equilibrated structures had similar microstructures to the short chain blends.

#### 4. Conclusion

This study shows that blends of HDPE and LLDPE microphase separate when the branch content of LLDPE exceeds 40 branches/1000 C. The level of microphase separation quantified by the radial distribution function was found to increase with increasing branch content. The conformations of the different polymers, characterized by the order parameter were found to be different as branch content increased. The MD simulation results can be used to explain rheological experimental results that showed NDB rheology.

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