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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1. Introduction

Commercial linear low-density polyethylene (LLD-PE) produced by Ziegler–Natta (ZN) catalysis is available in a range of densities from 0.900 to approximately 0.935 g/cm³ 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 hetero-geneity 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 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 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 CH$_3$/1000 C). However, when the BC is high (>80 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_{CED}, and Flory–Huggins interaction parameter, χ, were then calculated [32]. Miscibility was then predicted from χ 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 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 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 CH$_2$ segments each and two chains of HDPE composed of 250 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}C NMR as CH$_3$/1000 C. The density (ρ) in g/cm^3 was obtained as $\rho = 0.92$–0.012 BC. A thermal expansion coefficient of 2×10^{-4} cm^3/g/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 conditions were applied. The simulation temperature was limited to 500 K to simulate melt conditions and accelerate equilibration of the polymers. An integration time step of 0.001 ps was used. A relaxation constant of 0.1

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

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

for the relaxation heat variable bath was applied throughout the simulations. The compass force field potential was employed in the simulation [35]. The geometric and energetic parameters were as described by Sun [35]. The potential was validated for polyethylene and was found to reproduce the crystalline structure and experimental densities of HDPE [35]. Non-bonded interactions were modeled using a Lennard-Jones potential with a cut-off distance of 10 Å. Standard tail corrections were applied.

3. Results and discussion

Fig. 1a–d shows images of the final equilibrated conformations of the blends after 10 ns of simulation. It can be seen in Fig. 1a and b that the blends of HDPE and LLDPE containing 10 and 30 branches/1000 C are compatible and well mixed in the simulation box. The HDPE chains are shown in black while the m-LLDPE chains are shown in gray. No microphase separation was displayed by these two systems. However, increasing the branch content to 40 causes the two polymers to microphase separate as shown in Fig. 1c. The microphase separation becomes more evident at a branch content of

60/1000 C when chains occupy distinct domains in the simulation box as shown in Fig. 1d. The snapshots shown are representative of the structure of the melt. The systems containing LLDPE with 40 and 60 branches/1000 C were observed to display microphase separation after 2 ns of simulation and remain phase segregated for the remaining equilibration period. The level of self assembly increased as the branch content increased from 40 to 60/1000 C. For example, some overlap is observed between the two polymers in the case of 40/1000 C (Fig. 1c) while the polymers occupy totally distinct domains in the 60/1000 C case (Fig. 1d). In addition, a layered morphology is observed in the microphase separated blends (Fig. 1c and d).

In order to investigate the microstructure of the blend and the level of miscibility, we determined the unlike C–C radial distribution function (RDF) for backbone carbons belonging to HDPE and m-LLDPE. A comparison of the intermolecular RDF of the carbon atoms in the blend is shown in Fig. 2. It can be observed that unlike RDF (for carbons belonging to different types of PE) decreases with increasing branch content from 10 to 60. The level of intermolecular correlation is maximum for the blend with BC = 10 and decreases gradually as the branch content increases to 60. This
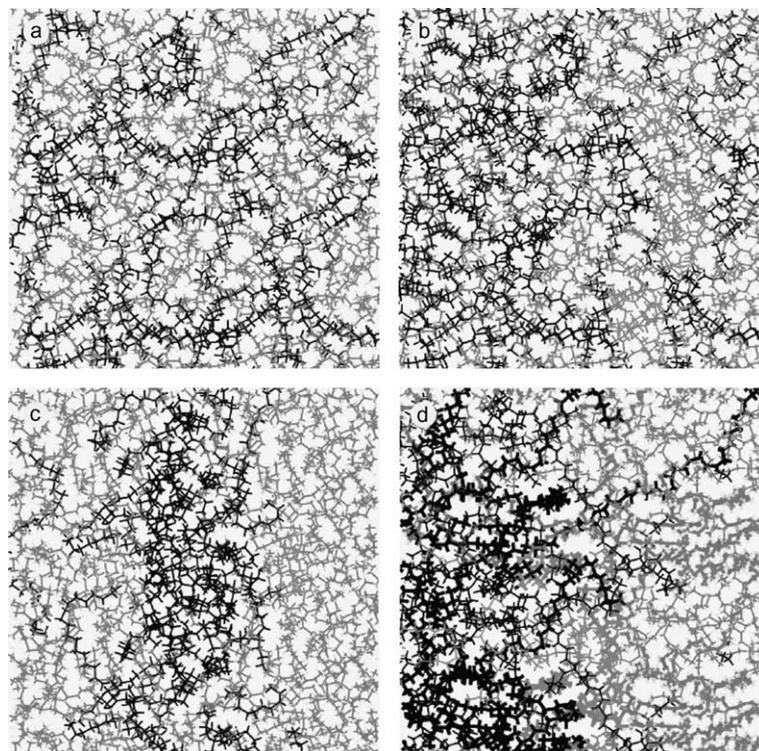

Fig. 1. (a) Configuration of the blend of HDPE with m-LLDPE containing 10 branches/1000 C. (b) Configuration of the blend of HDPE with m-LLDPE containing 30 branches/1000 C. (c) Configuration of the blend of HDPE with m-LLDPE containing 40 branches/1000 C. (d) Configuration of the blend of HDPE with m-LLDPE containing 60 branches/1000 C.
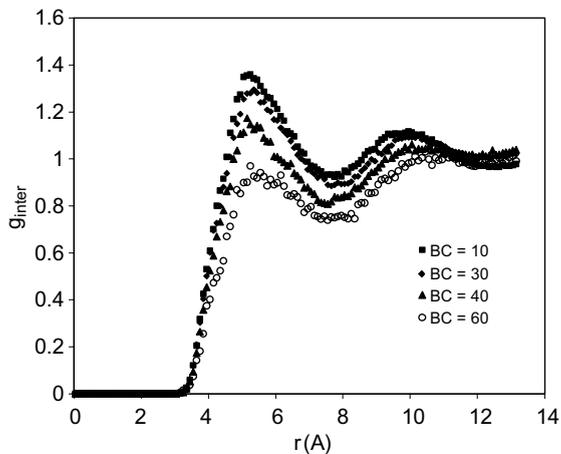
Fig. 2. Intermolecular RDF of CH_2 segments belonging to different type chains.

increase in intermolecular correlation with increasing branch content indicates that methylene segments belonging to the HDPE do not like to be in the neighborhood of LLDPE methylenes and prefer an environment of segments belonging to the same type HDPE. This tendency increases with increasing branch content.

For the miscible systems (BC = 10–30), the intermolecular RDF's are very similar. However, a large decrease in intermolecular RDF is observed for the microphase separated systems (BC = 40 and 60).

It is also observed that the two chain types assume different conformations in the melt in the immiscible systems. Fig. 3a–d show the intramolecular RDF for the C atoms in the blend for both the HDPE and m-LLDPE. It can be observed that at the low BC of 10, both the HDPE and LLDPE have very similar structures in the melt. However, as the branch content increases, the height of the first peak becomes smaller for the m-LLDPE than that for the HDPE. This indicates that the HDPE molecules maintain a denser and more ordered structure in the blend than the LLDPE molecules. This also indicates that structural heterogeneity increases with increasing branch content in the blend. Fig. 4 shows a comparison of the order parameters (Eq. (1)) determined from the simulation for the HDPE and the m-LLDPE with BC = 30 in the melt blend. The order parameter is a quantity that provides an indication of the structural source of incompatibility of the two polymers. The order parameter, $S(r)$, is defined by

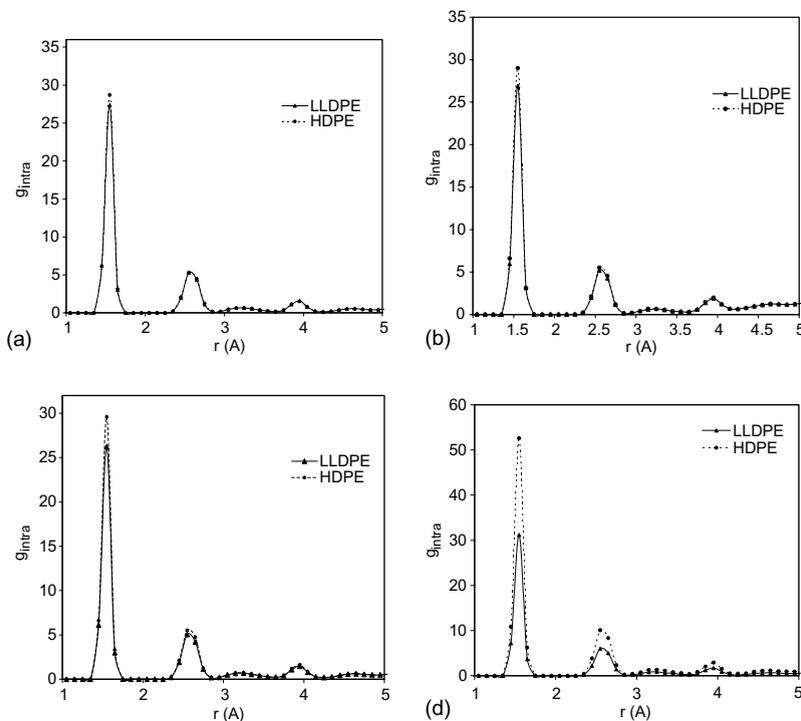$$S(r) = \frac{3\langle \cos^2 \theta \rangle - 1}{2} \tag{1}$$

(a)

(b)

(c)

(d)

Fig. 3. (a) Intramolecular RDF of CH_2 segments belonging to the HDPE and m-LLDPE chains with BC = 10. (b) Intramolecular RDF of CH_2 segments belonging to the HDPE and m-LLDPE chains with BC = 30. (c) Intramolecular RDF of CH_2 segments belonging to the HDPE and m-LLDPE chains with BC = 40. (d) Intramolecular RDF of CH_2 segments belonging to the HDPE and m-LLDPE chains with BC = 60.
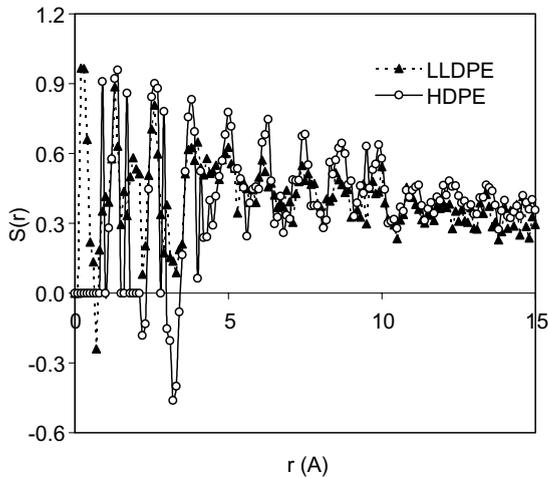
Fig. 4. Bond order correlation function for the two components of the blend (LLDPE with 30 branches/1000 C).

where θ is the angle between structural unit vector taken here as the vector connecting carbons separated by 10 bonds and the reference direction. It can be observed that at the branch content of 30, the HDPE and m-LLDPE chains have similar levels of order in the blend. However, as the branch content increases to 60, Fig. 5 shows that the level of order for the HDPE (open symbols) is much higher than that for m-LLDPE. These results suggest that the origin of the observed segregation in these simulations is the difference in the local structures of the two polymers in the blend at high branch content. In particular, the HDPE and the LLDPE with low branch content are capable of forming locally ordered structures in the fluid state in which a
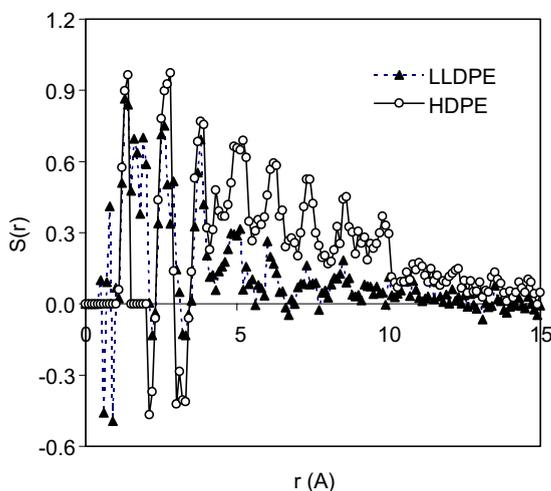
lower energy state is formed when CH_2 segments belonging to the same chain are neighbors to each other [36]. However, as the branch content exceeds 40, the low energy conformation of the HDPE is realized when CH_2 segments belonging to the same chain are neighbors.

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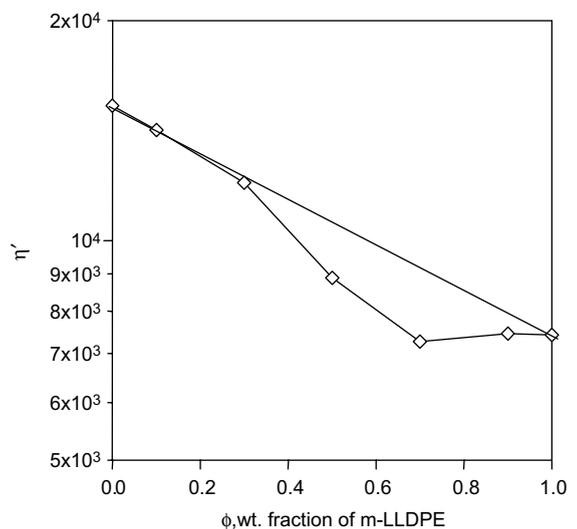

Fig. 5. Bond order correlation function for the two components of the blend (LLDPE with 60 branches/1000 C).

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

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.

Acknowledgements

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