



MOLECULAR DYNAMICS SIMULATION OF THE INFLUENCE OF BRANCH CONTENT ON THE MISCIBILITY OF HDPE IN METALLOCENE OCTENE-LLDPES

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ABSTRACT

Miscibility of linear high-density polyethylene (HDPE) and series of metallocene octene-based linear low-density polyethylene (m-LLDPE) with different branch contents were studied by molecular dynamic (MD) simulation. m-LLDPEs were modeled as ethylene-octene copolymers with octene uniformly distributed on the PE chain. In the MD simulation, chains were modeled using united atom approach in the NVT ensemble. The branch content (BC) was varied in the range 10–80 branches/1000C. The miscibility of HDPE/m-LLDPE blends was inferred from the steady-state conformation of the blend. Miscibility was found to be a function of BC. Miscibility was observed in blends of up to 40 branches/1000 C; however, blends were found to be immiscible in higher ranges (50-80 BC). MD Simulation results agree with previous experimental reports of Hill's group.

Keywords: Polyethylene, LLDPE, HDPE, blend miscibility, Molecular Dynamics Simulation

INTRODUCTION

The Phase behavior of polyethylene-polyethylene blends has attracted considerable interest both in the research community and industry. As a result, a better understanding of the miscibility behavior of polyethylene blends is crucial to meet requirement of processing and properties of final product.

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^3 depending on the amount of comonomer incorporated, usually 1-butene, 1-hexene, or 1-octene. In the past, significant research work has been conducted to study the influence of branch content and its distribution in LLDPE on the miscibility of LLDPE in high-density polyethylene (HDPE). A great deal of information has been obtained from the work of Hill's group [Hill et al., 1993, Hill and Barham, 1994] and [Alamo et al., 1997], [Morgan et al., 1999], and [Choi, 2000]. However, all of these studies used ZN-LLDPE, which is known for its structural heterogeneity, with substantial amounts of the polymer having either low or high degree of comonomer incorporated. The introduction of single-site catalyst (i.e. metallocene) has made possible the production of LLDPE with almost uniform distribution of branches [Bjor et al., 2001]. In the literature, different views have been expressed about the phase behavior of ZN-LLDPE/HDPE systems ranging from liquid-liquid phase segregation [Barham et al., 1988], [Hill, et al., 1991], [Hill and Barham, 1994], and [Hill et al., 1996] to complete homogeneity in the melt [Alamo et al., 1994, Alamo et al., 1997, Agamaian et al., 1999]. Most of the above studies have used either transmission electron microscopy (TEM) or small angle neutron scattering (SANS) techniques except the recent work of Fan et al. (2002) that used MD simulations with random distribution of branching mimicking ZN-LLDPEs. In this study, MD simulations were used to study the effect of branch content on the miscibility of m-LLDPE in HDPE with branch content ranging from 10 – 60 branches/1000 C.

MODEL AND METHOD

Models of HDPE and octene-based LLDPE with uniform distribution of branches were simulated using a molecular modeling software package Cerius2 (Version 4.2, Accelrys Inc.). Each model is composed of 500 ethylene monomer units (i.e. 1000 backbone carbons). Different m-LLDPEs were modeled with 10, 20, 30, 40, 50, 60 and 80 branches per 1000 C. The branches were uniformly spaced along the chain. The branches were composed of five methylene units and an end methyl unit simulating the copolymerization of ethylene with 1-octene. Each ethylene unit was treated as a united atom. In the absence of density constraints, segments composing the chain have more chances to reorient and assume their optimal configurations in a shorter time [Choi et al., 1995].

The dynamic simulations were run under canonical (NVT) ensemble at temperatures of 450 and 500 K, using the Nose method (1984). The time step was 0.001ps. The time-evolution for

isolated fully extended polyethylene of chain length 1000 CH₂ units is studied up to 1000 ps. Atomic force field used here is the Dreiding 2 potential [Mayo et al., 1990].

Molecular interaction energies can be described by the total energy E_{Tot} in the MD simulations: $E_{\text{Tot}} = E_{\text{S}} + E_{\text{b}} + E_{\text{T}} + E_{\text{vdw}}$ Where E_{S} is the bond-stretching energy, E_{b} is the bond bending energy; E_{T} is Van der Waals interaction (non-bonded interaction). Non-bonded interactions were modeled using a Lennard-Jones 12-6 potential [Flory, 1941]. The objective of this investigation is to study the influence of branch content on the miscibility of HDPE in Octene m-LLDPEs.

RESULTS AND DISCUSSIONS

The steady-state conformation for m-LLDPE/HDPE for m-LLDPE with 10 branches/1000 C is shown in Figure 1. In all Figures, the magenta line represents HDPE and the grey one is for m-LLDPE with branches colored in red. Chain folding in lamellar structures is evident for both HDPE and m-LLDPE with branch contents of 30 and 40 branches/1000 C as shown in Figures 2 and 3 respectively. Figures 1, 2, and 3 show the mingling of the linear and branched chains suggesting into each suggesting the miscibility of m-LLDPE in HDPE in the range up to 40 branches/1000 C. For higher branch content, results are shown for blends of HDPE with m-LLDPE with 50 and 60 branches/1000 C in Figures 4 and 5 respectively. In the last two Figures, it is clear that HDPE started to form a separate phase that is different from m-LLDPE and the trend is the same for higher branch contents (not shown here) up to 80 branches/1000 C. This suggests the existence of a critical branch content of 40 branches/1000 C where miscibility of m-LLDPE in HDPE cease to exist. These results are in agreement with previous experimental work of Hill's group [Hill and Barham, 1995] and also with recent work of Abu-Shark and Hussein on m-LLDPE where critical branch content was observed in MD simulations of pure m-LLDPEs. This work suggests that the reasons behind the observed immiscibility of these members of the PE family is due to the direct influence of the density of branching and its distribution on mismatch of conformations of m-LLDPE and HDPE. This seems consistent with theoretical findings [Fredrickson and Liu, 1995]; [Bates and Fredrickson, 1994] that acknowledge the important influence of the conformational and architectural "mismatch" between components of polyolefin blends on the miscibility of polyolefins.

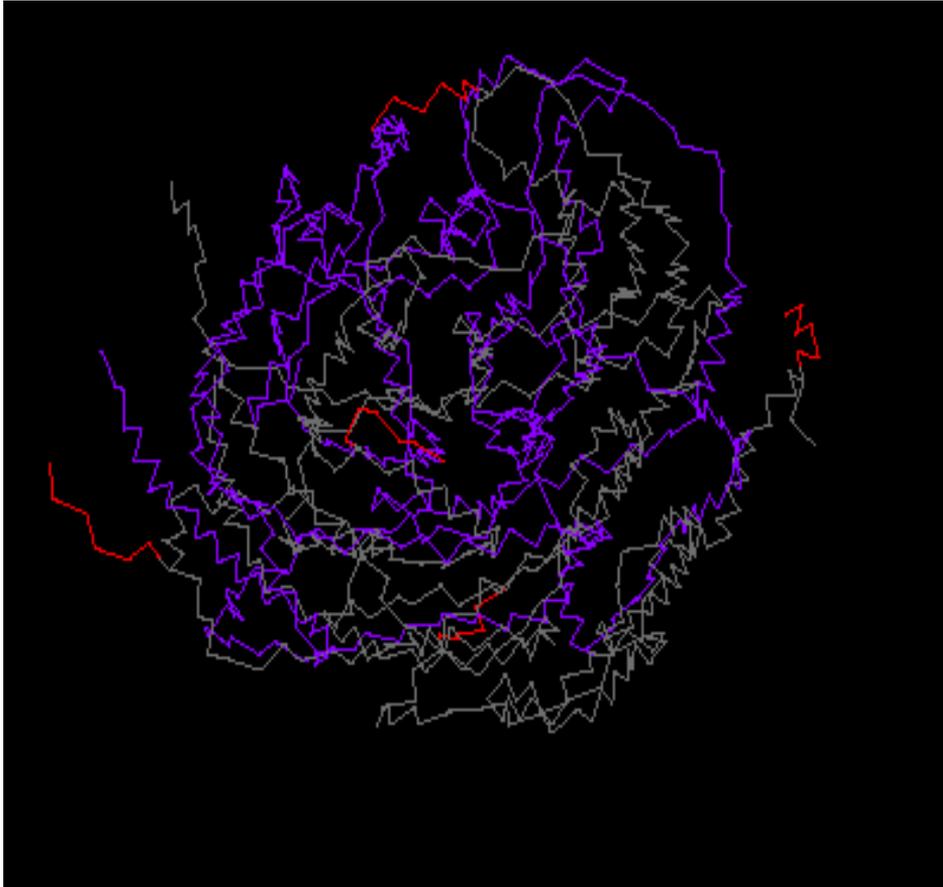


Figure 1: Blend of HDPE/m-LLDPE with 10 branches/1000 C at 500 K

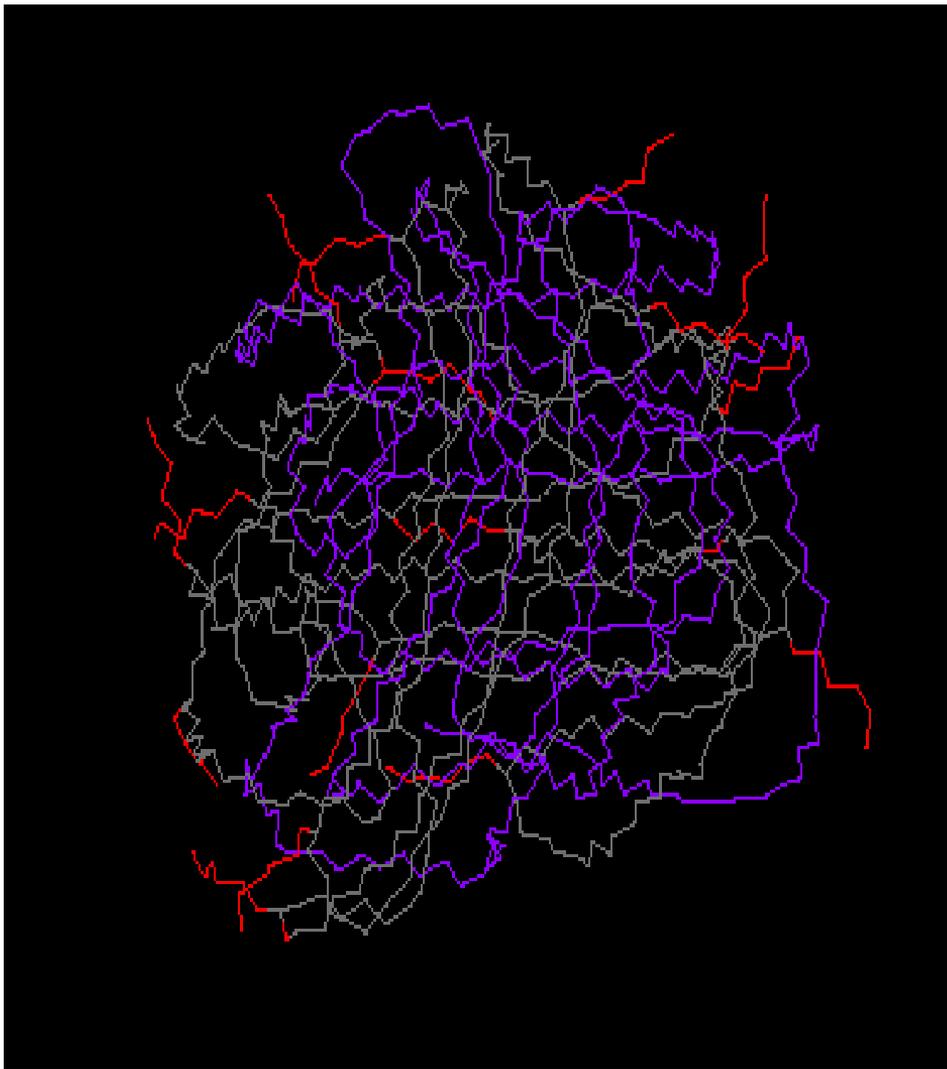


Figure 2: Blend of HDPE/m-LLDPE with 30 branches/1000 C at 500 K

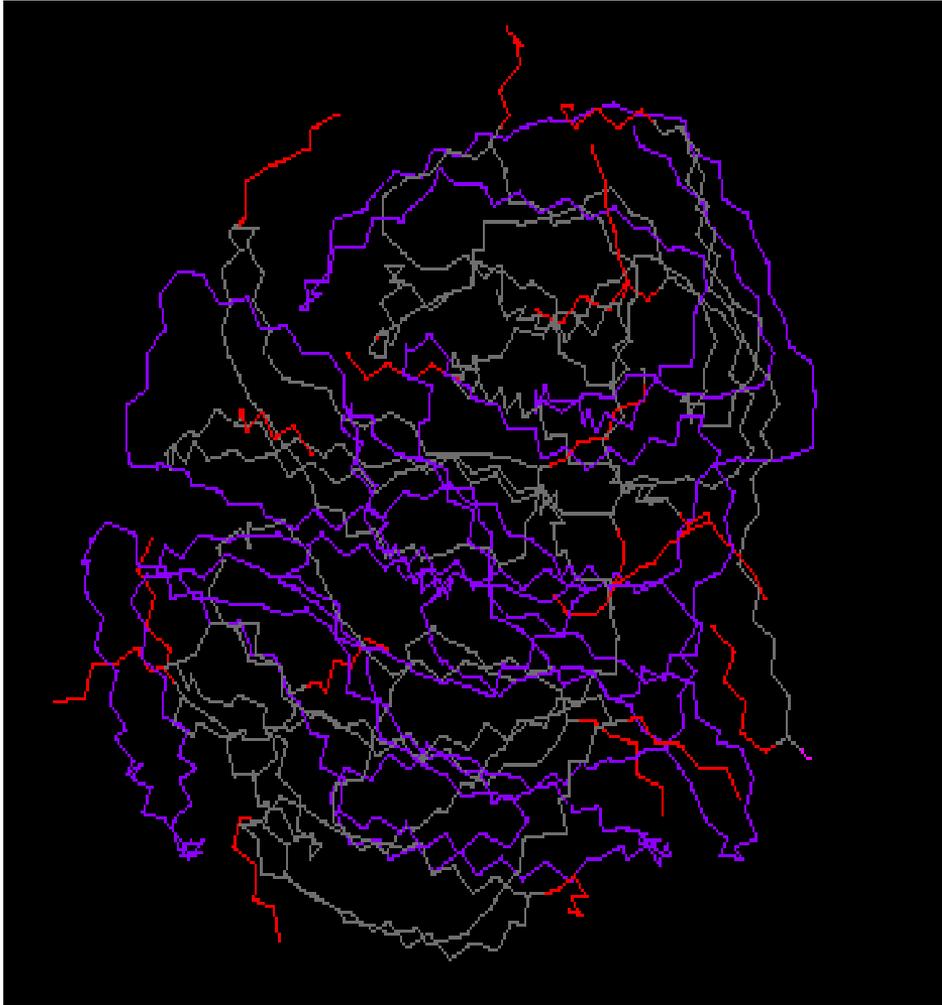


Figure 3: Blend of HDPE/m-LLDPE with 40 branches/1000 C at 500 K

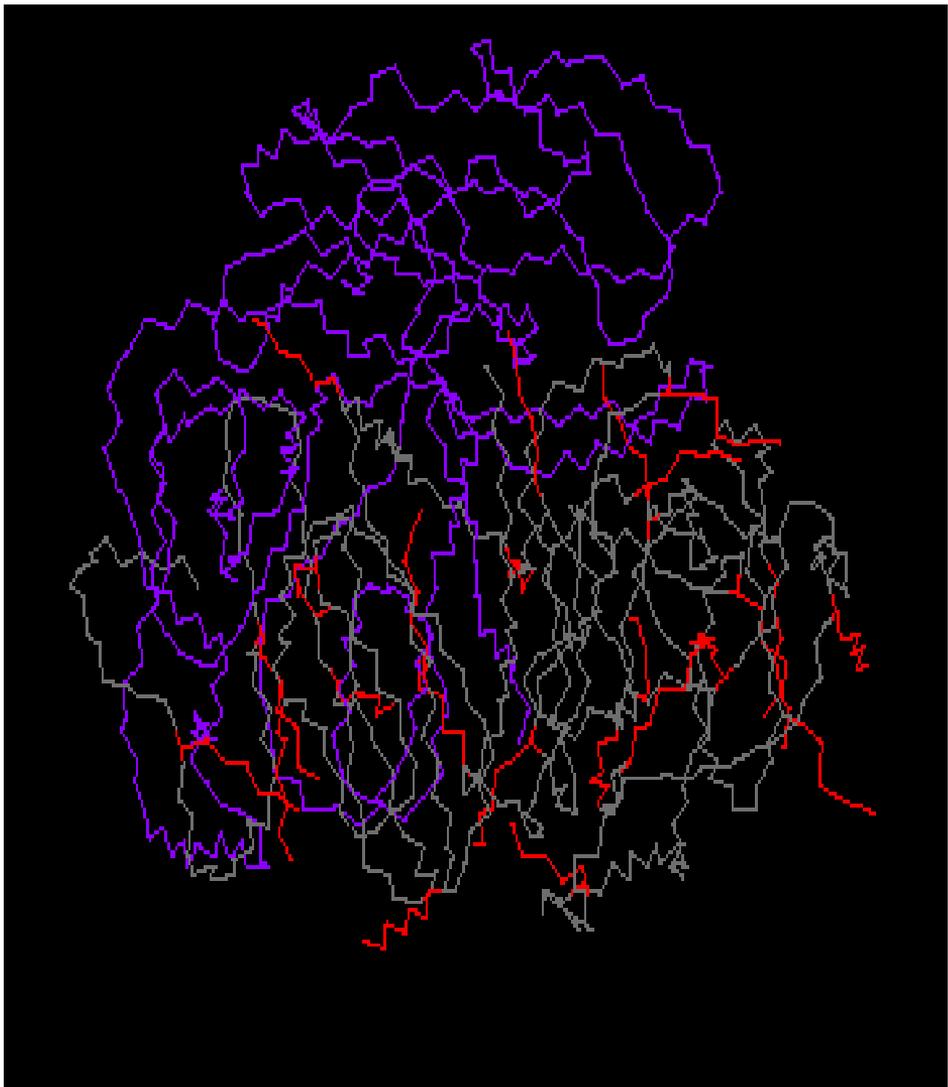


Figure 4: Blend of HDPE/m-LLDPE with 50 branches/1000 C at 500 K

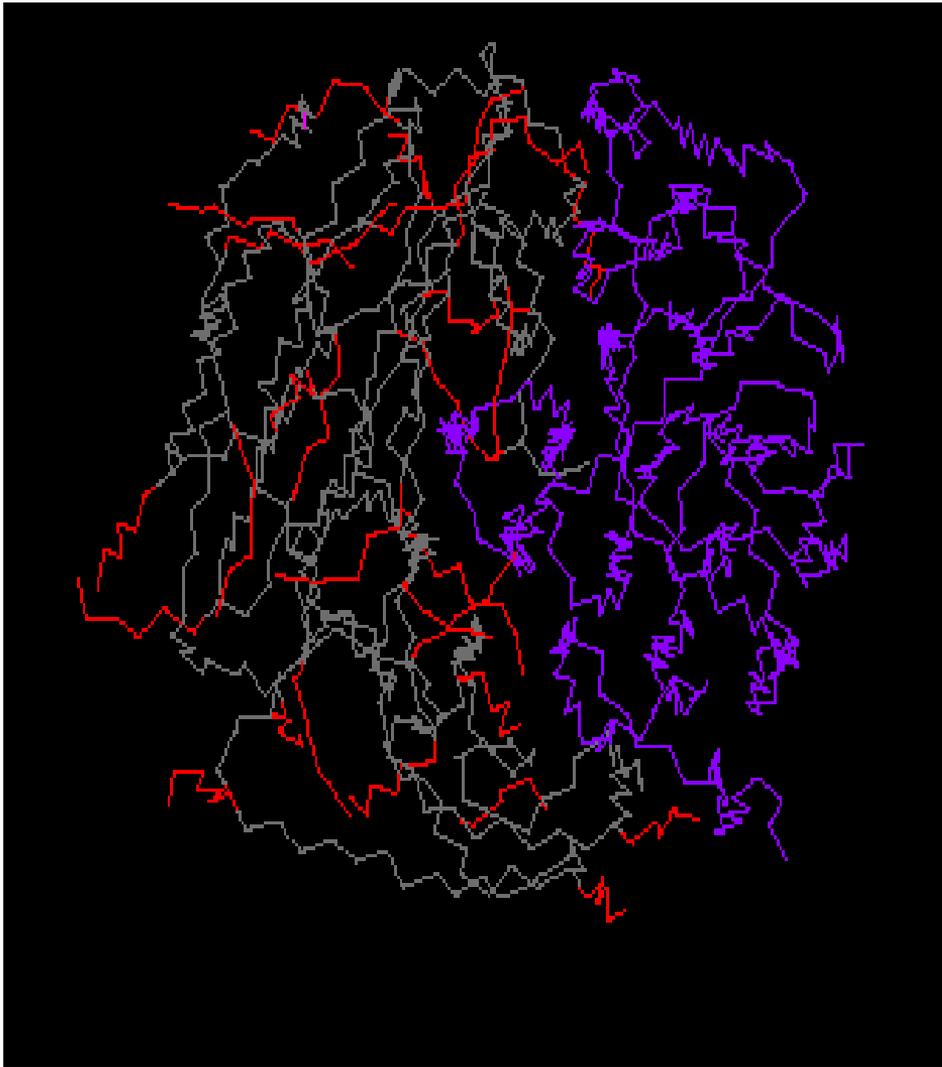


Figure 5: Blend of HDPE/m-LLDPE with 60 branches/1000 C at 500 K

CONCLUSIONS

Miscibility of m-LLDPE in HDPE was observed for m-LLDPE with branch content up to 40 branches/1000 C. However, blends are immiscible in higher ranges of branch contents.

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