

PHASE SEPARATION IN BIMODAL MOLECULAR WEIGHT HIGH DENSITY POLYETHYLENE WITH DIFFERING BRANCH CONTENTS BY MOLECULAR DYNAMICS AND MESODYN SIMULATION*

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Abstract The phase behavior of bimodal molecular weight high density polyethylene (BHDPE) in solid state was investigated. Hildebrand solubility parameters (δ) were calculated for the models of blends of higher molecular weight branch polyethylene (HBPE) with different branch contents and lower molecular weight linear polyethylene (LLPE), by using molecular dynamics (MD) simulations. These δ values were then used to calculate the corresponding Flory-Huggins interaction parameter (χ) between HBPE and LLPE models. In order to better understand the compatibility between LLPE and various HBPE, Mesodyn simulations were used to show the density profiles of the blends of LLPE with various HBPE at different compositions. The results indicated that the phase behavior of BHDPE was influenced by both the global branch content of the system and the local branch content, *i.e.*, the branch content of HBPE.

Keywords: Polyethylene; Phase behavior; Molecular dynamics; Mesodyn simulation.

INTRODUCTION

Polyolefin blends are very important and popular materials, which have much better properties compared with traditional pure polyolefins^[1]. The miscibility of the blends takes the key role since it determines the properties of the materials. Many researches have successfully described the liquid-liquid phase behavior of binary blends of linear polyethylene (LPE) and branch polyethylene (BPE) by both computer simulations and experimental methods^[2–7]. The results for phase behavior of the binary blends obtained by computer simulations are consistent with those from experiments. Wignall and coworkers confirmed that for BPE, the branch content was the major factor that controlled the miscibility of the blends, based on small angle neutron scattering (SANS) experiments. If the branch content (the number of branches per 100 backbone carbon atoms) is smaller than 4, the blends are homogeneous. When the content is higher than 8, the blends are phase separated^[2]. However, for heterogeneous BPE, a small fraction of highly branched molecules results in phase separation, even though the overall branch content is low (*i.e.* 1–2 branches/100 backbone carbon atoms)^[8]. In addition, Hill *et al.* found that the threshold value of branch content for LPE/BPE blends in liquid-liquid state phase separation was around 6 by transmission electron microscopy (TEM)^[3–5]. Choi and coworkers investigated the miscibility and the threshold value of branch content for LPE/BPE blends by MD simulations, which were in good agreement with available experimental data^[6, 7]. However, the studies on the miscibility of LPE and BPE in solid state are relatively scarce^[9].

BHDPE material is a “hot” research topic at present^[10–14]. It is shown that BHDPE consists of a higher molecular weight fraction with homogeneous branches to contribute the mechanical strength and a lower molecular weight fraction without branches to give the excellent processing ability. Due to their good processing

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and excellent mechanical properties, BHDPE are widely used in film, pipe and blow moulding applications. The phase behavior of BHDPE is of great commercial importance in polyethylene industry. However, there have been no comments on the miscibility of such blends till now. In this work, we investigate the phase behavior of BHDPE with different branch contents and different compositions by computer simulations. Compared with experimental method, simulation approaches can avoid the effect of the broad molecular weight distribution and branching composition distribution. Here we show the results on the effects of branch contents of higher molecular weight branch polyethylene (HBPE) on its miscibility with LLPE and the effect of compositions on the blend miscibility.

MOLECULAR DYNAMICS SIMULATION

MD simulations were completed by using a molecular modeling software package Cerius². The force field Dreiding 2.21 was adopted for energy minimizing and MD simulations, which had been used for similar systems, and reasonable results were obtained. In Dreiding force field, the total energy of the system E_T is represented by the sum of bonding and non-bonding interactions defined as:

$$E_T = E_b + E_{nb} \quad (1)$$

Where bonding interaction E_b includes bond stretching (E_s), bond angle bending (E_a), and torsion angle rotations (E_r); non-bonding interaction E_{nb} consists of van der Waals (E_{vdw}) and electrostatic (E_q). Thus, E_T can be represented as:

$$E_T = E_s + E_a + E_r + E_{vdw} + E_q \quad (2)$$

For the systems investigated in the present work, van der Waals interactions were the only non-bonding interactions considered. The non-bonding interaction energy was calculated using a spline function, where the spline-on distance was 0.8 nm and the spline-off distance was 0.85 nm. Actually, electrostatic interaction is not significant in this work. The force field is described in detail in Ref. [15].

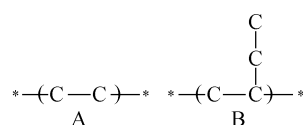
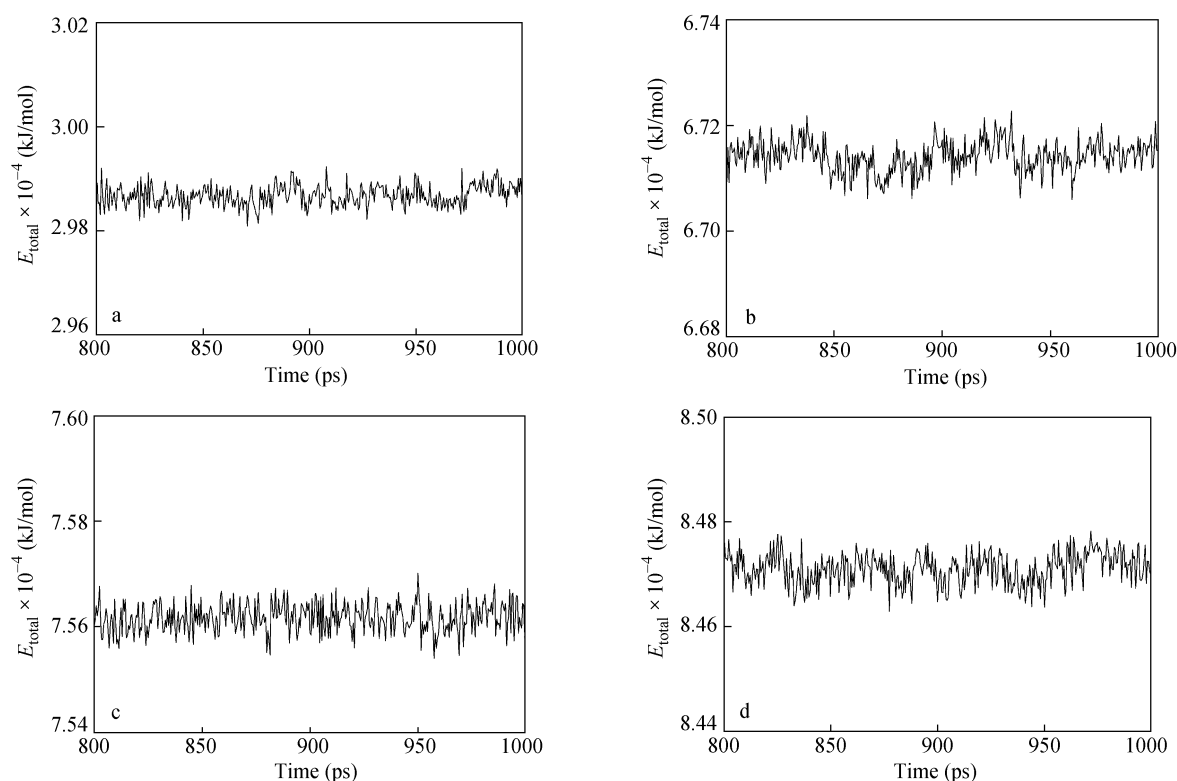
The monomeric units A as shown in Fig. 1 are polymerized to have a linear architecture, which represents the lower molecular mass fraction LLPE. The LLPE chain consisting of 500 monomeric units (1000 backbone carbons) is packed into a simulation box with 3-dimensional periodicity. In order to eliminate the unfavorable high-energy of the initial structure, three different initial structures of LLPE models are introduced (*i.e.*, model1, model2, and model3 mentioned below). Each structure is relaxed to avoid the overlaps between atoms by molecular mechanics (MM). Then, NVT ensemble is chosen for MD simulations with a density of 0.95 g/cm³ at 300 K. The T-Damping thermostat is used to set the temperature at the desired value. The simulation time is 1000 ps with a time step of 1 fs for all models, and the trajectory-saving interval is 0.5 ps. Figure 2 shows the time evolution of the total energies for LLPE and various HBPE model molecules. The simulation time is found to be long enough for the systems to reach thermodynamic equilibrium. For HBPE, monomeric units A and B as showed in Fig. 1 are copolymerized. Each HBPE chain contains 1000 monomeric units (sum of monomeric unit A and B). The MM and MD simulations for HBPE are the same to those for LLPE. The number of monomer units and the branch contents for different model systems are shown in Table 1. Once the system reaches equilibrium, the final 50 ps is chosen to calculate the energy for single chain in vacuum (E_{vac}) and the energy for the chain in amorphous condensed state (E_{cond}). The Hildebrand solubility parameter is then calculated as:

$$\delta = [(E_{vac} - E_{cond})\rho/M]^{1/2} \quad (3)$$

where $(E_{vac} - E_{cond})$ is the cohesive energy, ρ the mass density, and M the molar mass of the molecule. $(E_{vac} - E_{cond})\rho/M$ is thus the cohesive energy density. The Flory-Huggins parameter is obtained by:

$$\chi = (\delta_{LLPE} - \delta_{HBPE})^2 V_{mon} / RT \quad (4)$$

where T is the temperature, R the molar gas constant, and V_{mon} the volume of monomer unit ethylene.

**Fig. 1** Polymer monomers for LLPE and HBPE**Fig. 2** Total energies versus simulation time for LLPE and HBPE

a) For LLPE; b), c), d) For HBPE with branch content 5, 10 and 15, respectively

Table 1. Descriptions of the model systems of HBPE and LLPE

Branch content	Number of monomer A	Number of monomer B
0	500	0
4	920	80
5	900	100
6	880	120
7	860	140
8	840	160
9	820	180
10	800	200
15	700	300
20	600	400

MESOSCALE SIMULATION

The phase separation process of the blends at mesoscopic level is studied by using Mesodyn, which is one of the most popular tools to predict compatibility of polymer blends in recent years^[16–19]. The method is actually based on the dynamic variant of the mean-field density functional theory^[20, 21]. The polymer chains are modeled as ideal Gaussian chains consisting of coarsegrained beads. Each bead represents a number of monomers of the real polymer, and the free energy of the system is calculated according to the distribution function of the beads. The

Mesodyn chain length (N_{Meso}) is given as:

$$N_{\text{Meso}} = \frac{M_p}{M_n C_n} \quad (5)$$

where M_p is the polymer molecular weight, M_n the monomer molecular weight and C_n the characteristic ratio. The parameter of Mesodyn interaction energy between pair of interacting bead types is according to the equation:

$$v^{-1} \varepsilon_{ij} = \chi_{ij} RT \quad (6)$$

where χ_{ij} is the Flory-Huggins parameter obtained by atomistic simulations. $v^{-1} \varepsilon_{ij}$ is used as an input parameter for Mesodyn simulation. Here, for LLPE and HBPE, N_{Meso} is 40 and 4 units, respectively. The values of $v^{-1} \varepsilon_{ij}$ for all of the blends are shown in Table 2. The time step in Mesodyn simulation is set as 50 ns, and the total simulation time is 500 μ s for all blends. The simulation dimensions are chosen to be 64 nm $\times$ 64 nm $\times$ 64 nm.

Table 2. List of Mesodyn interaction energies and branch contents for blends at 300 K

	Branch content of	Branch content of blends		Mesodyn interaction energy (kJ/mol)
	HBPE	Composition 1/1	Composition 1/4	
A	4	2.67	3.56	0.275
B	5	3.33	4.44	1.209
C	6	4.00	5.33	1.737
D	7	4.67	6.22	2.210
E	8	5.33	7.11	0.665
F	9	6.00	8.00	0.187
G	10	6.67	8.89	0.001
H	15	10.00	13.34	0.560
I	20	13.34	17.78	4.190

RESULTS AND DISCUSSION

Table 3 shows the calculated Hildebrand solubility parameter, δ , of systems of HBPE and LLPE with three different initial configurations (denoted by model1, model2, and model3, respectively). The values of δ obtained in this research are smaller than those obtained by Choi *et al.* for low density systems^[6, 7]. The difference may be attributed to different density. The deviations $\Delta\delta$ of different initial configurations of HBPE with same branch content are larger than that of LLPE (with branch content 0). The larger $\Delta\delta$ values for HBPE are attributed to the differences in the local chain arrangements of the initial structures, as shown in Fig. 3. In the figure, A and B denote the monomer units as described in Fig. 1, and ss denotes that the monomer units are arranged shoulder by shoulder, tt tail by tail, and hh head to head. Obviously, BBtt is the most unfavorable structure for the strong repulsion between the branches, and BBhh and BABtt are the most favorable structures. In addition, the ratio of trans and gauche states of backbone is also important. The effect of the initial configuration on HBPE is larger than that on LLPE. Figure 4 shows the calculated Hildebrand solubility parameters versus branch content.

Table 3. Calculated Hildebrand solubility parameters of the models with different initial configurations

Branch content	δ_1 (model1)	δ_2 (model2)	δ_3 (model3)	δ_m (mean)	δ_{se} (Standard error)
0	6.09	6.13	6.12	6.11	0.015
4	6.15	6.20	6.28	6.21	0.038
5	6.19	6.27	6.48	6.31	0.085
6	6.26	6.37	6.43	6.35	0.050
7	6.22	6.42	6.51	6.38	0.086
8	6.13	6.21	6.45	6.26	0.097
9	6.01	6.25	6.31	6.19	0.091
10	6.04	6.09	6.17	6.10	0.037
15	5.84	6.18	5.92	5.98	0.100
20	5.89	5.84	5.66	5.79	0.068

According to Fig. 4, when the branch content is less than 7, δ values increase with increasing branch content; when the branch content is higher than 7, δ values decrease with increasing branch content. Choi *et al.* had showed that the δ values for BPE tend to decrease with increasing branch content in melt state when the branch content is larger than 10, which is in agreement with our results^[6,7]. However, there are no comments on the δ values when the branch content is smaller than 10.

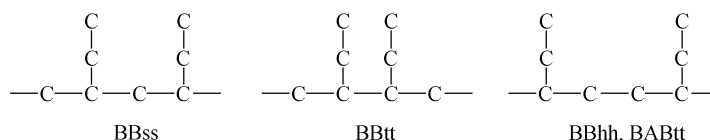


Fig. 3 The possible local arrangements of HBPE
A and B denote monomers shown in Fig. 1.

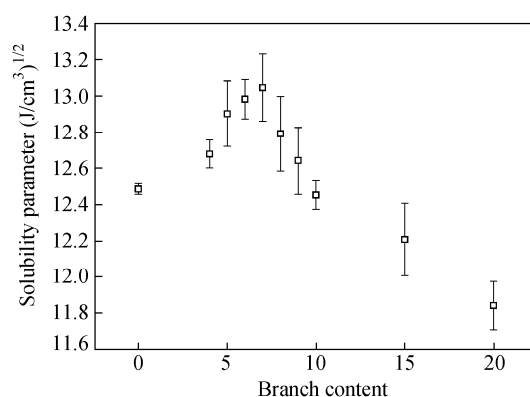


Fig. 4 Hildebrand solubility parameters of HBPE with different branch contents and LLPE (zero branch content)

The obtained δ is then used to calculate the χ values between LLPE and HBPE. The results are shown in Fig. 5. It shows the irregular branch content dependence of HBPE. The χ value reaches a local maximum when the branch content of HBPE is 7. χ tends to increase again with increasing branch content of HBPE when it is higher than 10.

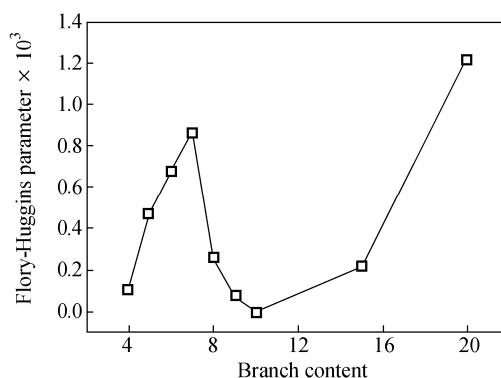


Fig. 5 Flory-Huggins parameters between HBPE with different branch contents and LLPE

In order to study the compatibility of LLPE and HBPE blends, Mesodyn simulations are applied on these systems. Figure 6 and Fig. 7 show the morphology of LLPE/HBPE blends with volume composition 1/1 and 1/4, respectively. The branch contents are shown in Table 2. For the blends with composition 1/1, as shown in Fig. 6, the blends with the branch content of HBPE from 8 to 15 (the content of branch for blends from 5.3 to 10) show

a homogeneous phase. When the branch content of HBPE is larger than 15 (the content of branch for blends is larger than 10), the phase separation takes place. The results are in reasonable agreement with SANS experiments that when the branch content of blends is higher than 8, the blends phase separate^[2]. However, when the branch content of HBPE is between 5 and 7 (the content of branch for blends is from 3.3 to 4.7), the phase separation also takes place. Obviously, when the branch content of blends is low (the branch content of blend is smaller than 5), the phase behavior is mainly controlled by the branch content of HBPE. The results for the blends with branch content of HBPE smaller than 8 are in good agreement with those obtained by Choi^[6]. On the contrast, when the branch content of HBPE is a little bit larger, the influence of branching is not strong. For blends with composition 1/4, as shown in Fig. 7, a homogeneous phase can not be achieved in this research. Thus the composition of the blends is also a major factor in the compatibility of LLPE and HBPE blends.

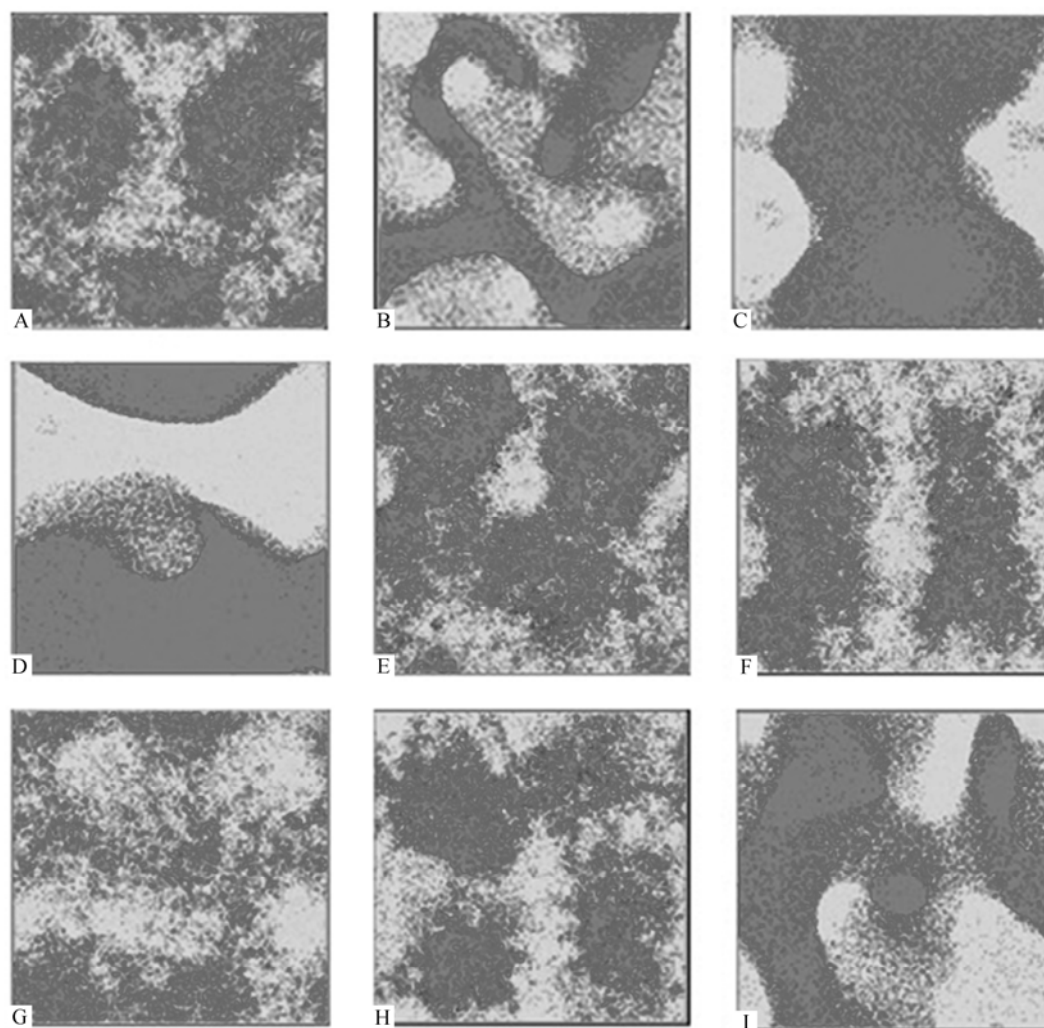


Fig. 6 The morphology of LLPE/HBPE blends with 1/1 composition, for the systems described in Table 2

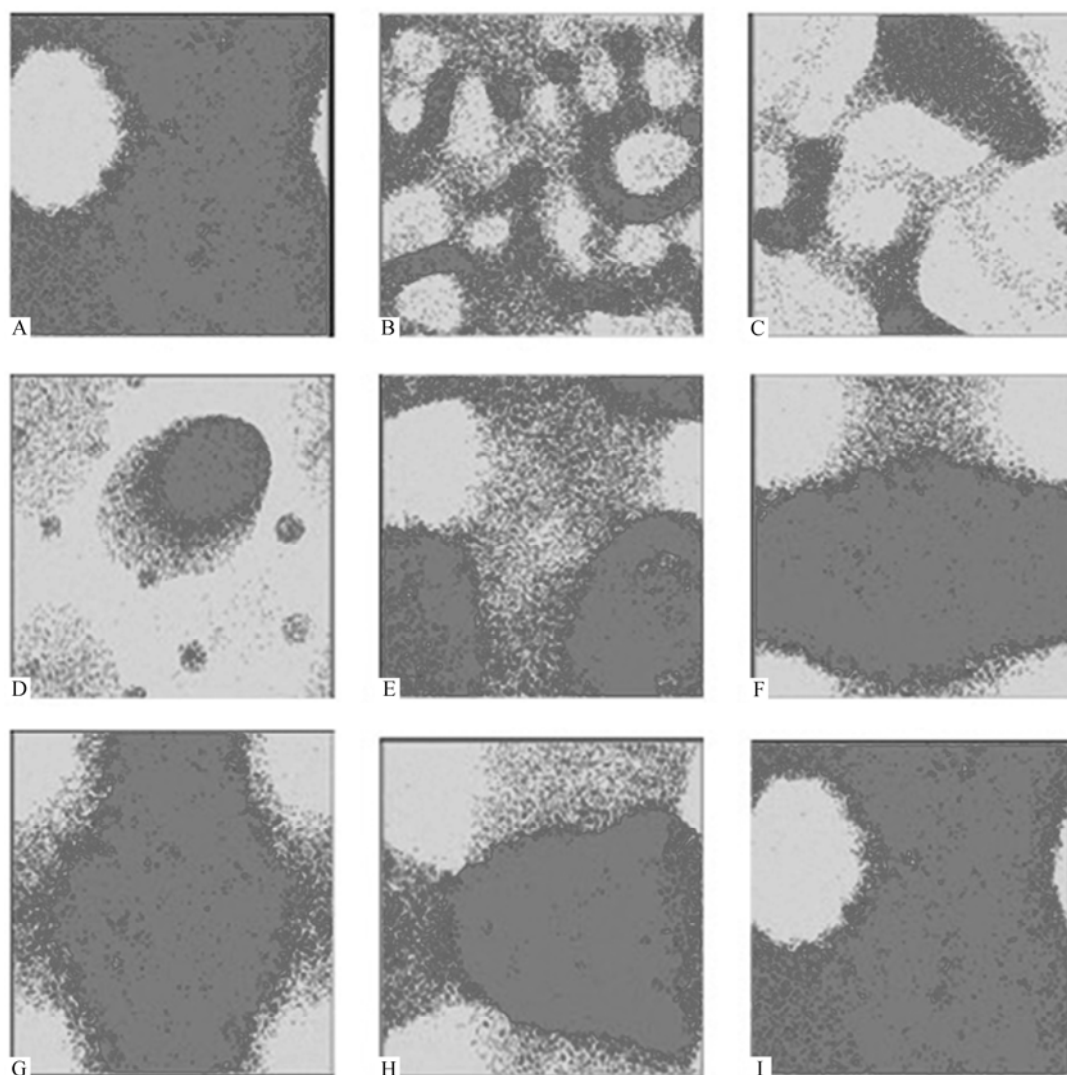


Fig. 7 The morphology of LLPE/HBPE blends with 1/4 composition, for the systems described in Table 2

CONCLUSIONS

In this paper, we study the miscibility of HBPE/LLPE blends by means of MD and Mesodyn simulation methods. In the case of LLPE/HDPE with composition 1/1, when the global branch content is smaller than 5.3, the local branch content controls the phase behavior, and the blends tend to phase separate with the branch content of HBPE being from 4 to 8; when the global branch content is larger than 10, which is similar to the value of 8 obtained by SANS^[2], the blends phase separate. Additionally, the results for LLPE/HDPE with composition 1/4 show that the blend composition is another important factor on phase behavior.

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