Molecular Simulation on Relationship between Composition and Microstructure of PP/PC Blend

Shanshan Dai,[1] Lin Ye,[2] Guo-Hua Hu[3,4]

[1]School of Chemistry and Chemical Engineering, Southwest Petroleum University, 615000 Chengdu, China
[2]State Key Laboratory of Polymer Materials Engineering, Polymer Research Institute of Sichuan University, 610065 Chengdu, China
[3]Laboratory of Chemical Engineering Sciences, CNRS-ENSIC-INPL, 1 rue Grandville BP 20451, 54001 Nancy, France
[4]Institute Universitaire de France, Maison des Universités, 103 Boulevard Saint-Michel, 75005 Paris, France

ABSTRACT: Simulations based on molecular dynamics and mesodyn theories were used to investigate the compatibility, morphology evolution of polypropylene/polycarbonate (PP/PC) blends, and the relationship between the composition and microstructure. Results of Flory–Huggins interaction parameters, integral structure factor, X-ray intensity, free-energy density, and order parameters all indicated that phase separations occurred in all PP/PC blend systems, and poor compatibility was exhibited for this polymer pair. The systems of PP/PC = 54/46, PP/PC = 31/69, and PP/PC = 18/82 showed stronger immiscibility and the faster separation process, while the systems of PP/PC = 82/18 and PP/PC = 5/95 showed less immiscibility and a slower separation process. Compared with the results of mechanical properties tests, the appearance of a cocontinuous structure obtained from simulation corresponds to the transition point of impact strength and tensile strength. After transition, the mechanical properties of the blends depended on the properties of the PC matrix, and the impact strength and tensile strength were both clearly enhanced. As the simulation steps increased, the morphology of PP/PC = 54/46 blend developed into a double-lamellar structure by coarsening of PC phase from initial homogeneous configuration. In addition, the compatibilizing effect of SEBS was also investigated at the microscale, and varying the content of PS block in SEBS has little effect on the morphology of blend. © 2012 Wiley Periodicals, Inc. J Appl Polym Sci 000: 000–000, 2012

Key words: polypropylene; polycarbonate; blending; compatibility; simulation

INTRODUCTION

Polypropylene (PP) is one of the most utilized polymers. However, it exhibits low impact strength, limiting its application potential greatly. Polymer blending provides a more practical and economic way of preparing new materials with combinations of properties not available in a single polymer, and the development of PP-based blends is often aimed at obtaining a processable material with high impact strength and sufficient stiffness.[1–13] Elastomer modification has been proved to be effective in toughening PP even at low temperatures, but a concomitant and adverse effect of elastomer toughening is significant reduction in modulus of the material. For this reason, a so-called "rigid–rigid polymer toughening" concept was developed, to improve the toughness of PP while retaining its rigidity as much as possible. PP blended with PC showed a significant improvement in impact toughness with a relatively good tensile strength in our previous investigation.[14–16]

With the development of hardware and software, molecular simulation has become one of the most important tools to predict or validate structure–property relationship of polyblends, blend compatibility, and phase behavior of polymers. Method of Quantum Mechanics provides the valuable information of configuration or conformation of isolated molecule in the vacuum at absolute zero. Monte Carlo method is a statistic simulation technique for architectural characteristic of molecules at different temperatures, which can not describe the development of mechanical state of molecules. In this work, method of molecular dynamics (MD), which is suitable to trace the morphology evolution, was chosen to apply on polymeric systems of PP/PC blends. Besides, the relationship between the composition and microstructure, including the effect of SEBS as a compatibilizer were also studied based on MD and Mesoscopic Dynamics (Mesodyn) theories.
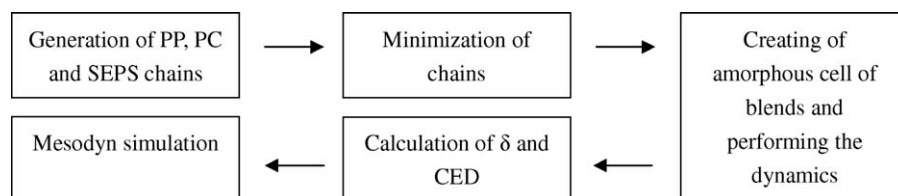
EXPERIMENTAL

Simulation methods

MD and Mesodyn simulations have been performed on PP/PC and the compatibilized blends

at ambient temperature (298 K) using the software packages of Mesodyn with Materials Studio Modeling (version 4.0) installed on Windows 2000. The whole simulation process is shown as follows:

```
┌─────────────────────┐      ┌─────────────────────┐      ┌─────────────────────┐
│  Generation of PP, PC │ ──→ │    Minimization of   │ ──→ │     Creating of      │
│   and SEPS chains     │      │       chains         │      │   amorphous cell of  │
└─────────────────────┘      └─────────────────────┘      │      blends and      │
                                                            │   performing the     │
┌─────────────────────┐      ┌─────────────────────┐      │      dynamics        │
│  Mesodyn simulation   │ ←── │  Calculation of δ and │ ←── └─────────────────────┘
└─────────────────────┘      │         CED          │
                             └─────────────────────┘
```

Initially, the bulk phases were constructed with the Amorphous Cell Program, which utilizes the combined use of arc algorithm developed by Theodorou and Suter[16] and the scanning method of Meirovitch.[17] Minimization was done using the conjugate gradient method (CGM), until the energy reached a minimum. The CGM used here worked on the Polak-Ribiere algorithm with a convergence level of 0.1 kcal mol^{-1} Å^{-1}. The initial configurations were refined by the dynamics of 100 ps after the amorphous cell was generated. The COMPASS[18] (condensed-phase optimized molecular potentials for the atomistic simulation studies) force field was used for modeling inter-atomic interactions. This is indeed the widely used all-atom force field, optimized to predict the structural, conformational, and thermophysical condensed phase properties for the most common molecules including polymers. As mentioned above, configurations were generated individually for each system to compute the cohesive energy density (CED). The MD simulations under constant temperature and density (NVT ensemble) were performed for each configuration using the Discover program. The energy of the system was monitored to ensure that it fluctuated around the average value, and this was considered as a criterion for having an "equilibrated" system. The phase separation dynamics of PP-based blends at the mesoscopic level were investigated by Mesodyn program. This approach is based on the dynamic variant of the mean-field density functional theory[19] that is similar to the classical dynamic random phase approximation (RPA).[20] Polymer chains are modeled as ideal Guassian chains consisting of beads, each representing the monomer chain (Kuhn statistical segments).

Mechanical test

PP (T30S) was produced by Dushanzi Petrochemical (China), with melt flow index (MFI) 2.5–3.5 g/10 min (230°C, 2.16 kg). PC (L1250Y) was supplied by Teijin (Japan), with MFI 6.7 g/10 min (300°C, 1.2 kg).

PP/PC blends with different molar ratio were prepared in a TSSJ-25/03, corotating, twin-screw extruder at a rotational speed of 90 rpm. The temperature of the barrel was in the range of 220–270°C. Corresponding extrudates were hauled into a quenching water trough prior to being palletized. Dried blends were molded to form impact and tensile specimens by using a K-TEC40 injection molding machine. The barrel temperature profile was 260°C (hopper)–280°C (nozzle) and the mold temperature was maintained at 50°C.

The tensile strength of the samples was measured with 4,302 material testing machine from Instron (USA) according to ISO527/1-1993 (E). The test speed was 50 mm min^{-1}, and the sample length between bench marks was 50 ± 0.5 mm. The notched charpy impact strength of the samples was measured with ZBC-4B impact testing machine from Xinsansi (Shenzhen of China) according to ISO179-1993 (E).

RESULTS AND DISCUSSION

Molecular dynamic simulations of PP/PC blend

The results of molecular dynamic simulations on PP/PC blend were used to investigate Flory–Huggins interactions between PP and PC at the molecular level. However, due to the space limitations of data storage of computer, simulations couldn't be performed with the actual size of polymer. Therefore, it's necessary to find out the minimum molecular size which is sufficient to represent the properties of real polymer, including some important thermodynamic parameters.

To determine the minimum size mentioned above, solubility parameters of PP and PC with different repeating units, namely, different molecular weight were computed up to a point. At this point, the values of solubility parameters won't change with the increase of the polymer molecular. As shown in Figure 1, the solubility parameters of PP levels off as
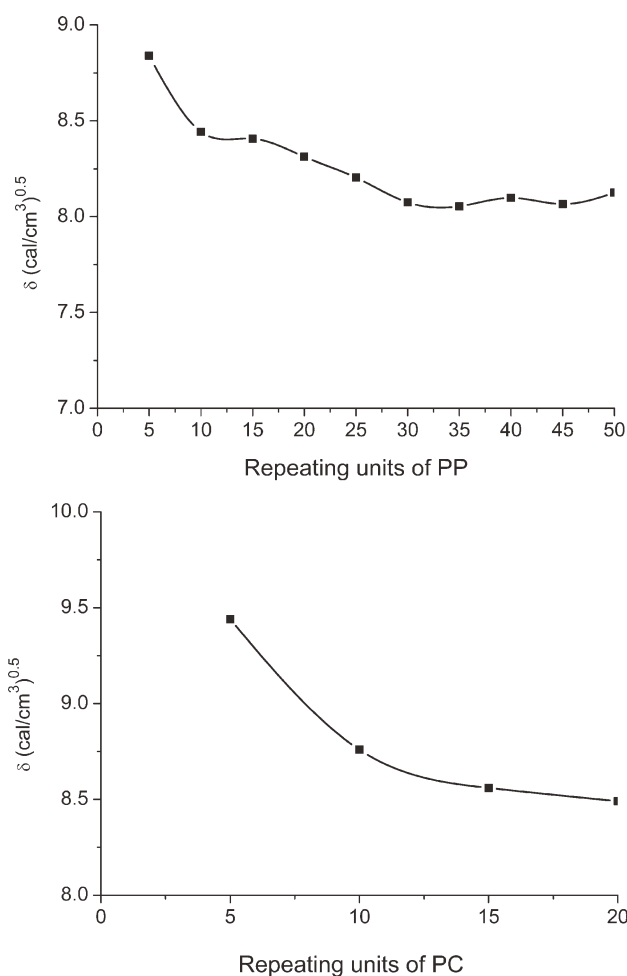
Figure 1 Dependence of solubility parameters (δ) of PP and PC on the number of repeating units.

the number of repeating units increases >30. For PC, the minimum number of repeating units is 10. Data of corresponding molecular weight and solubility parameters are calculated and listed in Table I. The model construction of PP/PC blends is established at different quantity ratios of PP to PC in the simulation cell. The number of polymer chains in each unit, the composition, the density and the molar volume of PP/PC blend are summarized in Table II. The Van Krecelen solubility parameters and molar volume of PP/PC/SEBS blend are summarized in Table III.

A typical snapshot unit cell for PP/PC = 54/46 (weight ratio) blend is shown in Figure 2 which contains 2900 atoms. The carbon atoms are grey, hydrogen, white, and oxygen, red. The original

TABLE II
Simulation Details of PP/PC Blends

Number of chains per unit cell	Composition (wt % PC)	Density (g cm^{-3})	Molar volume (cm^3 mol^{-1})
1 PP chain	0	0.9	1400
1 PC chain	100	1.2	2116
9 PP chain, 1 PC chain	18	0.93	1492
7 PP chain, 3 PC chain	46	0.99	1661
5 PP chain, 5 PC chain	69	1.05	1810
3 PP chain, 7 PC chain	82	1.11	1942
1 PP chain, 9 PC chain	95	1.17	2062

configuration must be optimized after construction because of the high level of energy.

Flory–Huggins interaction parameter χ is given by:

$$\chi = \frac{z \Delta E_{mix}}{RT} \tag{1}$$

where z is a coordination number, the value of which for the cubic lattice model is taken as 6, R is the molar gas constant (8.314 J mol^{-1} K^{-1}), and T is the temperature in Kelvin, at which simulation was performed. The energy of mixing, ΔE_{mix}, needed to compute χ was calculated as:

$$\Delta E_{mix} = \phi_A \left(\frac{E_{coh}}{V}\right)_A + \phi_B \left(\frac{E_{coh}}{V}\right)_B - \left(\frac{E_{coh}}{V}\right)_{mix} \tag{2}$$

where subscripts A, B, and mix represent CED values of PP, PC, and their blend, respectively. Φ_A and Φ_B represent the volume fractions of PP and PC, respectively. χ obtained from eq. (1) should be compared with the critical value to judge the compatibility between PP and PC. The critical value of χ is calculated by the following equation:

$$(\chi_{AB})_{critical} = \frac{1}{2} \left(\frac{1}{\sqrt{m_A}} + \frac{1}{\sqrt{m_B}}\right)^2 \tag{3}$$

where m_A and m_B are the degree of polymerization of A and B. Blends are miscible if $\chi < \chi_{\text{critical}}$. If χ is slightly greater than χ_{critical}, the blends are partially miscible. If χ is considerably greater than χ_{critical}, then the component polymers are totally immiscible.

As shown in Figure 3, χ_{critical} is 0.1244, which is indeed the line of demarcation for the blend to be

TABLE I
Solubility Parameters of PP and PC

Polymer	Repeating units	Molecular weight	Solubility parameters (cal cm^{-3})$^{0.5}$
PP	30	1260	8.07
PC	10	2540	8.76

TABLE III
Simulation Details of PP/PC/SEBS Blends

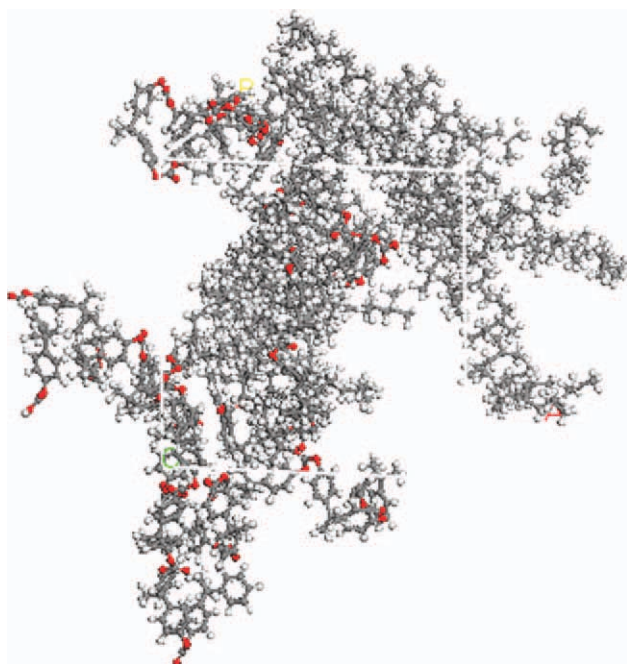| Polymer	Van Krecelen solubility parameters (J cm^{-3})$^{1/2}$	Molar volume (cm^3 mol^{-1})
PP	16.06	49.04
PC	19.40	211.92
PS	19.52	96.98
EB	16.49	48.89

Figure 2 Snapshot of the amorphous unit cell for a 54:46 blend of PP/PC. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

treated as miscible or not. It can be concluded the PP/PC blends are immiscible in the whole range of weight fraction of PC. Further insight into the figure, the blend with 5% PP is in comparatively better compatibility.

The structure factor $S(q,t)$ affected by the crystal structure could be calculated through the X-ray scattering with method of MD. q is the scattering vector equal to $(4\pi/\lambda)\sin(\theta/2)$, where λ and θ are the wavelength of light and scattering angle respectively, at regular time intervals.[21] When the value of S is equal to 0, the system is completely miscible due to the disappearance of diffraction. X-ray intensity
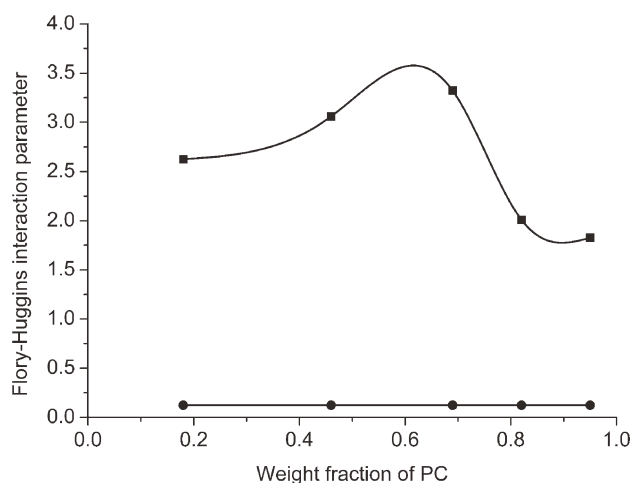
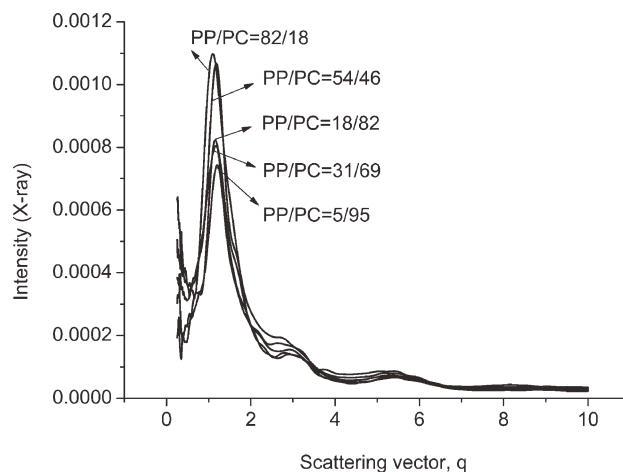**Figure 3** Flory–Huggins interaction parameters versus weight fraction of PC.

Figure 4 Intensity versus scattering vector plots for PP/PC blends.

plotted versus q of PP/PC blends with different weight ratio is shown in Figure 4. It is observed that the X-ray intensity of blends is higher for more immiscible systems (PP/PC = 82/18; PP/PC = 54/46; PP/PC = 31/69) and lower for less immiscible systems (PP/PC = 18/82; PP/PC = 5/95). The maximum peaks of curves appeared at the similar value of scattering vector with the increase of PC concentration, and all the blends represent obvious phase separation.

Mesoscopic dynamic simulations of PP/PC blend

The length of polymer chain could be determined from the degree of polymerization and characteristic ratios of polymer. The expression for length of Mesodyn chain (N_{meso}) is given by:

$$N_{Meso} = \frac{M_p}{M_m C_n} \tag{4}$$

where M_p is the polymer molecular weight, M_m is the monomer molecular weight, and C_n is the characteristic ratio $((C_n)_{PP} = 6.9, (C_n)_{PC} = 2.4)$.[22] The input parameter P for Mesodyn simulation is related to the Flory–Huggins interaction parameter χ_{ij} by the following equation:

$$P = \chi_{ij}RT \tag{5}$$

where the χ_{ij} is taken from the atomistic simulation carried out for each blend at different composition, R is the molar gas constant, and T is taken to be 298 K. To analyze the effects of blend composition on its mesoscopic morphology, PP/PC binary blend with different weight ratio were investigated in detail. Figure 5 shows the morphologies of the blends and the corresponding iso-density surfaces of PC after
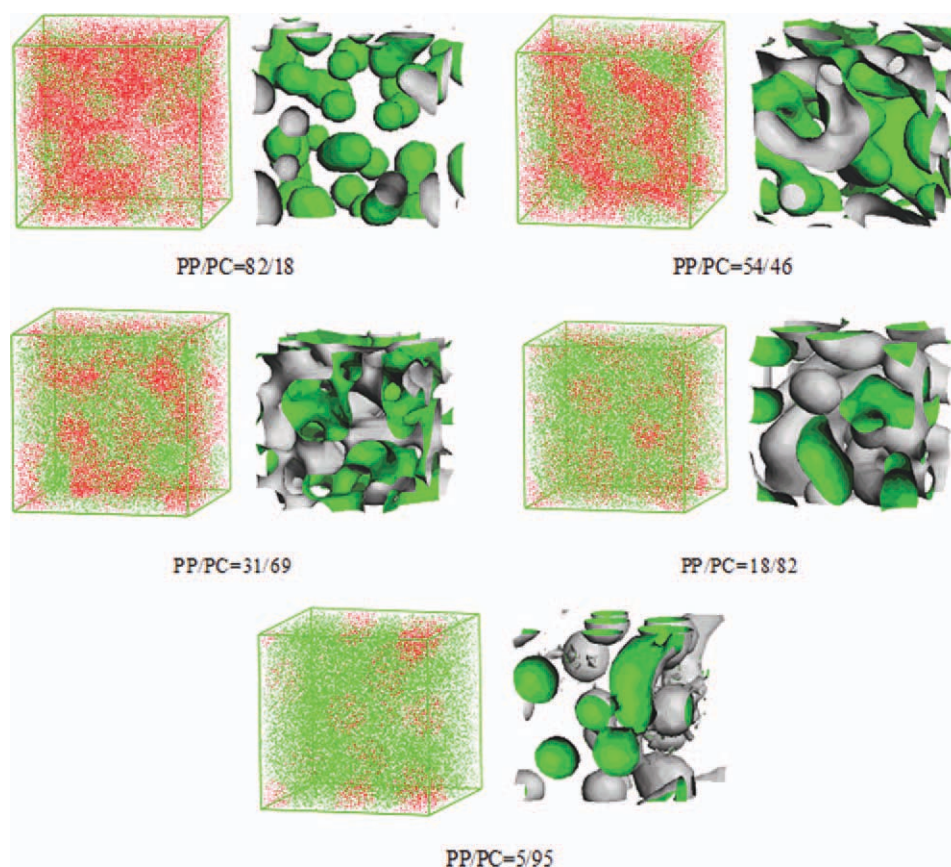
Figure 5 Morphology of PP/PC blends (left) and isodensity surface of PC (right) after 1×10^3 steps simulation from random initial configuration (the red and green beads represent PP and PC, respectively). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

1×10^3 time steps Mesodyn simulation from random initial configuration. PC particles disperse in the PP matrix as spherical shape at a lower loading of PC. As the concentration of PC increases to 46%, phase size of PC increases and bicontinuous phase appears. At 69% concentration of PC, the bicontinuous phase of blend is more perfect. When the concentration of PC reaches 82%, reversal of phase happens, and PP disperses in PC matrix as spherical shape. As the concentration of PC increases to 95%, phase size of PP particles decreases.

Compared with the results of mechanical properties tests shown in Figure 6, the appearance of cocontinuous structure obtained from simulation corresponds to the transition point of impact strength and tensile strength. Before transition, the mechanical properties of blends mainly depend on the properties of matrix PP because of the bad compatibility between PP and PC. After transition, the mechanical properties of blends depend on the properties of matrix PC, hence, the impact strength and tensile strength enhance obviously.

During the simulation, free energy asymptotically approaches a stable value when the system attains dynamic equilibrium as shown in Figure 7. However, the free-energy density obtained here is not for real polymer systems, and it's impossible to compare with the experimental data directly. Even though, the evolution of free energy is a good measure of the stability of a system. The free-energy density of blends decreases with the increase of simulation steps, and finally reaches at a stable stage. The
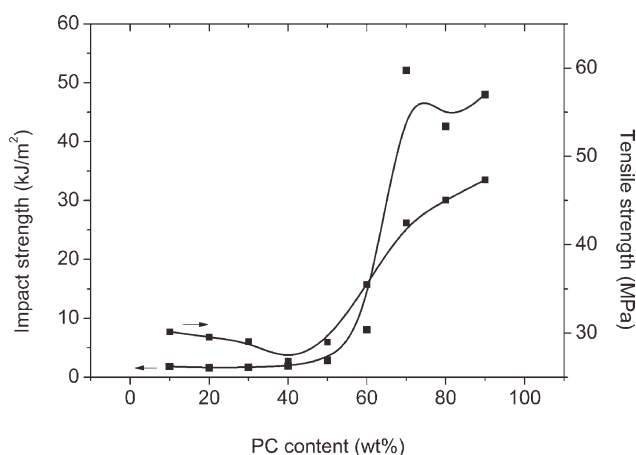

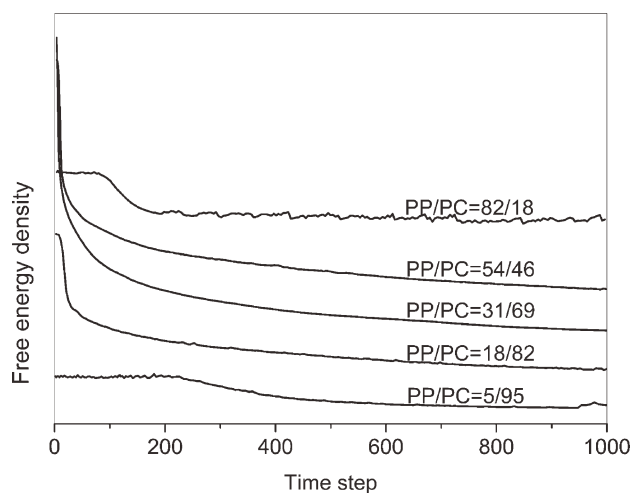**Figure 6** Impact strength and tensile strength of PP/PC binary blends.

Figure 7 Plot of free-energy density versus time step for PP/PC blends.

Figure 8 Mesophase order parameter of PC versus time step.

systems of PP/PC = 82/18 and PP/PC = 5/95 experience a comparatively longer time to reach the equilibrium state, namely, a slower separation process. The systems of PP/PC = 54/46, PP/PC = 31/69,
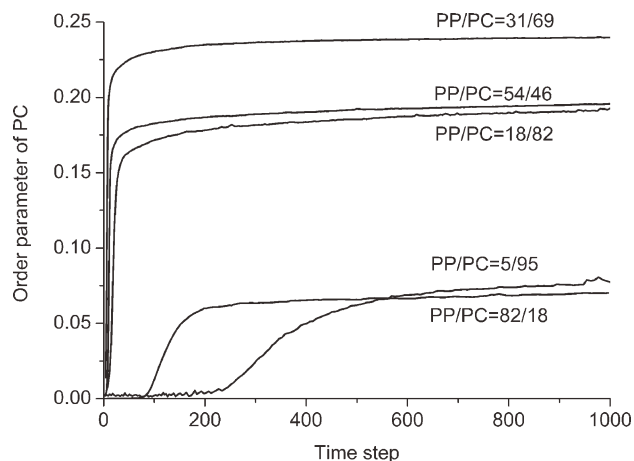
and PP/PC = 18/82 with stronger immiscibility show the faster separation process.

The order parameter, P_i, defined as the volume average of difference between local density squared and the overall density squared, is given by:
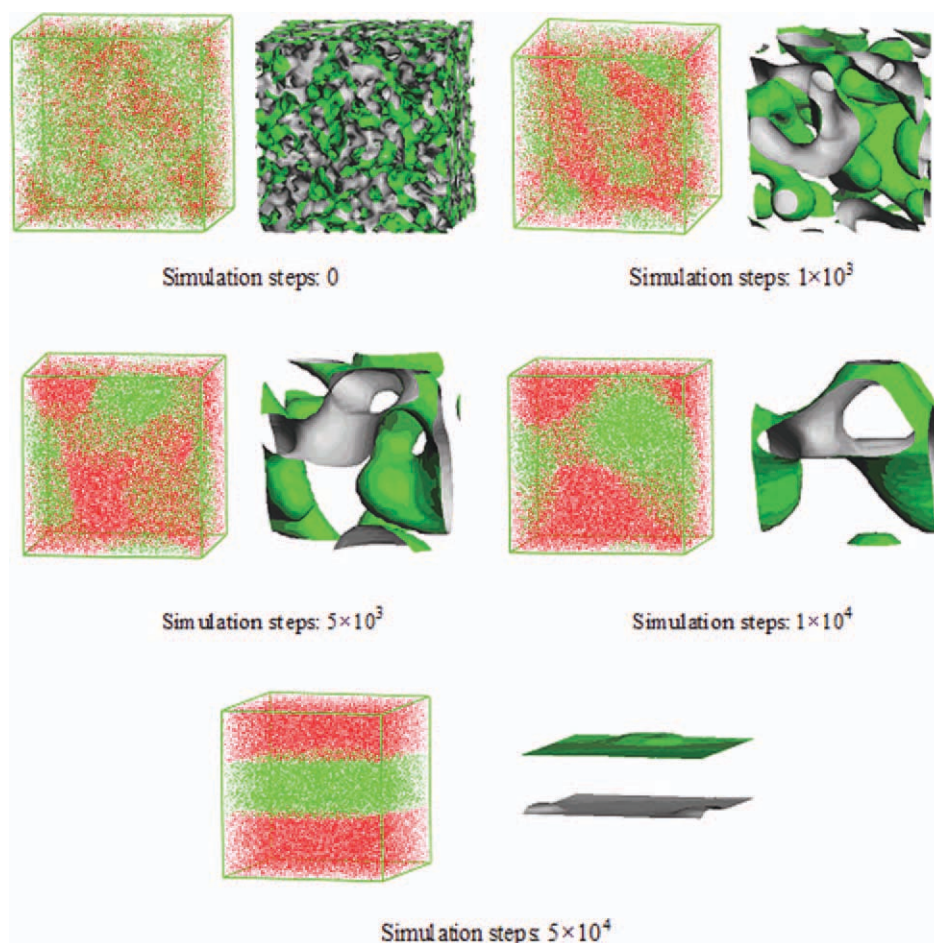

Figure 9 Time evolution of morphology of PP/PC = 54/46 blends (left) and isodensity surface of PC (right) from random initial configuration (the red and green beads represent PP and PC, respectively). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE IV
$\chi_{ij}RT$ between Polymer i and j

Species	PP	PC	PS	EB
PP	0	1.456	0.867	0
PC	1.445	0	0	1.104
PS	0.867	0	0	0.661
EB	0	1.104	0.661	0

$$P_i = \frac{1}{V}\int_v [\eta_i^2(r) - \eta_i^2]dr \qquad (6)$$

where η_i is dimensionless density (volume fraction) for species i. As shown in Figure 8, the systems of PP/PC = 54/46, PP/PC = 31/69, and PP/PC = 18/82 with larger value of order parameters indicates the strong phase segregation, more immiscibility, and the faster separation process. The systems of PP/PC = 82/18 and PP/PC = 5/95 have the comparatively better compatibility and slower separation process, which is consistent with the results of free-energy density.

The time evolution of the morphologies of PP/PC = 54/46 blend was investigated as an example, and snapshots of the morphologies in the evolution process are shown in Figure 9. The bicontinuous phase is developed from homogeneous initial configuration after 1×10^3 of simulation steps. With increasing simulation steps, PC phase continues to grow and coarsen till 1×10^4 of simulation steps. Morphologies of blend finally developed into double-lamellar structure after 5×10^4 of simulation steps.

Dynamic simulation of effect of SEBS on morphologies of PP/PC blend

SEBS is a triblock copolymer with polystyrene extremes and a copolymer of ethylene and butylene in the interior. The blocks are incompatible and phase separation is known to occur. The length of the individual blocks in SEBS varies from sample to sample, and we will assume block lengths at our convenience ($N_{Meso}(PS) = 10$; $N_{Meso}(EB) = 10$). The solubility parameters δ can be used to derive Flory–Huggins interaction values using:

$$\chi = \frac{V_{ref}(\delta_i - \delta_j)^2}{RT} \qquad (7)$$

where V_{ref} is a reference volume, taken to be the molar volume of one of the monomers (actually the mean volume of the two monomers). The calculated parameters used in the simulation are listed in Table IV.

Take morphology evolution of PP/PC = 54/46 blend as an example. As shown in Fig. 10, addition of SEBS slows down the separation of PP/PC blend.

Addition of SEBS slows down the separation of PP/PC blend. Bicontinuous phase is developed from homogeneous initial configuration after 1×10^3 of simulation steps. With increasing of simulation steps, PC phase continues to grow and coarsen till 1×10^4 of simulation steps. Morphologies of blend finally developed into an imperfect double-lamellar structure after 5×10^4 of simulation steps. The compatibilizer prefers to locate in the interface of PP and PC, and the structure of PC encapsulated by SEBS is
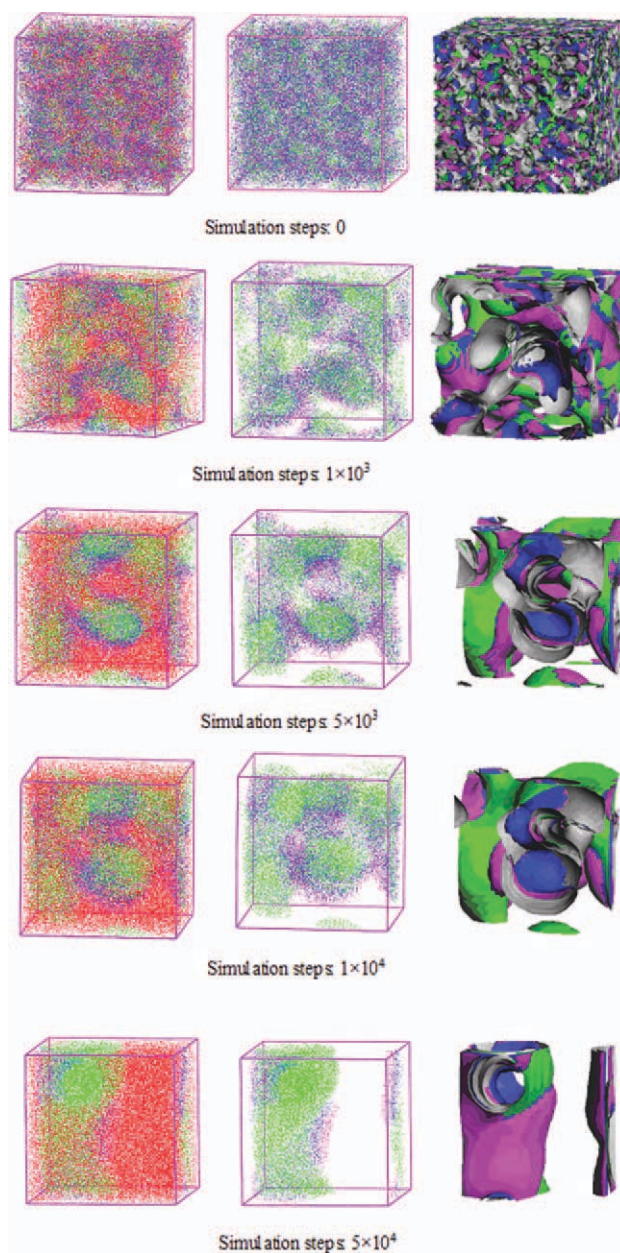

Figure 10 Time evolution of morphology of PP/PC/SEBS blends (left, middle) and isodensity surface of PC and SEBS (right) from random initial configuration (the red, green, blue, and pink beads represent PP, PC, PS block, and EB block, respectively). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
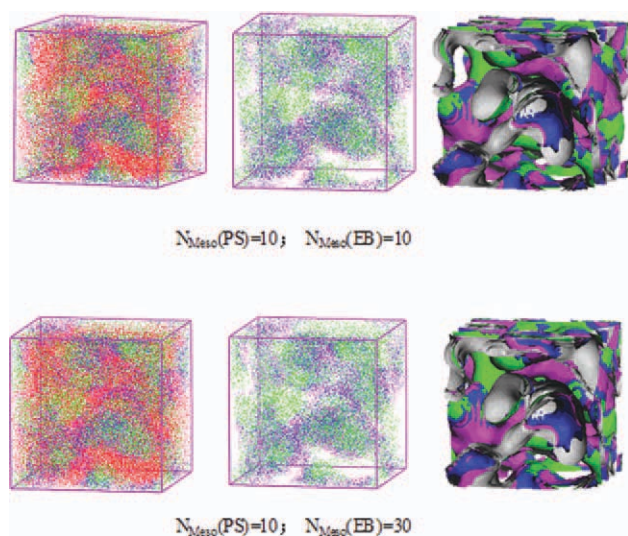
Figure 11 Morphology of PP/PC/SEBS blends (left, middle) and isodensity surface of PC and SEBS (right) after 1×10^3 steps simulation from random initial configuration (the red, green, blue, and pink beads represent PP, PC, PS block, and EB block, respectively). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

consistent with the results of SEM images discussed in our previous work.[14–16] Two systems with different content of PS block in SEBS have similar trends of evolution, which is shown in Fig. 11. The evolution of free energy and order parameter of compatibilized blends are shown in Figures 12 and 13, respectively.

CONCLUSION

Both molecular dynamics and mesodyn theories have been used to simulate the compatibility, morphology evolution of PP/PC blends and the relation-
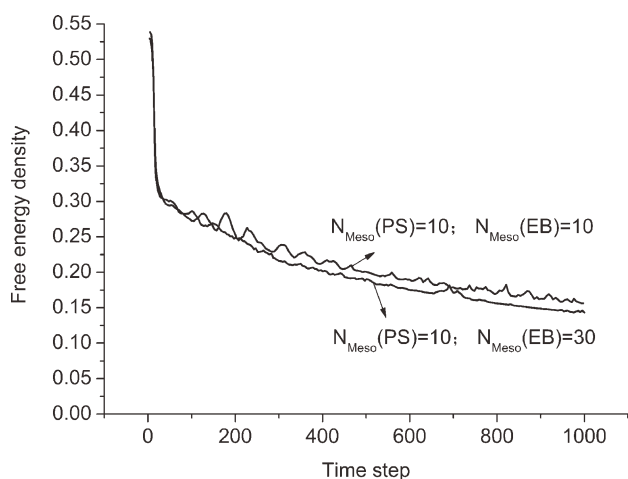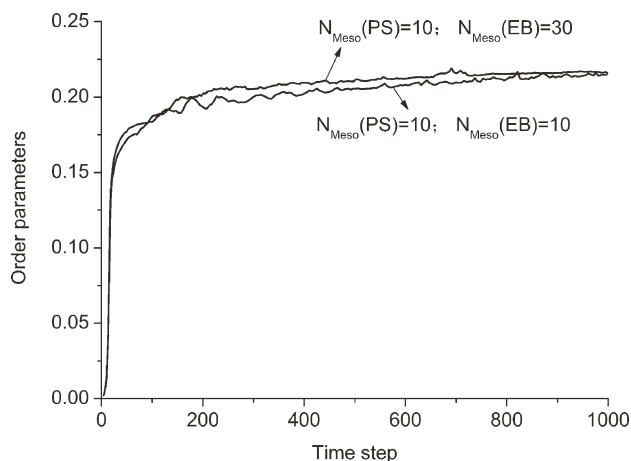

Figure 13 Mesophase order parameter of PC versus time step.

ship between the composition and microstructure. Flory–Huggins interaction parameters between PP and PC with different weight ratio were always higher than the critical value, indicating the poor compatibility of this polymer pair. Integral structure factor of blend wasn't equal to zero, which indicated phase separations occurred in all the blend systems. The X-ray intensity of blends was higher for more immiscible systems (PP/PC = 82/18; PP/PC = 54/46; PP/PC = 31/69) and lower for less immiscible systems (PP/PC = 18/82; PP/PC = 5/95). PC as particles existed in PP matrix when the concentration of PC was low. Cocontinuous structure appeared with the increase of PC concentration. Phase reversion occurred with further increasing PC, and PP as particles existed in the PC matrix. The size of PP reduced a bit when the concentration of PC continued to increase. Compared with the results of mechanical properties tests, the appearance of cocontinuous structure obtained from simulation corresponds to the transition point of impact strength and tensile strength. Before transition, due to the bad compatibility between PP and PC, the advantages of dispersed phase (PC) were almost invisible, and mechanical properties of blends mainly depended on the properties of matrix PP. After transition, the mechanical properties of blends depended on the properties of matrix PC, and the impact strength and tensile strength both enhanced obviously. The free-energy density of blends decreased with the increase of simulation steps, and finally dropped to a stable stage. The systems of PP/PC = 54/46, PP/PC = 31/69, and PP/PC = 18/82 with larger value of order parameters showed the stronger immiscibility and the faster separation process. The systems of PP/PC = 82/18 and PP/PC = 5/95 reached the equilibrium state after a comparatively longer time, and showed less immiscible systems and a slower separation process, which was

Figure 12 Plot of free-energy density versus time step for PP/PC/SEBS blends.

consistent with the results of free-energy density. With the increase of simulation steps, morphology of PP/PC = 54/46 blend developed into a double-lamellar structure by coarsening of PC phase from initial homogeneous configuration. Addition of SEBS slowed down the separation of PP/PC blend. The compatibilizer existed in the interface of PP and PC, and encapsulated PC. Varying the content of PS block in SEBS has little effect on the morphology of blend.

References

1. Yang, H.; Zhang, X. Q.; Qu, C.; Li, B.; Zhang, L. J.; Zhang, Q.; Fu, Q. Polymer 2007, 48, 860.
2. Yang, J. H.; Zhang, Y.; Zhang, Y. X. Polymer 2003, 44, 5047.
3. Bai, S. L.; Wang, G. T.; Hiver, J. M.; G'sell, C. Polymer 2004, 45, 3063.
4. Chang, S. Q.; Xie, T. X.; Yang, G. S. J Appl Polym Sci 2006, 102, 5184.
5. Sung, Y. T.; Han, M. S.; Song, K. H.; Jung, J. W.; Lee, H. S.; Kum, C. K.; Joo, J.; Kim, W. N. Polymer 2006, 47, 4434.
6. Sahnoune, F.; Lopez Cuesta, J. M.; Crespy, A. Polym Eng Sci 2003, 43, 647.
7. Wilkinson, A. N.; Clemens, M. L.; Harding, V. M. Polymer 2004, 45, 5239.
8. Yang, H.; Zhang, Q.; Guo, M.; Wang, C.; Du, R. N.; Fu, Q. Polym 2006, 47, 2106.
9. Lach, R.; Schneider, K.; Weidisch, R.; Janke, A.; Knoll, K. J Eur Polym 2005, 41, 383.
10. Liu, X. H.; Wu, Q. J.; Berglund, L. A.; Fan, J. Q.; Qi, Z. N. Polym 2001, 42, 8235.
11. Kim, S. J.; Kim, D. K.; Cho, W. J.; Ha, C. S. Polym Eng Sci 2003, 43, 1298.
12. Shu YC, Hsiao KJ. Eur Polym J 2006, 42, 2773.
13. Yin, J.; Zhang, J.; Yao, Y. J Appl Polym Sci 2006, 102, 841.
14. Dai, S. S.; Ye, L. Polym Adv Tech 2008, 19, 1069.
15. Dai, S. S.; Ye, L. J Appl Polym Sci 2008, 108, 3531.
16. Dai, S. S.; Ye, L.; Hu, G. H. Polym Adv Tech 2010, 21, 279.
17. Meirovitch, H. J Chem Phys 1983, 79, 502.
18. Rigby, D.; Sun, H.; Eichinger, B. E. Polym Inter 1997, 44, 311.
19. Fraaije, J. G. E. M.; Van Vlimmeren, B. A. C.; Maurits, N. M.; Postma, M.; Evers, O. A.; Hoffman, C.; Altevogt, P.; Goldbeck-Wood, G. J Chem Phys 1997, 106, 4260.
20. Fan, C. F.; Cagin, T.; Chen, Z. M.; Smith, K. A. Macromolecules 1994, 27, 2383.
21. Debye, P. W. Ann Phys 1915, 46, 809.
22. Brandrup, J.; Immergut, H. I.; Grulke, E. A. Polymer Handbook; Wiley: New York, 1999.