

Monte Carlo Simulation of the Compatibility of Graft Copolymer Compatibilized Two Incompatible Homopolymer Blends: Effect of Graft Structure

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ABSTRACT: Compatibility of graft copolymer compatibilized two incompatible homopolymer A and B blends was simulated by using Monte Carlo method in a two-dimensional lattice model. The copolymers with various graft structures were introduced in order to study the effect of graft structure on the compatibility. Simulation results showed that incorporation of both A-g-B (A was backbone) and B-g-A (B was backbone) copolymers could much improve the compatibility of the blends. However, A-g-B copolymer was more effective to compatibilize the blend if homopolymer A formed dispersed phase. Furthermore, simulation results indicated that A-g-B copolymers tended to locate at the interface and anchor two immiscible

components when the side chain is relatively long. However, most of A-g-B copolymers were likely to be dispersed into the dispersed homopolymer A phase domains if the side chains were relatively short. On the other hand, B-g-A copolymers tended to be dispersed into the matrix formed by homopolymer B. Moreover, it was found that more and more B-g-A copolymers were likely to form thin layers at the phase interface with decreasing the length of side chain. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 105: 1591–1596, 2007

Key words: graft copolymer; compatibilization; Monte Carlo simulation; polymer blends

INTRODUCTION

In most cases, polymers are incompatible with each other due to the low entropy gain upon mixing.¹ The incompatible polymers blends usually exhibit poor mechanical properties because of weak interactions at the interfaces. Therefore, compatibilization of the immiscible polymer blends has been widely attended in the past decades.

Studies have demonstrated that graft copolymer is a highly effective compatibilizer,^{2–21} which can reduce the interfacial tension, enhance adhesion between two immiscible components, and slow the phase coarsening. Gersappe et al.³ combined Monte Carlo (MC) method and experimental studies to design graft copolymers that enhanced the strength of the polymer composites. They found that the graft

copolymers were localized at the phase interface. D'Orazio et al.⁷ added the graft copolymers of unsaturated propylene with methyl methacrylate (PP-g-PMMA) to improve the compatibility of the binary blends of isotactic polypropylene (iPP) and atactic poly(methyl methacrylate) (PMMA). Soares et al.⁸ investigated the influence of poly[(ethylene-co-vinyl acetate)-g-polystyrene] (EVA-g-PS) on the mechanical and morphological properties of polystyrene and the blends with EVA copolymers. They pointed out that the addition of a small amount of EVA-g-PS graft copolymers provided an improvement on mechanical properties of the resulting blends. Dong et al.⁹ used a graft copolymer SMA-g-PA6 to improve the compatibility of PA 6 and PVC. In addition, Chuayjuljit et al.¹⁰ chose polystyrene grafted natural rubber copolymers (NR-g-PS) as the compatibilizer to compatibilize the natural rubber/polystyrene (NR/PS) blend. Recently, Inoue and coworkers^{11,12} studied the pull-out of *in situ*-formed graft copolymers from the interface between two phases during the melt-mixing process. More recently, Edgecombe et al.¹³ toughened the PS/PVP interface by introducing PS-g-PS(OH) graft copolymer and found that enhancement of the interfacial fracture toughness depended on the lengths of the PS and PS(OH) blocks. Moreover, some research groups^{14–16} introduced

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polymers with functional groups to *in situ* generate graft copolymers to compatibilize the immiscible polymer blends. Though a lot of attention has been paid to this field in recent years, it is still not so clear about the existence mode of graft copolymer in the resulting blends and is hard to know how to choose an effective compatibilizer for a given incompatible polymer blend system.

On the other hand, MC simulation has been proved to be a powerful tool that can give a direct insight into microstructures of the dynamic process of the polymer blends. Sahlin and Peppas²² employed MC simulation to study grafted chains at interfaces. Liang and coworkers^{23,24} have successfully employed this method to study the compatibilizing effects of the diblock and triblock copolymers in the A/B/copolymer ternary mixtures. Kamath and Dadmun²⁵ studied the effect of copolymer sequence distribution on the dynamic of copolymers in a homopolymer matrix using MC simulation. In our previous work,²⁶ we have studied the compatibility of ternary polymer mixtures coupled with chemical reaction by MC method. However, it is known that the chain architecture of graft copolymer is more complex than that of linear copolymer. Therefore, the existence mode of graft copolymer in polymer blends is much different from those of linear diblock or triblock copolymers. To our knowledge, the compatibility of A/B/graft copolymer has not been studied by MC method up to now. In this article, MC method was used to study the compatibility of graft copolymer compatibilized two incompatible homopolymer A and B blends. The copolymers with various graft structures were introduced. The purpose is to reveal the effect of graft structures on the compatibility of the blends.

MODEL AND SIMULATION

A two-dimensional lattice model was employed to provide a direct inspection of the polymer configuration and coarsening of the phase-separated structure. Cifra et al.^{27,28} showed that there is no essential difference in the phase behavior between a two- and a three-dimensional simulation.

In order to deal with the branching points, we adopted the four-site model proposed by Carmesin and Kremer.²⁹ In this model, one bead occupies the whole space of a square with four neighboring lattice sites. The bond vector connecting two successive effective beads may have length between l_{\min} and l_{\max} . In the four-site model, the length of a Kuhn segment can take six discrete values, i.e. 2, $\sqrt{5}$, $\sqrt{8}$, 3, $\sqrt{10}$, and $\sqrt{13}$, and the segment orientation can take 36 discrete angles.

Multiple-chain configurations were generated on a planar square 600×600 lattice. The system contained

3000 homopolymer chains and 500 graft copolymer chains. Moreover, each homopolymer and graft copolymer chains had 20 and 28 segments, respectively. Each segment occupied four neighboring lattice sites, resulting in a polymer concentration as high as 0.82, so that it could be regarded as a bulk. The vacancy of 0.18 is handled as free volume. A standard periodic boundary condition was imposed on the lattice to mimic an infinite-size system.³⁰ Considering such a high polymer concentration, we adopted "vacancy diffusion" algorithm suggested by Lu and Yang³¹ to improve the MC simulation efficiency. Excluded volume interactions are also enforced. Not only can two beads not occupy the same lattice, but also the intersection of chains in the course of a sequence of motions is forbidden. If the attempted move violates the excluded volume condition or the bond length restriction or the bond crossing, it will be rejected. Thermal interactions are catered by a short range intermonomer potential. The cutoff range of this potential was set at $r = \sqrt{8}$, a choice to ensure that only the nearest-neighbor pairs of segments have the intermonomer potential. Attempted moves that satisfy both the excluded volume condition and bond length restrictions are accepted or rejected according to Metropolis rules,³² i.e., an attempted move is accepted if the energy change $\Delta E = (N - N_0)\varepsilon$ is negative, or accepted with probability $p = \exp(-\Delta E/kT)$, if ΔE is positive, where ΔE is the change in energy that accompanies with the attempted move, where N and N_0 are the numbers of the nearest-neighbor pairs of segments within the cutoff range after and before the attempted move. ε is the interaction energy, which is won if the two nearest-neighbor segments within the cutoff range that are taken by monomers of different kinds. When $\bar{\varepsilon} = \varepsilon/kT$ is negative (the interaction between the different monomers is attractive) and positive (the interaction between the different monomers is repulsive), the system will be in its homogeneous state and heterogeneous state, respectively.

In this study, we first set $\bar{\varepsilon} = -1$. After the system reaches a completely compatible state, we set $\bar{\varepsilon} = 1$ to observe the change of domain structure in the phase separation.

RESULTS AND DISCUSSION

In the simulation, the chain numbers of homopolymer A, homopolymer B and graft copolymer were 900, 2100, and 500, respectively. Both homopolymer A and homopolymer B had the same length (20 segments). However, the graft copolymer had 28 segments, including one main chain (20 segments) and one or more side chains (the total length of side chains is fixed as 8 segments). Therefore, the volume

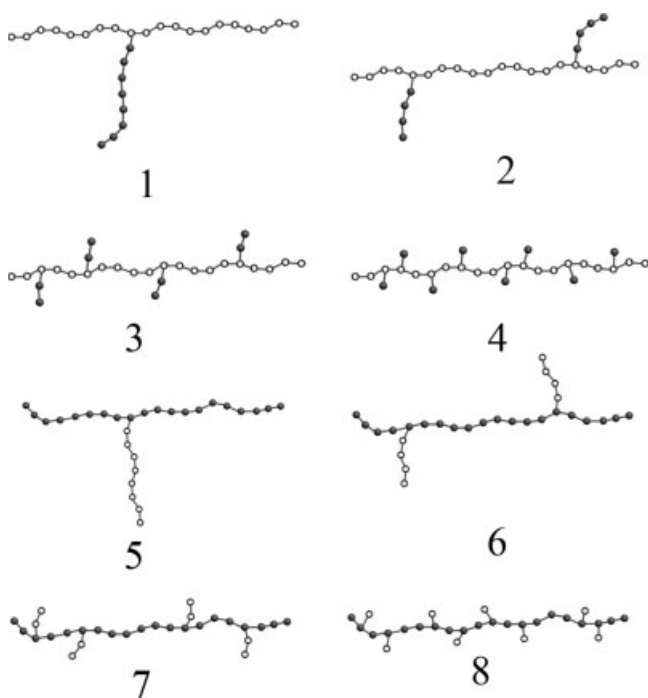


Figure 1 Schematic diagrams showing various architectures of the graft copolymers investigated in the simulation. \circ and \bullet refer to block A and block B segments for the graft copolymer, respectively. Structures 1–4 and 5–8 are A-g-B and B-g-A copolymers.

fractions of homopolymer A, homopolymer B, and graft copolymer were 0.243, 0.568, and 0.189, respectively. The compatibilizing effects of A-g-B and B-g-A copolymers with various graft structures (Fig. 1) were investigated in this study. By fixing the total length of the side chains as 8, the length of the side chain was varied from 1 to 8, namely 1, 2, 4, 8. Accordingly, the number of grafts onto the main chain was 8, 4, 2, and 1. Therefore, all the graft copolymers contained the same main chain and side chain components. Moreover, the grafting sites of each side chain were previously generated with random distribution on the backbones of the main chains.

Figure 2(a–i) show the snapshots of dispersed phase A for various blends at 150,000 MC time. In Figure 2(a), without copolymer, it is seen that polymer A tends to form relatively smooth spheres, and the phase domains are considerably large, indicating that the interfacial tension between homopolymers A and B is quite high. However, after introducing graft copolymer (A-g-B or B-g-A) into the A/B polymer blends, the domain size of the dispersed phase A is evidently reduced [Fig. 2(b–i)]. Moreover, the interface between phases A and B is irregular, which shows the interfacial tension between them is decreased and the compatibility of the blend is much improved.

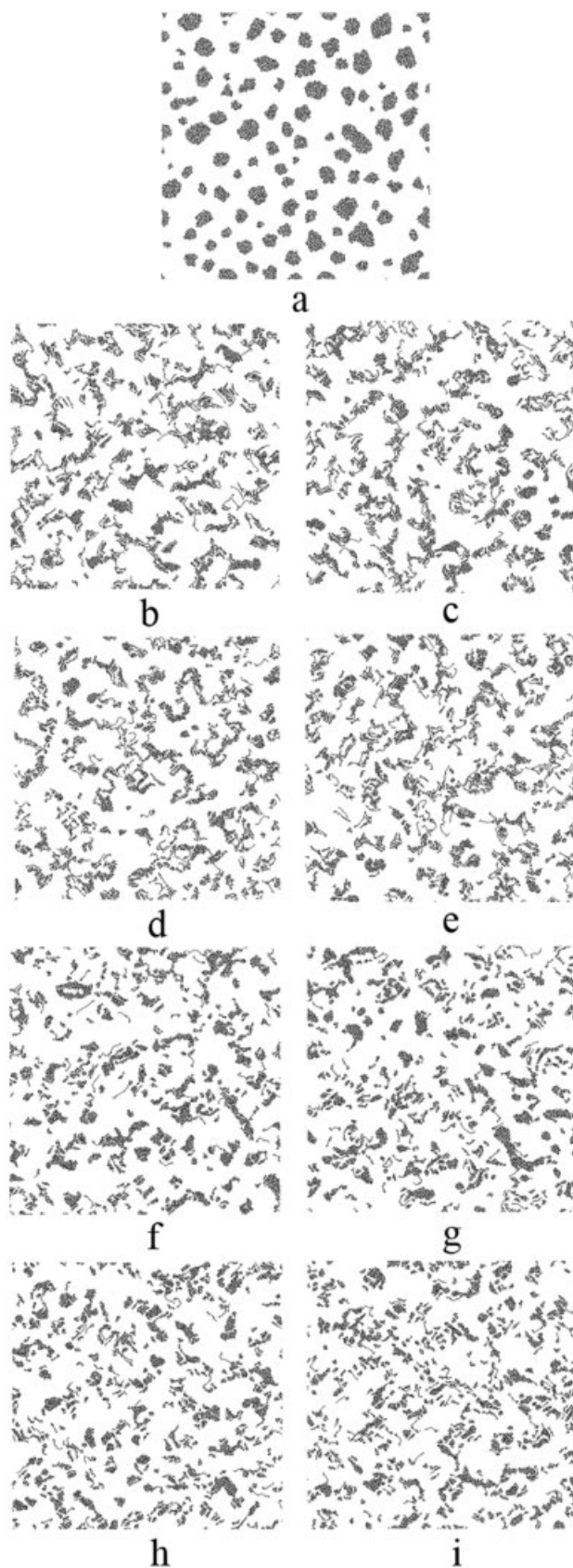


Figure 2 Domain patterns of the dispersed phase A at 150,000 MC time: (a) without graft copolymer; (b–i) adding graft copolymer 1–8, respectively.

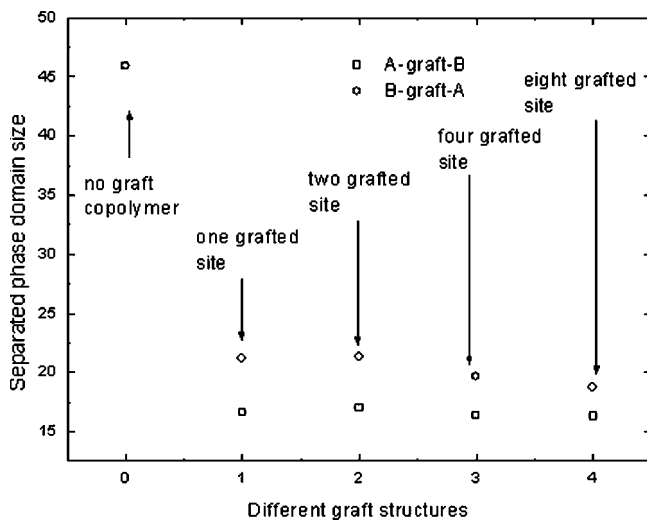


Figure 3 Variation of polymer A domain size with the graft copolymer structures at 150,000 MC time.

Quantitative relationship between the average domain sizes (D) of dispersed phase and the graft architectures is presented in Figure 3. The average domain size (D) is defined as $N \times 0.243/N_d$, where N and N_d are the lattice numbers and the dispersed phase numbers on the line drawn parallel to the borderline, and 0.243 is the volume fraction of dispersed phase A. From Figure 3, it is found that the average domain size of dispersed phase with introducing A-g-B copolymer was somewhat smaller than that of introducing B-g-A copolymer.

It is known that the existence mode of compatibilizers can affect the compatibility of the resulting blends. Figure 4(a-d) show the enlarged snapshots by introducing different A-g-B copolymers as compatibilizer at 150,000 MC time, from which we can distinctly observe the chain configuration in the resulting blends. Though containing the same graft

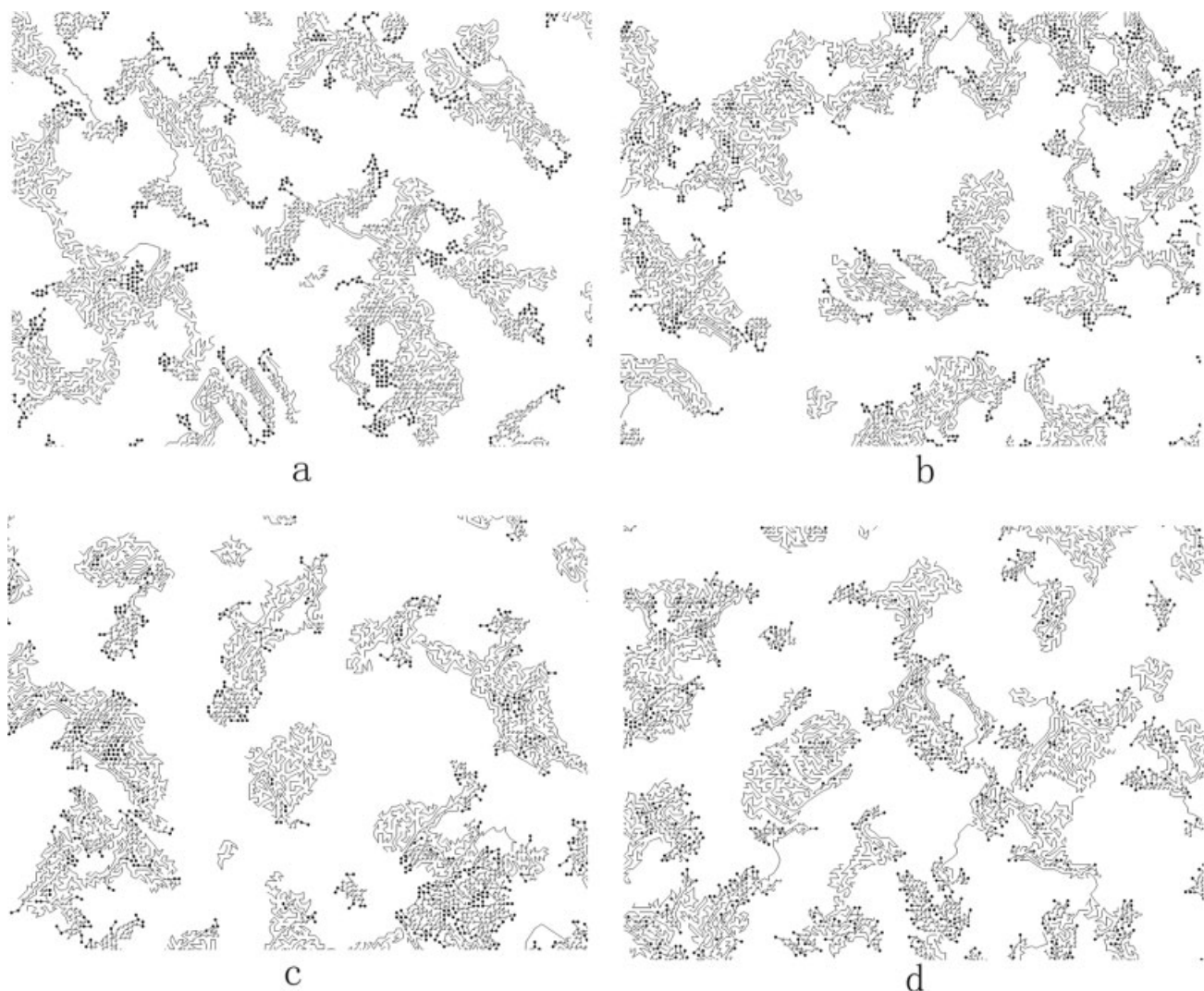


Figure 4 Enlarged snapshots of the blends with adding various A-g-B copolymers at 150,000 MC time. -, O, and ● refer to homopolymer A and A-block and B-block of the graft copolymer, respectively, and white area represents homopolymer B. (a-d) are added graft copolymer 1-4, respectively.

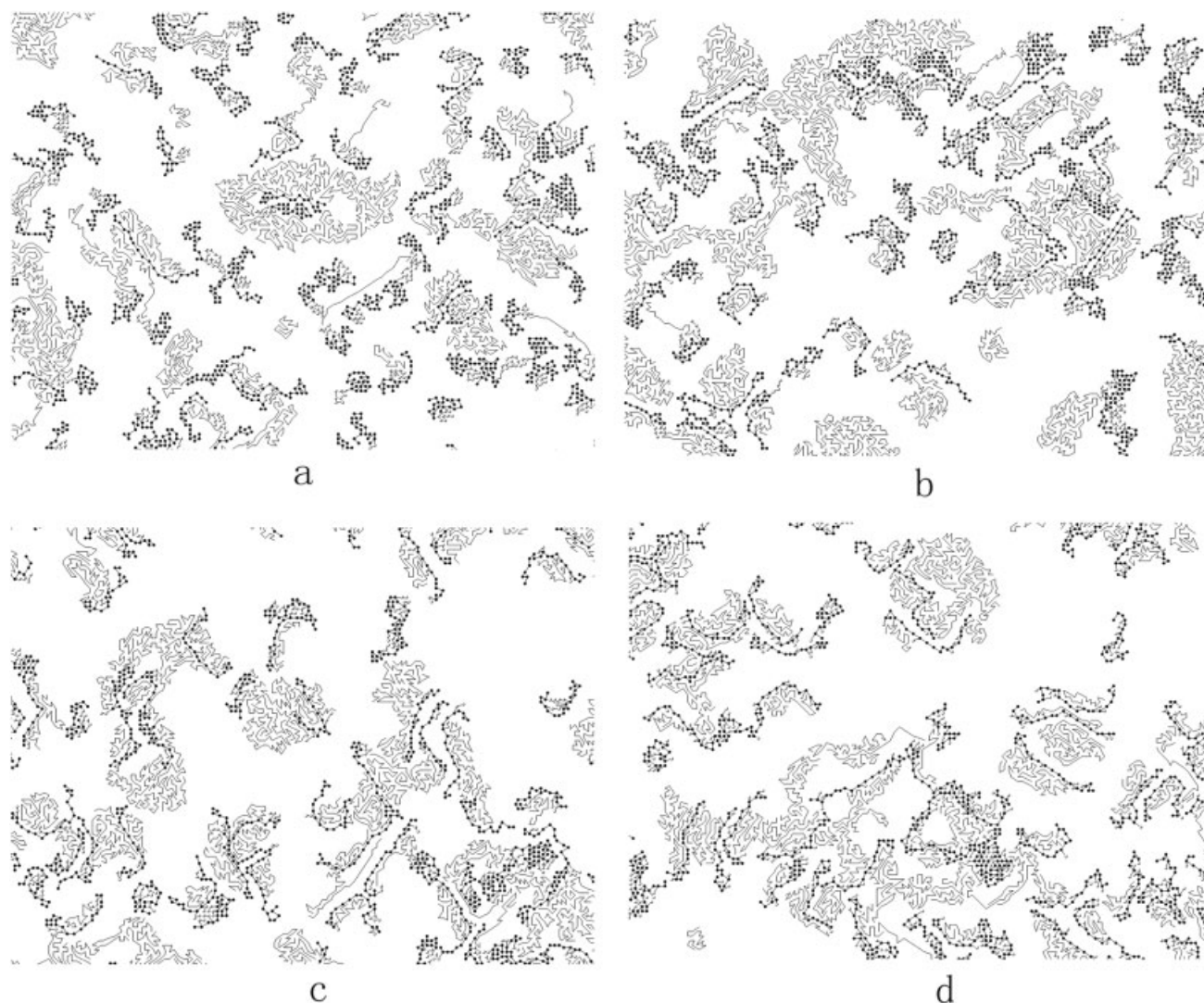


Figure 5 Enlarged snapshots of the blends with adding various B-g-A copolymers at 150,000 MC time. —, ○, and ● refer to homopolymer A and A-block and B-block of the graft copolymer, respectively, and white area represents homopolymer B. a-d are added graft copolymer 5-8, respectively.

component, the A-g-B copolymers with different grafting architectures exhibit disparate existence modes in the blends. In Figure 4(a,b), we find that most A-g-B copolymers with relatively long side chains (8 or 4 segments) are likely to locate at the interface between A phase and B phase. Moreover, it is seen that the side chain (B block) and main chain (A block) anchor B phase and A phase, respectively. Obviously, the graft copolymer connected two immiscible components by the “bridge” effects, which can strongly enhance the mechanical properties of the polymer composites. On the other hand, in Figure 4(c,d), it shows that a majority of A-g-B copolymers with short side chains (1 or 2 segments) are dissolved into the dispersed phase. In this case, the copolymers have less contribution to the mechanical properties. Edgecombe et al.¹³ have pointed out that the interfacial fracture toughness had few

improvements when the side chain of the graft copolymer is extremely short.

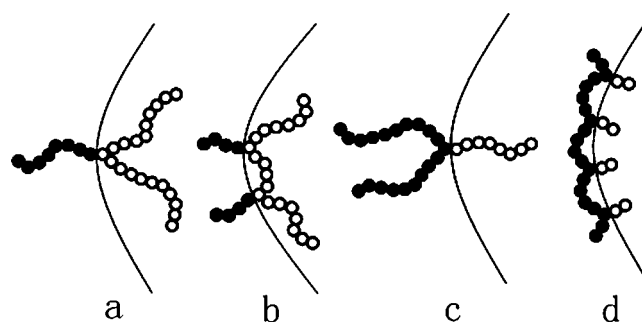


Figure 6 The schematic diagrams of the existence models of A-g-B and B-g-A copolymers in the resulting blends. ○ and ● refer to A-block and B-block of the graft copolymer, respectively. (a-d) show the existence models of graft copolymer 1, 2, 5, and 7, respectively.

Figure 5(a–d) show a dissimilar existence mode of B-g-A copolymers in the resulting blends. It is seen that a small quantity of copolymers are dissolved into the matrix phase, which have less effect on compatibilization. Moreover, it is also observed that more and more copolymers tend to form thin copolymer layers and cover on the phase interface with decreasing the length of side chain. Though those thin copolymer layers can suppress the coalescence of dispersed phase, they are not sufficient to anchor A and B phases together to promote a strong adhesion at the A/B interface. Therefore, the mechanical properties of the composites with this kind of existence mode should have few improvements. By comparing the existence modes of graft copolymer 1–8, it can be concluded that the graft copolymer with long side chain is benefit to compatibilize the blends. For greater clarity, we present some representative schematic illustrations of the existence modes of A-g-B and B-g-A copolymers in Figure 6(a–d). It is clear that the copolymers are not sufficient to anchor A and B phases together when their side chains are extremely short.

CONCLUSIONS

Monte Carlo simulation was successfully employed to study the compatibility of incompatible A/B blends by introducing graft copolymer (A-g-B or B-g-A). Simulation results showed that incorporation of both A-g-B (A was backbone) and B-g-A (B was backbone) copolymers could improve the compatibility of the blends very much. However, A-g-B copolymer was more effective to compatibilize the blend if homopolymer A formed dispersed phase. Furthermore, simulation results indicated that A-g-B copolymers tended to locate at the interface and anchor two immiscible components when the side chain is relatively long. However, most of A-g-B copolymers were likely to be dispersed into the dispersed homopolymer A phase domains if the side chains were relatively short. On the other hand, B-g-A copolymers tended to be dispersed into the matrix formed by homopolymer B. Moreover, it was found that more and more B-g-A copolymers were likely to form thin layers at the phase interface with decreasing the length of side chain.

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