Effect of the molecular structure of graft copolymer on the interfacial behavior between two immiscible homopolymers: A Monte Carlo simulation

Joon Sik Park[1], Ho Cheol Kim[2], Won Ho Jo[1,]*

[1] Department of Fiber and Polymer Science, Seoul National University, Seoul 151-742, Korea
[2] Central Research Institute, Hyosung T&C Co., Anyang 430-080, Korea

Summary

The effects of molecular structure of graft copolymer on the interfacial properties are investigated using a Monte Carlo simulation. The interfacial activity is analyzed by calculating the surface coverage and the concentration profile of graft copolymer at the interface. At low interaction energy between two segments, the graft copolymer having fewer grafting sites and longer grafting chains locates better at the interface than the graft copolymer having more grafting sites and shorter grafting chain. At high interaction energy, this situation is reversed: the graft copolymer with more grafting sites locates better than the copolymer with fewer grafting sites.

Introduction

The method giving interfacial activity by adding block or graft copolymers to an immiscible polymer pair has been well established (1). Generally, when an AB block or graft copolymer is added to an A/B immiscible binary blend thus forming an A/B/AB ternary blend, the following major effects are observed: reduced interfacial energy between two phases, better dispersion of minor phase, better adhesion between two phases, and stabilization of dispersed phase against coalescence. It has been known that the compatibilizing efficiency of copolymer strongly depends on its molecular architecture: the simpler the architecture of copolymer, the easier the penetration of copolymer segment into the corresponding homopolymer phase (2). Therefore, it is expected that block copolymers are more efficient in compatibilization than random or graft copolymers, and that diblock copolymer is more efficient than triblock or multi-block copolymers. However, the block copolymers have been some limitations to use as a compatibilizer, i.e., the production cost is relatively high and the variation of chemical structure is rather limited. Graft copolymers are, however, easily produced in large-scale and commonly used as compatibilizers in industrial processes (1). Although the use of graft copolymer is now well established, there have been few fundamental studies to investigate the effect of comb architecture of graft copolymer on its compatibilizing efficiency.

In this study, we investigate the effect of the molecular architecture of graft copolymers, such as number and length of grafting chain, on the compatibilizing activity using a Monte Carlo computer simulation.

---

* Corresponding author

Model and simulation method

The simulations are performed on a simple cubic lattice of 70 x 70 x 70 sites with periodic boundary conditions in the X and Y directions. As schematically illustrated in Figure 1, this cubic lattice is separated into two regions along the Z axis. The upper half of the box (Z = 0 ~ 34) represents homopolymer A region and the lower half (Z = 35 ~ 69) represents homopolymer B region. There exists an interface at the center of the Z axis in the cubic box (i.e., Z = 34 and Z = 35).

In the simulation, we consider two types of graft copolymers denoted by Graft-1 and Graft-2, where the numerals 1 and 2 represent the number of grafting site per chain. The backbone chain and grafting chain are composed of A and B segments, respectively. The length of backbone chain is fixed at 10, and the length of grafting chain is varied from 2 to 10. The numerals following the name Graft-1 and Graft-2 denote the total length of grafting chains. For example, the Graft-2-10 represents a graft copolymer having two grafting sites with the grafting chain length at each site being 5. Note that in a Monte Carlo simulation one segment always represents one Kuhn's segment. Figure 2 shows schematic structures of two graft copolymers. The initial configurations of graft copolymers are randomly generated as follows. The first segment of the first chain is placed at a randomly chosen lattice site in the cubic lattice, and chains are grown simultaneously by adding bonds to the end of growing chains in a direction selected randomly from the bond set, with the segments avoiding each other. A total of 10 graft copolymers are generated in the cubic lattice. After the chains are completely generated in the cubic lattice, the structures are equilibrated by allowing the chains to move randomly without interaction for 10^8 Monte Carlo steps (MCS). The interaction between A and B segment is modeled by an energy cost ε_{AB} if two segments are neighbors of each other. Two segments are considered as a neighbor if they are separated by one of the displacement vectors $\{(2,0,0), (2,1,0), (2,1,1)\}$ (plus those obtained from symmetry operations). The value of the interaction energy (ε_{AB}) varies from +0.05 to +0.5, while the interaction energies between the same segments are set to be zero, i.e., $\varepsilon_{AA} = \varepsilon_{BB} = 0$.

We adopt in this study the bond fluctuation model to simulate the motion of the polymer chains on the lattice (3-5). In this model, each segment occupies eight lattice sites of a unit cell, and each site can be a part of only one segment (self-avoiding walk condition). This condition is necessary to account for the excluded volume of the polymer chains. For a given chain, the bond length between two successive segments can have all possible length from 2 to $10^{1/2}$, restricted to a particular set of vectors (6). For a cubic lattice, the possible vectors can be derived from the basic set $\{(2,0,0), (2,1,0), (2,1,1), (2,2,1), (3,0,0), (3,1,0)\}$. This set of bond vectors guarantees that no two bonds will cross each other during the course of their motion and thus entanglement is automatically taken care of.
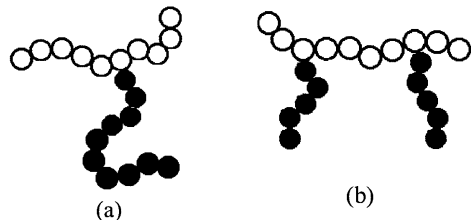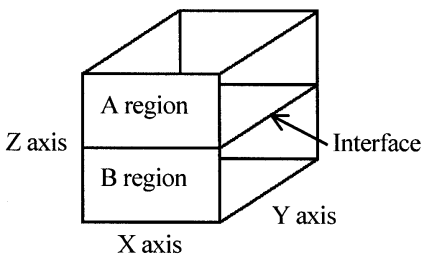

Figure 1. Model of cubic lattice used in the simulation.

Figure 2. Schematic illustration of the molecular structure of graft copolymers: (a) Graft-1-10; (b) Graft-2-10.

The specific scheme for moving polymer chains proceeds as follows: First, a chain is chosen at random and then a segment on the chain is also picked randomly. An attempt is made to move the segment in one of six possible directions. If no other segment is present in the new location and if the bond length of the new bond satisfies the bond length constraint, the move is accepted and the simulation proceeds by choosing another chain and segment at random. If, however, the excluded volume conditions and the bond length constraint are not fulfilled, the move is rejected and the segment is restored to its original position.

The interaction energies exert an effect through the Metropolis algorithm (7). Here, moves that reduce the energy of the system are accepted with unit probability, but moves that increase the energy of the system are accepted with the probability $\exp(-\Delta E/kT)$, where ΔE is the energy change associated with the move of the segment, k is the Boltzmann constant, and T is temperature.

Results and discussion

Figure 3 shows the surface coverage of graft copolymers as a function of interaction energy ε_{AB}. Here the surface coverage is defined as the ratio of the interfacial area occupied by copolymer chains to the total interfacial area. Irrespective of the number of grafting site, the surface coverage increases with increasing ε_{AB} and then levels off. At lower value of ε_{AB}, the grafting chain composed of B segments can still remain at the A homopolymer region and the backbone chain of A segments can also stay at the B homopolymer region. As the value of ε_{AB} increases, the interaction between A and B segments becomes energetically unfavorable. As a result, the grafting side chain is forced to move into the B homopolymer region while the backbone chain is segregated into the A homopolymer region, thereby the surface coverage of graft copolymer becomes larger. Figure 3 also shows that the surface coverage of graft copolymers increases with increasing the length of grafting chain. This phenomenon is explained by enthalpic effect, i.e., the longer the grafting chain, the stronger the repulsive energy. The strong repulsive energy forces the copolymer chain to move to the interface, resulting in higher surface coverage. In Figure 3, the surface coverage of Graft-1-10, Graft-2-8 and Graft-2-6 shows a maximum as the interaction energy increases. This unexpected maximum might come from poor statistics of simulation, because it seems not to be plausible at present to explain thermodynamically this phenomenon.
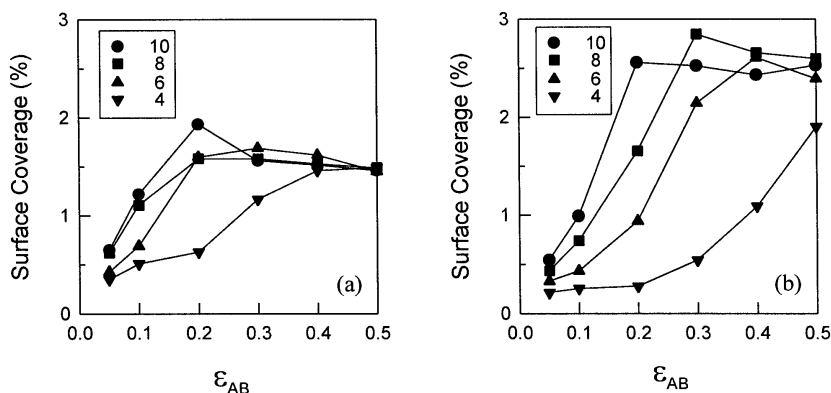

Figure 3. Surface coverage of graft copolymers having different grafting chain length as a function of ε_{AB}: (a) Graft-1; (b) Graft-2. The numbers for symbols in inset denote the total length of grafting chains.
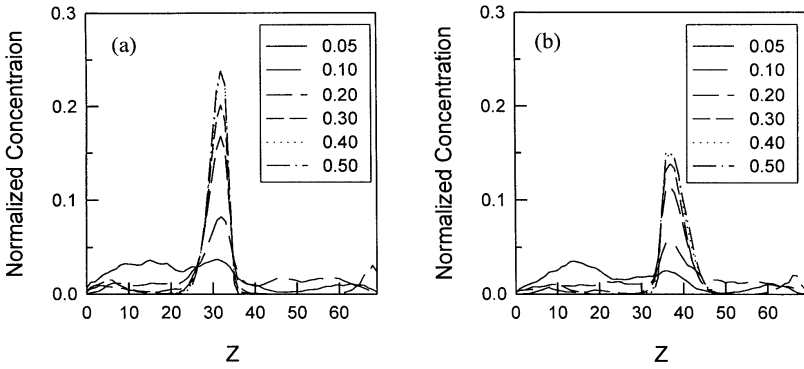
Figure 4. Normalized concentration profiles of Graft-1-8 for various interaction energies: (a) backbone segment; (b) grafting segment.
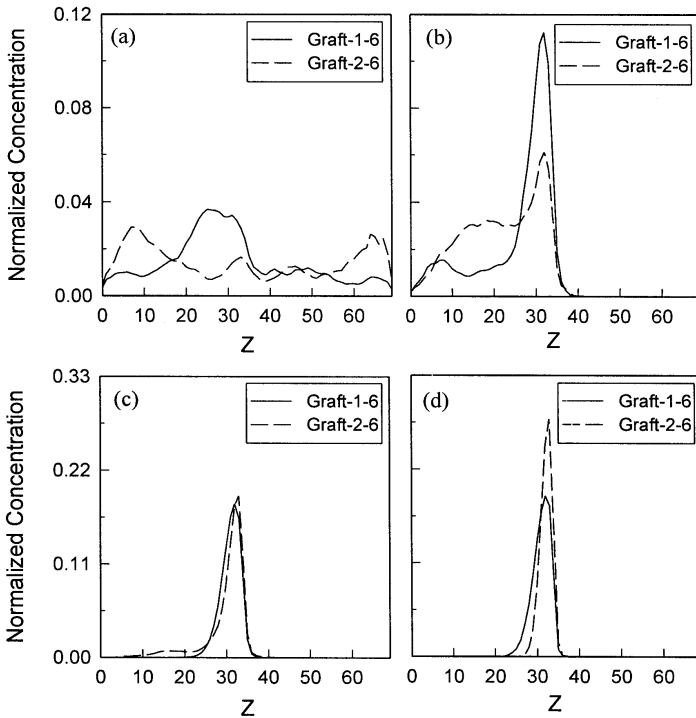

Figure 5. Normalized concentration profiles of backbone segments of Graft-1-6 and Graft-2-6 for various ε_{AB}: (a) $\varepsilon_{AB} = 0.05$; (b) $\varepsilon_{AB} = 0.20$; (c) $\varepsilon_{AB} = 0.30$; (d) $\varepsilon_{AB} = 0.50$.

Figure 4 shows the normalized concentration profiles of Graft-1-8 for various values of ε_{AB}. For both backbone and grafting chain, the width of the profiles is relatively broad at low value of ε_{AB}. The width of the profiles decreases with increasing ε_{AB}, indicating that graft copolymers are more localized at the interface. This result is well consistent with the result shown in Figure 3. Considering the fact that the interface exists between

Z=34 and Z=35 in this simulation model, it is apparent that the backbone segments localize near the region of Z<34 while the grafting segments localize near the region of Z>35. The effect of the magnitude of ε_{AB} on the normalized backbone concentration profiles of Graft-1-6 and Graft-2-6 is shown in Figure 5. The profiles clearly show that the peak height of Graft-1-6 is one and half times higher than that of Graft-2-6 at lower interaction energy, e.g., $\varepsilon_{AB} = 0.20$, whereas the peak height of Graft-2-6 becomes larger than that of Graft-1-6 at higher interaction energy, e.g., $\varepsilon_{AB} = 0.5$. This result indicates that there exists an interaction energy at which Graft-2 localizes better at the interface than Graft-1, so-called crossover interaction energy. In order to examine the crossover phenomenon in more detail, we may return to the surface coverage data as a function of interaction energy as shown in Figure 6. At lower interaction energy, Graft-1s have higher surface coverage than Graft-2s, but at higher interaction energy Graft-2s have higher surface coverage energy than Graft-1s. These results can be explained by considering both enthalpic and entropic effects due to localization of block copolymer at the interface. If a A/B graft copolymer (or a block copolymer) locates at the interface between A and B phases, the entropic term has an unfavorable effect while the enthalpic term has a favorable effect on the free energy of the system. Therefore, enthalpic and entropic effects compete with each other. If the enthalpic effect becomes large enough to compensate the unfavorable entropy loss due to localization at the interface, the junction point of graft copolymer can locate at the interface between two phases. In this study, Graft-1 and Graft-2 have one and two junction points in their structure, respectively. Thus, the entropy loss of Graft-2 is larger than Graft-1, when the graft copolymers are located at the interface. On the other hand, the enthalpic term depends upon the magnitude of the interaction energy between A and B segments. The enthalpic effect becomes larger as the interaction energy increases. Therefore, the copolymer chain is forced to move to the interface as the interaction energy increases. Since the graft copolymer having more junction points experiences larger entropy loss at the interface, it may require larger enthalpic energy to drive the copolymer to the interface. Consequently, Graft-2 requires more enthalpic energy than Graft-1 to locate the copolymer at the interface, because Graft-2 undergoes larger entropy loss than Graft-1. At low interaction, the enthalpic energy is enough to move Graft-1 to the interface, but Graft-2 needs more enthalpic interaction. As a result, Graft-1 shows higher surface coverage than Graft-2 at low interaction energy. As the interaction energy increases,
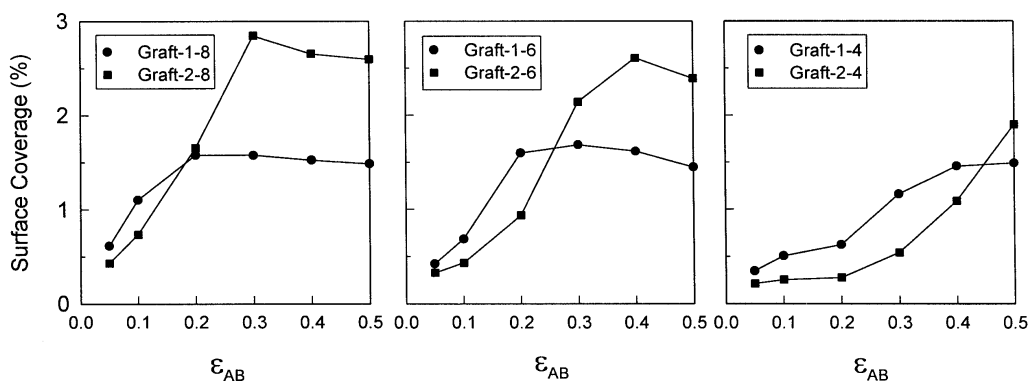

Figure 6. Surface coverage of graft copolymers having the same total length of grafting chain as a function of ε_{AB}.

Graft-2 overcomes large entropy loss and locates at the interface. Thus Graft-2 shows higher surface coverage than Graft-1 at high interaction energy, because a single chain of Graft-2 has higher surface coverage than that of Graft-1 when they are located at the interface. The enthalpic term also depends upon the total length of grafting chain, since the length of backbone chain is fixed at 10.

The enthalpic effect becomes larger as the total length of grafting chain increases. When crossover interaction energy is plotted against the length of grafting chain in Figure 7, it shows that the crossover interaction energy decreases with increasing the total length of grafting chain. This is because the graft copolymer having longer grafting chain needs less interaction energy to compensate the entropy loss due to localization at the interface.
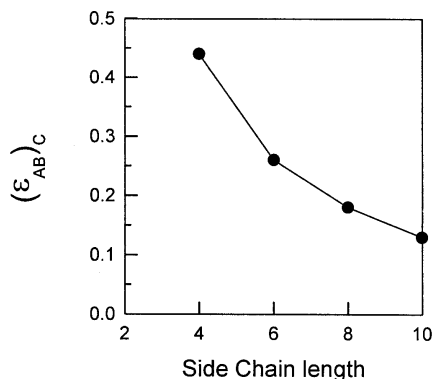

Figure 7. Crossover interaction energy, $(\varepsilon_{AB})_C$ as a function of grafting chain length.

Conclusions

The surface coverage of graft copolymer increases with increasing the repulsive interaction energy ε_{AB} between A and B segment. The surface coverage of Graft-1 is larger than Graft-2 at low interaction energy, but at high interaction energy Graft-2 has higher surface coverage than Graft-1. This is explained by considering the competition between enthalpic and entropic contribution when the graft copolymers are located at the interface. The results obtained from this simulation may provide a guideline for designing the molecular structure of graft copolymer to be used for an effective compatibilizer.

Acknowledgements

References

1. Paul DR, Newman S (1978) Polymer Blends. Academic Press, New York
2. Paul DR, Barlow JW (1980) J. Macromol. Sci., Rev. Macromol. Chem. 19:109
3. Carmesin I, Kremer K (1988) Macromolecules 21:2819
4. Jo WH, Ko MB (1993) Macromolecules 26:5473
5. Jo WH, Kim SH (1996) Macromolecules 29:7204
6. Deutsch HP, Binder K (1992) J. Chem. Phys. 94:2294
7. Metropolis N, Rosenbluth AW, Rosenbluth MN, Teller AH, Teller E (1953) J. Chem. Phys. 21:1087