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Monte Carlo Computer Simulation-Based Study on Interface Properties of Ternary Polymer Blend System

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Multi-polymer blending with complementary properties is a direct and efficient way to obtain materials with improved properties. However, it is difficult to mix between different types of polymers. Block and graft polymers are commonly used incompatible polymer mixed solubilizers, exhibiting interfacial activity at the interface, but their interfacial properties are difficult to predict. Based on Monte Carlo computer simulation technology, this paper studied the effects of molecular chain length and concentration of the ternary polymer blend system on the interface of the system. The simulation result showed that the interface of the ternary block or graft polymer blend interface exhibits no stretching in the direction perpendicular to the interface direction, and the graft polymer branch exhibits interface stretch in the direction perpendicular to the interface direction. The thickness of the interface increases with the increasement of the block or graft polymer. This study on the interfacial properties of ternary polymer blend system not only contributes to the development of new polymer materials, but also enhances the theoretical understanding of the interfacial properties of multi-polymer blend system and the intrinsic link of copolymer solubilizers.

1. Introduction

As the demand for new materials with superior functionality continued to increase, polymer science faced increasingly great challenges (Sun and Guo, 2011). In recent years, a large number of researchers had discovered a new method to meet the needs of polymer manufacturing, which is to mix the homopolymers of different components with complementary properties to achieve the performance improvement of polymer materials, providing materials with better performance for many important technologies and industries (Lu et al., 2016; Shokoohi and Arefazar, 2010). The ternary polymer blend material formed by homopolymer/copolymer/homopolymer not only had the characteristics of ordinary binary polymer blend, but also had a large difference from the ordinary binary polymer blend materials in terms of physical and mechanical properties (Sangeetha et al., 2016). The comprehensive influence of factors such as molecular chain length and chain topology between the ternary polymers and the interaction parameters between the incompatible units made it difficult to provide accurate predictions and descriptions of the properties and behavior of the complex interface of the ternary polymer blend system (Malik et al., 2011).

When the content of the copolymer solubilizer in the ternary polymer blend system exceeded the critical micelle concentration, the interface tension between the incompatible homopolymers no longer changed as the copolymer solubilizer content increased (Wang et al., 2018; Letuchii and Miroshnikov, 2015). The emergence of computer simulation methods combines the structure and performance of materials to predict the physical and mechanical properties and microstructure of materials on a computer, effectively reducing research and development costs and greatly improving research and development efficiency (Wright et al., 2016). The Monte Carlo simulation method was a randomness numerical simulation method that had great advantages in studying the relationship between physical and chemical properties and structures of polymers (Pike et al., 2011). The compatibilizing efficiency of the ternary polymer copolymer to the interface was primarily dependent on the copolymers that were concentrated at the interface of the mixture, and the blocks of each copolymer penetrated into the corresponding polymer phase (Roestorff and Chirwa, 2018). Based on Monte Carlo computer simulation technology, this paper studied the effects of molecular chain length and

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concentration of ternary polymer blend system on the interface of the system, and revealed the intrinsic relationship between the interfacial properties of the multipolymer blend system and the copolymer solubilizer.

2. Simulation Method and Model Theory

2.1 Principles and Steps of Monte Carlo Computer Simulation Technology

In recent years, computer simulation technology had assisted experimental research to accelerate the pace of scientific research. The method that people used computer simulation to study, analyze and solve problems was referred to as "computer experiments" (Zare, 2016). The lattice model and the non-lattice model were Monte Carlo models. Utilizing random walking or self-avoiding random walking was a common way for people to obtain samples in equilibrium (Barrozo et al., 2018; Mukhanov et al., 2015). The steps included coarse granulation modeling of the blend system, initial conformation of the simulation system, random moving links, checking the bond length of the attempted movement, and the difference in chain link energy before and after the change of the attempted movement position (Dhar et al., 2015). During the simulation, when the particles moved from the inside of the simulation box to the outside, the particles re-entered the interior of the simulation box according to the evolution equations of Equations 1 and 2:

$$if(\chi i(t+h) \leq -L/2), \chi i(t+h) = \chi i(t+h) + L \quad (1)$$

$$if(\chi i(t+h) \geq -L/2), \chi i(t+h) = \chi i(t+h) - L \quad (2)$$

wherein: L is the size of the simulation box

2.2 Lattice and Non-lattice Models

The commonly used lattice model was a two-dimensional model (bond fluctuation model), and the single-position and eight-position models were commonly used lattice models in 3D simulation (Tang and Wang, 2014). Assuming that each chain link occupies one lattice point, the bond length between adjacent chain links takes a value of 1 and$\sqrt{2}$, the bond length and bond angle between the copolymers are determined by the fluctuation of the bond length. The three-dimensional space is more realistic in reflecting the simulation system. The three-dimensional lattice model consists of a two-dimensional lattice model and a position model. The fluctuation range of the bond length is improved, and a more complex system can be solved. In the non-lattice model, the bond angle of the copolymer can be serialized, and there are no conditions corresponding to the chain link and the lattice, and the discrete conditions are closer to the multi-polymer blend. The physical quantities commonly used in simulation include the coordinate components of the mean square radius of gyration and the spatial direction, the orientation parameters, and the interface thickness.

3. Monte Carlo Simulation of Interfacial Properties of Three Ternary Block Polymer Blend System

3.1 Simulation Method and Model Establishment

The difference in free energy makes the compatibility of different polymers poor. The addition of a copolymer solubilizer improves the interfacial properties. The block polymer is an effective solubilizer compatible and expandable at the polymer interface. Compared with the binary block copolymer, the ternary block copolymer has a stronger solubilizing effect, and it is easier to form micelles. It has been found that the addition of a ternary block copolymer reduces the interfacial tension of the polymer blend system by more than 85%. In this section, ABA ternary block copolymer was studied. It was assumed that the length of the A block was equal to half the length of the B block. The effect of the ternary block copolymer concentration and the chain length on the interface thickness was studied respectively. The concentration of the ternary block copolymer increased from 0.01 to 0.05 and the molecular chain length increased from 8 to 60. The blend interface was perpendicular to the z-direction, and the system was balanced by computer simulation. The system was sampled every 10^4MCS for a total sampling of 100 times.

3.2 Simulation Results and Discussion

The interfacial properties of the blend system were related to distribution density, distribution width and penetration degree at the interface. The interface thickness can be used to represent the interfacial properties. Figure 1 showed the dependence of the interface thickness on the molecular chain length of the ternary block copolymer. It can be seen that the interface thickness decreased as the molecular chain length of the ternary block copolymer increased. Figure 2 showed the mean square radius of gyration of the copolymer and its components in three directions. It can be seen that the interface thickness in both directions parallel to the blend interface was almost the same, larger than the z direction. Figure 3 was the Dependence of the

orientation parameter on the molecular chain length of the ternary block copolymer. It can be seen that the orientation of the chain decreased as the molecular chain length of the ternary block copolymer increased, and the ternary block copolymer did not stretch in the direction perpendicular to the interface.

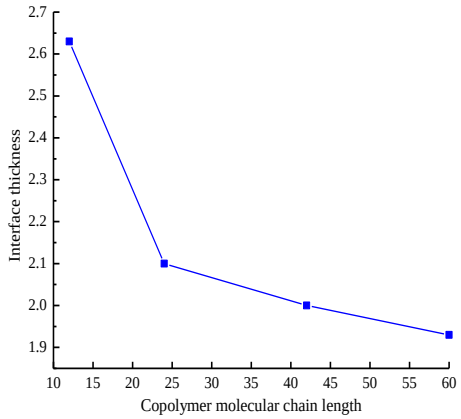


Figure 1: The dependence of interface thickness on the molecular chain length of ternary block copolymer

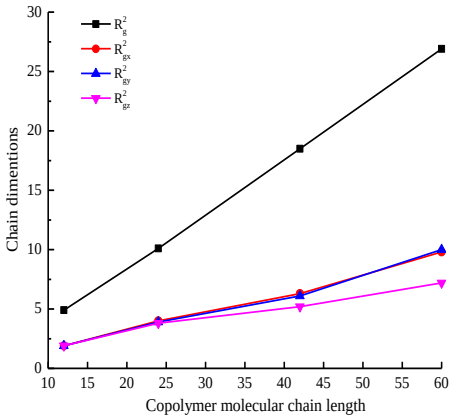


Figure 2: The mean square radius of gyration of the copolymer and its component in three directions

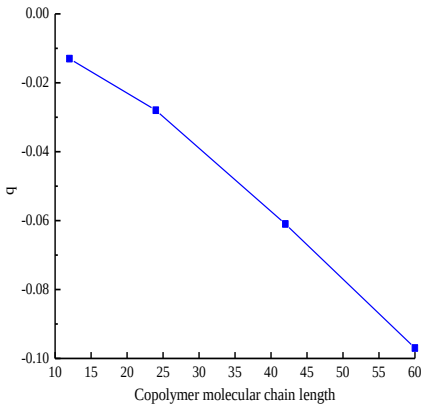


Figure 3: Dependence of orientation parameters on molecular chain length of ternary block copolymer

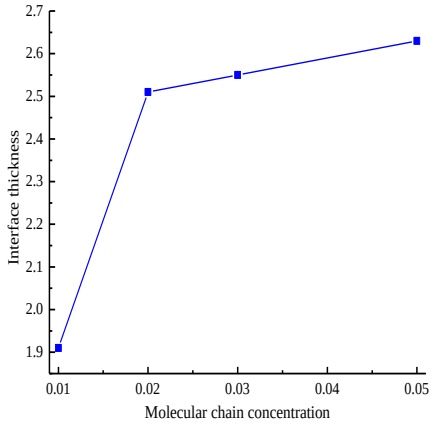


Figure 4: The dependence of interface thickness on the molecular chain concentration of ternary block copolymer

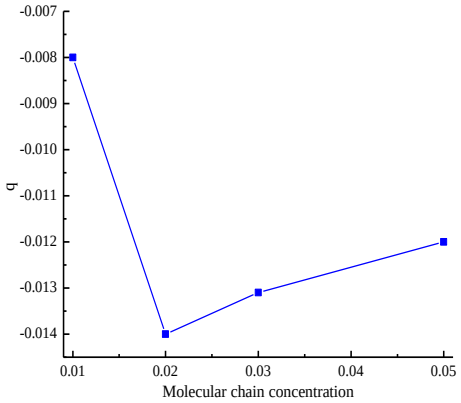


Figure 5: Dependence of molecular chain orientation parameters of copolymer on molecular chain concentration of ternary block copolymer

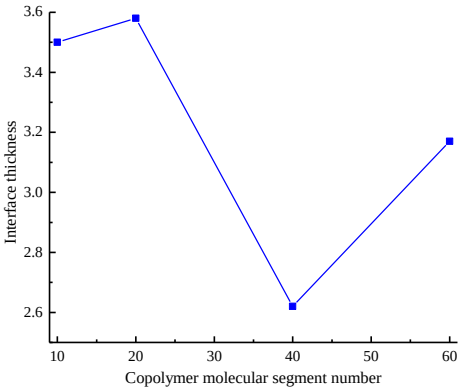


Figure 6: The dependence of interface thickness on the number of molecular segments of graft copolymer

Figure 4 showed the dependence of the interface thickness on the molecular chain concentration of the ternary block copolymer. The interface thickness increased along with the increasement of the ternary copolymer in the system, and the interface thickness increased faster when the molecular chain concentration of the copolymer was lower. Figure 5 showed the dependence of the molecular chain orientation parameter of the copolymer on the molecular chain concentration of the ternary block copolymer. Q was less than zero when the molecular chain concentration of the ternary block copolymer was increased from 0.01 to 0.05, that is, the ternary polymer blend did not stretch in a direction perpendicular to the interface.

4. 4. Monte Carlo Simulation of Interfacial Properties of Ternary Graft Polymer Blend System

4.1 Simulation Method and Model Establishment

The adhesion stress between incompatible polymer units was extremely low, and the addition of an appropriate amount of graft polymer can significantly reduce the interfacial tension of the incompatible polymer and the interface. There were few studies on ternary graft polymers. The experimental study on the interface properties of ternary graft polymers had limitations. The theory and simulation were still unclear. This paper studied the conformational interface properties of the main chain and the branched chain of the ternary graft copolymer with Monte Carlo computer simulation technology, including the density distribution and interface thickness of the copolymer. The number of molecular chain segments of the graft polymer ranged from 10 to 60, the molecular chain concentration ranged from 0.01 to 0.05, and the number of samples was 500. The remaining simulation methods were the same as those in the previous section.

4.2 Simulation Results and Discussion

Studies have shown that all of the graft polymers aggregated at the interface, independent of the number of molecular chain segments. Figure 6 showed the dependence of the interface thickness on the number of molecular chain segments of the graft copolymer. The thickness of the interface showed a trend of increase-decrease-increase along with the increase of the number of molecular chain segments of the graft copolymer, and the thickness of the interface was the maximum when the number of molecular chain segments was 20. Figure 7 was the mean square radius of gyration of the main chain and the branch chain on the graft copolymer and its component in three directions. The interface thickness of the main chain and the branch chain in the thickness direction parallel to the interface was the same, and the scale of the main chain was smaller than the branch chain in the direction perpendicular to the interface. Figure 8 was the dependence of the orientation parameter on the number of the chain segments. The orientation parameter q of the main chain was less than zero, which meant that the interface did not stretch in the direction perpendicular to the interface, and the branch chain showed interface stretch in the direction perpendicular to the interface. Figure 9 was topography of a ternary graft polymer blend system. In the figure, red indicated polymer A, yellow indicated polymer B, green indicated graft polymer main chain A unit, and blue indicated graft polymer branch chain B unit. It can be seen that the graft polymer aggregated at the interface, and as the number of molecular chain segments increased, more graft polymer main chains and branch chains gathered at the interface. Figure 10 and Figure 11 showed the dependence of the interface thickness on the molecular chain concentration of the graft copolymer when Nc = 10 and 60, respectively. The interface thickness increased with the increase of the graft polymer content in the ternary blend material.

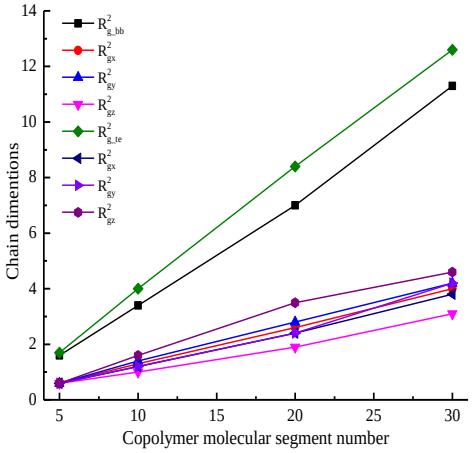


Figure 7: The mean square radius of gyration of the

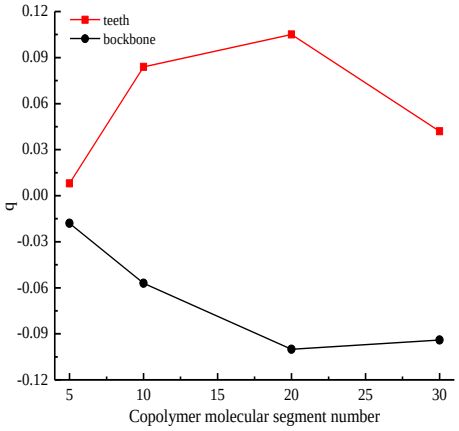
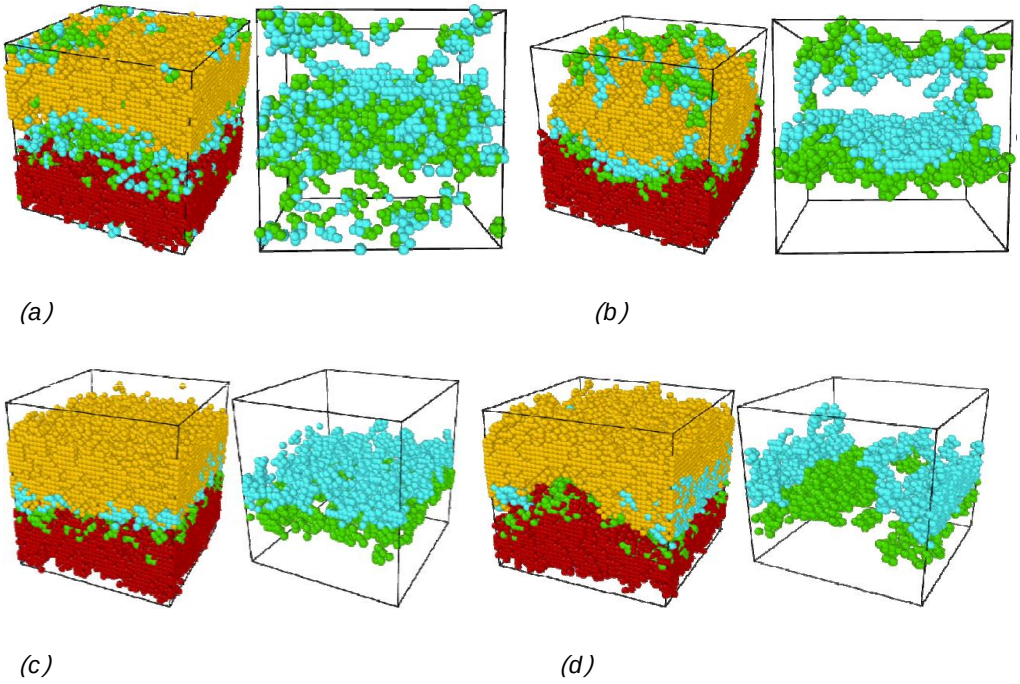


Figure 8: The dependence of orientation parameters

main chain and the branch on the graft copolymer and its component in three directions

on the number of segments



(a) *(b)*

(c) *(d)*

Figure 9: Topography of ternary graft polymer blend system

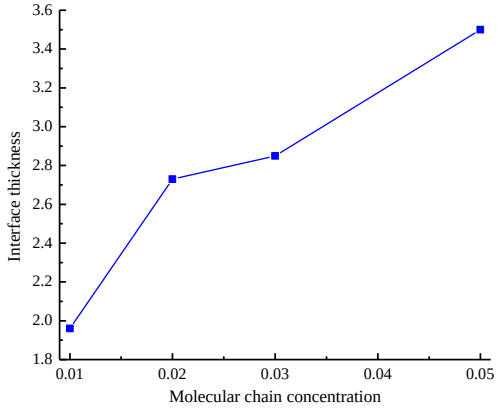


Figure 10: The dependence of interface thickness on the molecular chain concentration of graft copolymer when Nc=10

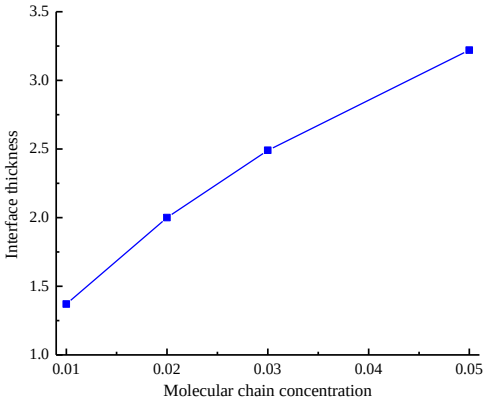


Figure 11: The dependence of interface thickness on the molecular chain concentration of graft copolymer when Nc=60

5. Conclusion

Based on Monte Carlo computer simulation technology, this paper studied the effects of molecular chain length and concentration of the ternary polymer blend system on the interface of the system. The specific conclusions were as follows:

(1) The three-dimensional space is more realistic to reflect the simulation system. The three-dimensional lattice model consists of a two-dimensional lattice model and a position model. The fluctuation range of the bond length is improved, and a more complex system can be solved. The physical quantities commonly used in computer simulation include the coordinate components of the mean square radius of gyration and the space direction, orientation parameters, and interface thickness.

(2) The thickness of the interface decreases with the increase of the molecular chain length of the ternary block copolymer, and the orientation of the chain decreases as the molecular chain length of the ternary block

copolymer increases, and the ternary block copolymer did not strength in the direction perpendicular to the interface.

(3) The interface thickness showed a tendency of increase-decrease-increase with the increase of the number of molecular chain segments of the graft copolymer. The interface thickness of the main chain and the branch chain in the direction parallel to the interface thickness was the same, and the scale of the main chain in the direction perpendicular to the interface is smaller than the branch.

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