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Effects of Competition between Phase Separation and Ester Interchange Reactions on the Phase Behavior in a Phase-Separated Immiscible Polyester Blend: Monte Carlo Simulation

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Abstract: The effects of rate ratio of phase separation to ester interchange reactions and the repulsive pair interaction energy on the phase behavior in a phase-separated immiscible polyester blend are investigated using a Monte Carlo simulation method. The time evolution of structure factor and the degree of randomness are monitored as a function of homogenization time. When the phase separation is dominant over ester interchange reactions, the domain size slowly increases with homogenization time. However, when the pair interaction becomes less repulsive, the domain size does not significantly change with homogenization time. On the other hand, when ester interchange reactions are dominant over the phase separation, the homogenization proceeds without a change in the domain size. The higher the extent of phase separation, the lower the increasing rate of the DR. However, when the phase separation is sufficiently dominant, the effect of the extent of phase separation on the increasing rate of the degree of randomness become less significant.

Keywords: Immiscible polyester blends, Phase separation, Ester interchange reactions, Phase behavior, Monte Carlo simulation

Introduction

Most of immiscible polyester blends have phase-separated structures unless ester interchange reactions occur. Therefore, their phase behaviors are greatly influenced by ester interchange reactions which are dependent upon mixing condition and residual catalyst used in polymerization[1]. Yoon *et al*.[2] reported that competition between phase separation and ester interchange reactions controls the coarsening, melting and stabilization mechanisms in immiscible polyester blends: When the phase separation is dominant over ester interchange reactions, global structure becomes coarsened. On the other hand, when ester interchange reactions are dominant over the phase separation, global structure becomes melted.

In our previous study[3], the homogenization process controlled by competition between phase separation and ester interchange reactions in phase-separated immiscible polyester blends was studied using the Monte Carlo simulation method. It was found that the homogenization of phase-separated polyester blends proceeds by ester interchange reactions through the reduction of the concentration difference between two phases without a change in the domain size. It was also found that the more repulsive the pair interaction is, the slower the homogenization process is. However, the effects of relative rates of phase separation and ester interchange reactions on the phase behavior in phase-separated immiscible polyester blends were not systematically investigated in the previous study. Practically, it is very difficult to experimentally control relative rates of phase separation and ester interchange reactions because these two phenomena are strongly coupled with each other and are also strongly dependent on the annealing temperature[4].

In this study, the homogenization of immiscible polyester blends having different extent of phase separation is simulated to investigate the effects of relative rates of phase separation and ester interchange reaction and the repulsive pair interaction energy on their phase behaviors.

Model and Simulation Method

The model and simulation methods used in this study are detailed in the previous paper[3]. The simulations are performed on a simple cubic lattice of 50×50×50 ($L_x \times L_y \times L_z$) sites with periodic boundary conditions[5]. The cubic lattice is filled with homopolyesters A and B at a blend ratio of 25/75 v/v, where 60% of the lattice sites are occupied by polymer segments. The initial chain length is set at $N_A = N_B = 19$, and consequently the numbers of homopolyester chains A and B are 938 and 2812, respectively. All the chains are arranged initially at randomly chosen positions with fully extended chain conformation. This initial structure is relaxed under athermal conditions through the bond diagonal method (BDM)[6], a kind of one-site bond fluctuation model, in a way of self- and mutual-avoiding walk on the lattice. In this method, to accommodate more chain conformations particularly for dense polymer system, the chain movement trial positions are prepared so as to satisfy the nearest-neighbor (*NN*) condition automatically where the bond length must be equal to 1 or $\sqrt{2}$ in two dimensions and 1, $\sqrt{2}$, or

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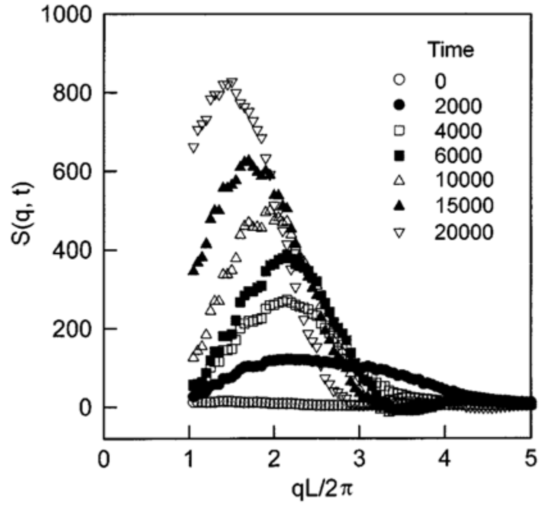

Figure 1. Time evolution of collective structure factor $S(q,\ t)$ during the phase separation with $E_{AB} = 0.1$.

$\sqrt{3}$ in three dimensions. If the moving segment is an end of a chain, all possible end rotations are equally considered. After the conformational state of polymer chains reaches an equilibrium, the ester interchange reactions between the same kind of segments (homo-ester-interchange) are implemented to prepare polyesters with the most probable molecular weight distribution (MWD). In this work, two kinds of ester interchange reactions such as end attack and bond flip corresponding alcoholysis (or acidolysis) and direct ester-ester interchange reaction, respectively, are performed on a homogeneous blend of immiscible polyesters, as suggested by Mansfield[7,8].

After each polyester with polydisperse MDW is prepared, phase separation is then induced by introducing the reduced pair interaction energy $E_{AB}(=\varepsilon_{AB}/k_BT$ where ε_{AB} is a pair interaction energy parameter between segments A and B, k_B is the Boltzmann constant, and T is temperature). During the phase separation, E_{AB} is set at 0.1. The phase-separated structures with different extent of phase separation are prepared by varying phase separation time from 2000, 4000, 6000 to 10000 MCS (Figure 1). In order to examine the effect of relative rates of phase separation and ester interchange reaction, and the repulsive pair interaction energy on their phase behaviors, the values of repulsive pair interaction energy (E_{AB}) between segments A and B are varied from 0.01, 0.05 to 0.1 and the trial ratio of phase separation to ester interchange reactions (P/E) is also varied from 5/1, 500/1, to 3000/1. The trial of phase separation, homo-ester-interchange or hetero-ester-interchange reaction is attempted with given values of E_{AB} and P/E for a segment randomly chosen. Homo- and hetero-ester-interchange reactions have the same probability of occurring only if the geometric condition is satisfied. As the time unit, a Monte Carlo step (MCS) is defined as one attempted trial per segment to move or react on the average.

To monitor the phase separation of immiscible polyester blends as a function of time, the time-dependent collective structure factors are calculated at a constant time interval and spherically averaged in the same way as described in the previous paper[3]. In order to trace the copolymerization by hetero-ester-interchange reaction, the degree of randomness (DR) is calculated by using the following relation[9]:

$$DR = PP_{AB} + PP_{BA} \tag{1}$$

where PP_{AB} is the probability of finding a B unit after an A unit and PP_{BA} the probability of finding an A unit after a B unit along a polymer chain. To enhance the statistics of results, three independent runs are performed for each case, and all the results are reported by averaging the data from the three independent runs.

Results and Discussion

In order to prepare various phase-separated structures with different extent of phase separation, the phase separation time was varied. Figure 1 shows the time evolution of structure factor $S(q,\ t)$ plotted against the scattering vector during the phase separation with $E_{AB} = 0.1$. As the phase separation proceeds, the structure factor shows a maximum and its value increases, while the peak position $q_{\max}$, where the maximum structure factor $S_{\max}$ is observed, shifts toward smaller q, reflecting the coarsening process in the late stage of phase separation. Initial structures with different extent of phase separation are prepared by varying phase separation time from 2000, 4000, 6000 to 10000 MCS.

The effects of rate ratio of phase separation to ester interchange reactions on the phase behavior in phase-separated immiscible polyester blends are investigated by monitoring time evolution of structure factor and DR with homogenization time. Figure 2 shows the time evolution of the collective structure factor during homogenization process of phase-separated structures with $P/E = 5/1$, 500/1, and 3000/1 at $E_{AB} = 0.1$. Here two initial structures with different extent of phase separation are prepared by varying phase separation time 4000 and 10000 MCS, and are used for further homogenization. The time evolution of the structure factor is strongly dependent on P/E, as can be seen in Figure 2. At $P/E = 5/1$, the $S_{\max}$ value decreases while the $q_{\max}$ value remains nearly unchanged with increasing MCS, indicating that the domain size does not significantly change during the homogenization process when ester interchange reactions readily occur. At $P/E = 500/1$, both the $S_{\max}$ value and the $q_{\max}$ value decrease with increasing MCS, indicating that the domain slowly grows during the homogenization process due to the higher phase separation ratio. At $P/E = 3000/1$, where the phase separation becomes more dominant, the $S_{\max}$ value first increases and eventually decreases while the $q_{\max}$ value continuously decreases with MCS.

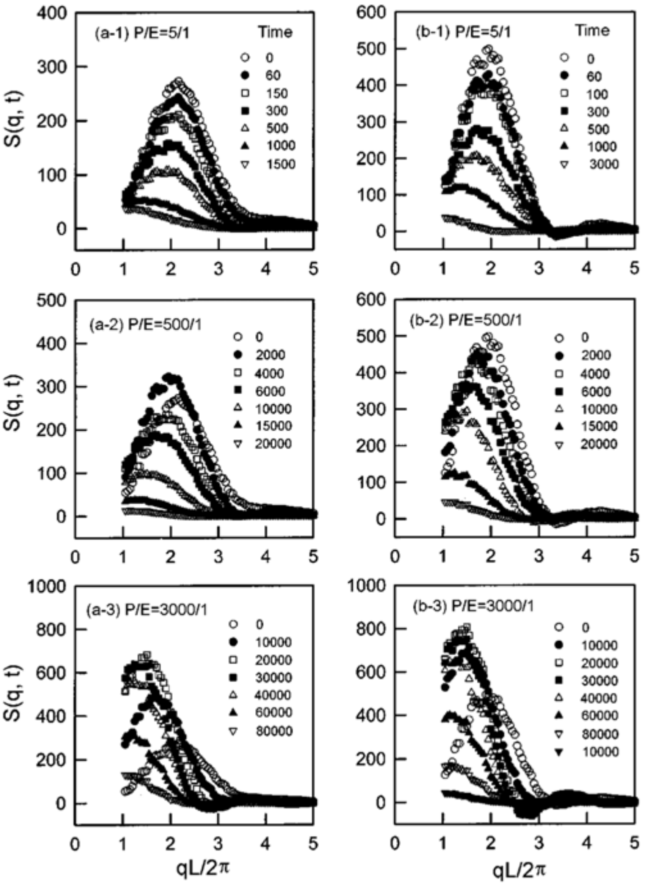

Figure 2. Time evolution of collective structure factor during the homogenization process of phase-separated structures taken after (a) MCS = 4000 and (b) MCS = 10000 from the result shown in Figure 1 with various *P/E*'s at $E_{AB} = 0.1$.

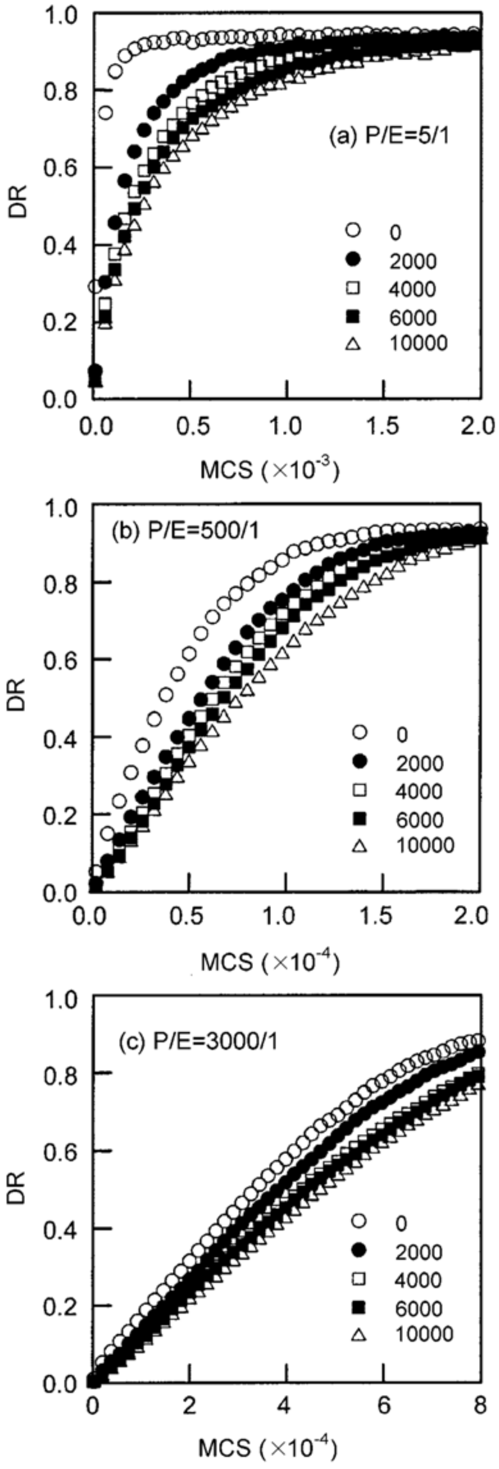

Figure 3. Changes of the degree of randomness during the homogenization process of phase-separated structures taken after MCS = 0, 2000, 4000, 6000, and 10000 from the result shown in Figure 1 with various *P/E*'s at $E_{AB} = 0.1$.

It is clear from the above results that the phase behaviors in phase-separated polyester blends are strongly dependent on the rate ratio of phase separation to ester interchange reactions. These results are in good accordance with experimental ones obtained in the immiscible blend of polycarbonate (PC)/poly(ethylene terephthalate) (PET) copolymer[2]. The rate ratio of phase separation to ester interchange reactions was dependent upon annealing temperature (T_a). At $T_a < 200^{\circ}C$, the global structure coarsens due to the dominance of phase separation over ester interchange reactions. At $200^{\circ}C < T_a < 220^{\circ}C$, ester interchange reactions start to dominate phase separation process. At $T_a > 220^{\circ}C$, the global structure melts due to the dominance of ester interchange reactions over phase separation. However, since these two processes are strongly coupled with each other and are differently dependent on the temperature[4], it is very difficult to systematically control the rate ratio of phase separation to ester interchange reactions. Moreover, these rates are largely affected by the presence of residual catalysts used in polymerization and can therefore be significantly modified by adding new catalysts[10-12].

In our previous study[3], the chain movement using the

BDM was attempted at every ester interchange reaction, which corresponds to *P/E* = 1/1. In this condition, the domain size was not changed during the homogenization process. The results obtained at *P/E* = 1/1 and 5/1 are in good accordance with experimental ones obtained in the homogenization process of PC/PET and PC/polyarylate blends, in which the domain size is almost independent of time and slightly increases only in the late stage[4]. This agreement indicates that these blends are readily homogenized due to the dominance of ester interchange reactions. Practically, most of studies on ester interchange reactions have been conducted at high temperature where ester interchange reactions can readily take place. Therefore, it can be concluded that these simulation conditions are very close to the real system.

Figure 3 shows the variations of DR with MCS at *P/E* = 5/1, 500/1 and 3000/1. Here, various phase-separated structures with different extent of phase separation are prepared by varying phase separation time from 0, 2000, 4000, 6000 and 10000 MCS and are used as initial structures for further homogenization. In the early stage, the DR increases by hetero-ester-interchange reactions at the interface between phases A and B. As expected, in cases of *P/E* = 5/1 and 500/1, the higher the extent of phase separation, the lower the increasing rate of the DR. This is probably due to the different probabilities of hetero-ester-interchange reactions depending upon the extent of phase separation. However, in the case of *P/E* = 3000/1, the change of DR with MCS shows nearly the same increase irrespective of initial structures, particularly the initial structures taken after phase separation times of 4000, 6000, and 10000, although they have different probabilities of hetero-ester-interchange reactions. As reveled by the time evolution of structure factor in Figure 2(a-3) and (b-3), the increasing rate of the DR is not influenced significantly by the extent of phase-separated structures due to the dominance of phase separation.

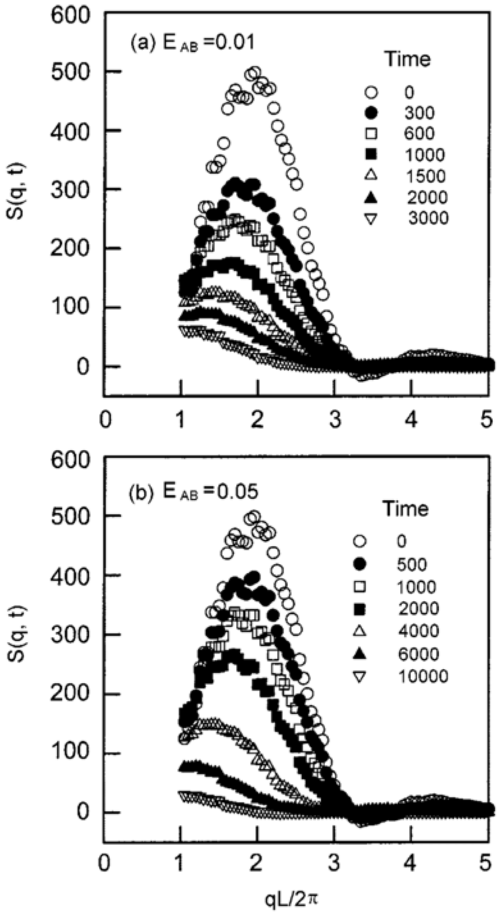

Figure 4. The effect of repulsive interaction energy on the time evolution of collective structure factor during the homogenization process in phase-separated structures taken after MCS=10000 from the result shown in Figure 1.

In our previous study[3], several values of E_{AB}(= 0.05, 0.1, 0.15 and 0.2) were used in order to investigate the effect of temperature on the phase behavior of phase-separated immiscible polyester blends. Although the magnitude of E_{AB} is an important factor affecting the homogenization process, the domain size was not significantly changed during the homogenization process for all E_{AB}'s due to the dominance of ester interchange reactions (*P/E* = 1/1). However, as shown in Figure 2, the homogenization process was largely influenced when the relative rate of phase separation at E_{AB} = 0.1 is increased. In this study, a simulation is performed under the condition where the relative rate of phase separation is high but the pair interaction is less repulsive. Figure 4 shows the time evolution of the collective structure factor of a phase-separated structure taken after 10000 MCS when *P/E* = 500/1 at E_{AB} = 0.01 and 0.05. It is found that the domain size is not significantly changed at a lower E_{AB}, although the phase separation is the dominant process. Consequently, it can be concluded that phase behaviors of phase-separated immiscible polyester blends are strongly dependent on the competition between phase separation and ester interchange reactions as well as the repulsive interaction energy.

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