Structure Development in Epoxy Resin Modified with Thermoplastic Polymer: A Monte Carlo Simulation Approach

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ABSTRACT: The time evolution of the collective structure factor $S(q,t)$ for epoxy resin cured in the mixture with thermoplastic polymer is simulated using a Monte Carlo technique. The simulation shows that the growth rate of the structure factor increases and then decreases, showing a maximum as the reactivity between an epoxide group and a cross-linking agent increases. It is also observed that the segmental interaction energy between the epoxy prepolymer and the thermoplastic polymer is an important controlling factor of the morphology of two-phase structure.

Introduction

Rubber-modified plastics have been the subject of continued interest in the field of polymer alloys.[1] Thermoset epoxy resins are generally known to be brittle. Hence, the utilization of epoxy as a neat resin is not practical in many industrial applications. The incorporation of a second phase of dispersed rubbery particles or thermoplastic polymers in epoxy resins can greatly increase their toughness without any significant loss of the other desirable engineering properties.[2] It has been realized that the extent of improvement critically depends upon the size of rubbery or thermoplastic particles, their dispersion, and interfacial adhesion between the dispersed phase and the matrix in the final cured system.

When an epoxy resin is modified with a thermoplastic polymer, initially, the mixture of an epoxy prepolymer and a thermoplastic polymer is homogeneous; but at a certain thermoset conversion the thermoplastic polymer begins to be phase separated from the epoxy-rich matrix. The morphology development continues until the thermoset matrix reaches a conversion close to the gel point or vitrifies (if the glass transition takes place before gelation). The final morphology of the cured system depends on the competition between the cross-linking reaction and phase decomposition during cross-linking. Thus the understanding of reaction kinetics and phase-separation dynamics is of crucial importance in order to achieve optimum phase structure. However, it seems that the systematic studies on this competition have not been established yet.

Since polymers are very complicated topological objects, computer simulations often are the best tool to obtain precise theoretical information on the proposed model or to estimate the qualitative decoupled informations. Especially, the Monte Carlo method is a powerful simulation technique to study nonequilibrium processes including a large-scale relaxation like the cure process of epoxy resins modified with thermoplastics.

One decade ago, Herrmann et al.[3] studied the problem concerning the irreversible gelation of radical polymerization as a result of a kinetic process. However, their approach has some serious drawbacks in that a polymerizable unit was allowed to move only if connected by at most one occupied bond to another unit. Thus any polymerizable unit connected by more than one bond cannot exchange sites with solvent molecules. Even though many lattice algorithms that obey Rouse dynamics are also given in the literature,[4-7] these algorithms have the disadvantage that the relaxation of branched structures cannot be achieved using these algorithms. However, Carmesin and Kremer[8] proposed a bond fluctuation algorithm and simulated the dynamics of a branched polymer with this dynamic algorithm.

In this study we applied this bond fluctuation algorithm for the simulation of structure development on a cubic lattice when an epoxy prepolymer is cured with a cross-linking agent in the presence of thermoplastic polymers. The effects of the reactivity between an epoxide group and a cross-linking agent and those of the interaction energy between a thermoplastic polymer and an epoxy prepolymer on the development of phase morphology were systematically studied in terms of the growth of a collective structure factor. In this paper, however, we are not concerned about percolation transition but mainly about the change of phase morphology.

Model and Simulation Technique

In this study we have adapted the two-dimensional bond fluctuation algorithm proposed by Carmesin and Kremer[8] for the dynamics of linear and/or corss-linked chains. Figure 1A gives an illustration of their model. A star polymer is placed on a square lattice with lattice constant 1. Each segment occupies four lattice sites of a unit cell, and each site can be a part of only one segment (self-avoiding walk (SAW) condition). This condition is necessary to account for the excluded volume of polymer chains. The bond length is required to be less than 4 and may have lengths in the range between a minimum length and a maximum. This fluctuation in the length of the bond vector can be considered to correspond to the fluctuation in the length of the physical "Kuhn segment", the latter being due to the fact that the sequence of chemical segments which form the Kuhn segment may take on many different conformations. Once a lattice site occupied by a segment is chosen at random, for instance, segment E in Figure 1A, it tries to randomly jump the distance of one lattice constant in one of four lattice directions. Here the segment labeled E moves downward. The move is accepted if the move complies with both the bond lengths restriction and the SAW condition.

We extended Carmesin-Kremer's two-dimensional method to a three-dimensional one on a simple cubic lattice (SC). Thus each segment of thermoplastic or epoxy prepolymer occupies eight sites of a unit cell. For convenience, we assume that an uncured epoxy prepolymer corresponds to one Kuhn segment and thus occupies eight sites of a SC lattice. A thermoplastic polymer is depicted

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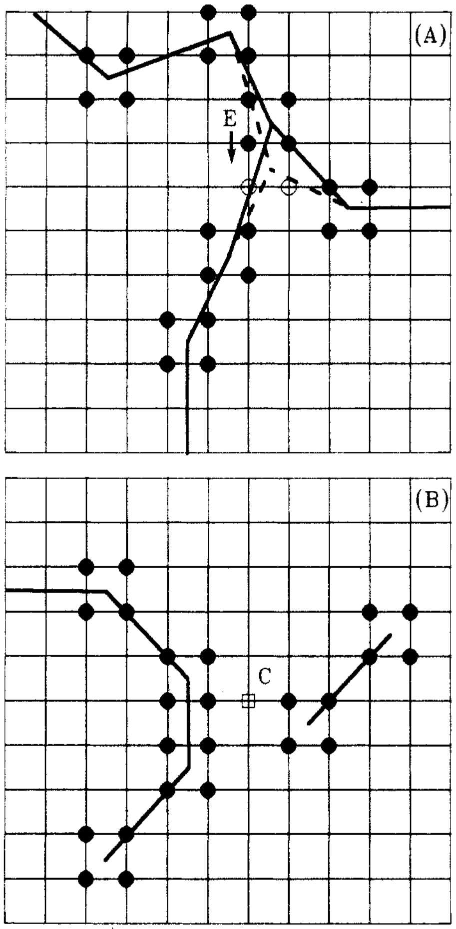

Figure 1. Schematic illustration of the two-dimensional Carmesin–Kremer bond fluctuation model[8] (A) and cross-linking reaction (B). Lattice sites taken by statistical segments of epoxy prepolymer and cross-linking agent are denoted by full dots and an empty square, respectively. The lattice sites of no notation indicate vacancies. In Figure 1A, the empty circle denotes a part of the statistical segments of epoxy prepolymer after the segment moves. The solid lines and dashed lines are denoted for the purpose of describing the linking between the statistical segments in succession before and after moving, respectively.

as one comprised of some effective units referred to the volume of an epoxy prepolymer upon a coarse-grained model for linear polymers. In this model the bond length l, i.e., the distance between two linked segments, is not fixed. The minimum value for any l is 2, and the maximum is 4.[9] In between, the bond length l can have values such as $5^{1/2}, 6^{1/2}, 8^{1/2}, 3, 10^{1/2}, 12^{1/2}, 13^{1/2}$, and $14^{1/2}$. A randomly selected segment may move the distance of one lattice constant in one of six SC lattice directions subjected to four conditions: the self-avoiding and mutally avoiding walk condition, the bond length restriction, the energetic transition criterion, and no bond crossing.

Since the condition of the upper limit of bond length will not exclude the possibility of bond crossing in the three-dimensional case, we further analyzed all possible cases in which an attempted move might cut through other bonds. If any of the bonds in the new set of bond vectors cuts through an existing bond during its formation, bond crossing occurs and the attempted move is aborted. Our program proceeds by calculating the area swept out by a bond in the projected move and then by systematically searching for any other bond that intersects that area.[10] If such an intersection is found, the move is rejected; otherwise, it is accepted. Finally, one more criterion, i.e., the Metropolis transition probability as an energetic criterion, is also used. In order to consider the effect of a repulsive interaction energy between an epoxy prepolymer segment and a thermoplastic polymer segment on the time evolution of structure development, the configurational energy change, ΔE, between before and after each move is appropriately taken into account with a transition probability $W = \min\{1, \exp(-\Delta E/kT)\}$. The unit w is defined as the magnitude of the repulsive interaction energy per one lattice site between epoxy prepolymer and thermoplastic polymer, irrespective of the distance between two units as long as the distance is below 3 lattice constants. Thus the interaction energies between the same molecules are assumed to be zero. The time unit, a Monte Carlo step (mcs), is defined as one attempted trial per segment on the average.

In this model a cross-linking agent occupies one lattice site (Figure 1B). Suppose that a randomly chosen cross-linking agent C comes into contact with a part of the epoxy prepolymer segment in one of the six nearest coordinates selected at random. The reaction probability, p, is assumed to be equal to the product of the reactivity, the number of unreacted functional groups of the chosen cross-linking agent, and the probability that the selected nearest site of the epoxy prepolymer should have an unreacted epoxide functional group; this probability corresponds to the number of unreacted epoxide groups in a selected nearest epoxy prepolymer divided by 8. If p exceeds a random number between 0 and 1, the reaction between the functional group of the cross-linking agent and the epoxide group is allowed. For simplicity, it is assumed that any intramolecular reaction in the same epoxy prepolymer cannot happen. No linkage between epoxy prepolymers is formed after one functional group in a cross-linking agent reacts, one linkage is formed after two functional groups are consumed, three linkages are formed after three functional groups react, and so on. If a randomly selected lattice site of six nearest coordinates around the cross-linking agent is an empty void, the chosen cross-linking agent moves into this empty void. However, if the chosen cross-linking agent is bound by at least one epoxy prepolymer, it moves into this empty void with the constraint that the chosen cross-linking agent could not deviate above the length of 3 lattice constants from all epoxy prepolymer segments linked to this cross-linking agent. This condition ensures that cross-linking agents are distributed homogeneously through the mixture.

In order to investigate the time evolution of the long-range ordering, we computed the collective structure factor of the system. The starting point of the description is a Flory–Huggins lattice model of the polymer mixture, where a local concentration variable Φ^j_P is equal to 1 if the lattice site j is taken by a thermoplastic polymer segment and otherwise zero and Φ^j_E is equal to 1 if it is taken by an epoxy prepolymer segment and otherwise zero. Then the time-dependent collective structure factor of an $L \times L \times L$ lattice, with L being equal to 45 and periodic boundary conditions applied, is given by eq 1,[11] where $\langle\ \rangle$ denotes

$$S(\vec{q},t) = \langle [\sum_{\vec{r}_j} \exp(i\vec{q}\cdot\vec{r}_j)(\Phi^j_P - \Phi^j_E - \langle \Phi^j_P - \Phi^j_E \rangle)]^2 \rangle / L^3 \tag{1}$$

a thermal statistical average. This quantity represents the Fourier transform of the pair-correlation function and was spherically averaged as eq 2, with $q = (2\pi/L)n$, where

$$S(q,t) = \sum_{\vec{q}} S(\vec{q},t) / \sum_{\vec{q}} 1 \tag{2}$$

$n = 1, 2, \ldots$ denotes that for a given n a spherical shell is taken as $n - {}^1/_2 \le qL/2\pi \le n + {}^1/_2$.

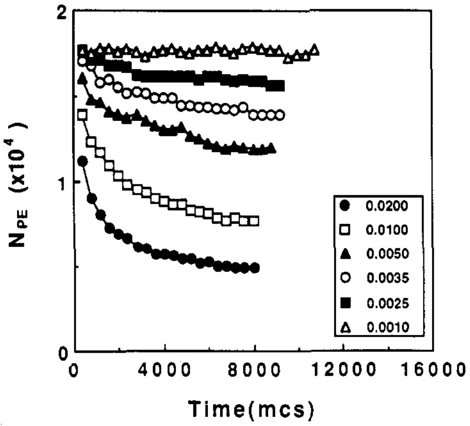

Figure 2. Plot of the number of hetero-pair contacts versus Monte Carlo step for various reduced segmental interaction energies as indicated in the legend.

Results and Discussion

Simulations for the cure process were performed for the system in which the number of statistical segments of a thermoplastic polymer is 5. A trifunctional cross-linking agent and bifunctional epoxy prepolymer are used in this simulation. In order to study the effects of the reactivity between an epoxide group and a cross-linking agent and those of the interaction energy between an epoxy prepolymer and a thermoplastic polymer on the phase morphology, a random mixture is initially generated, where the volume fractions of the epoxy prepolymer and thermoplastic polymer are 0.289 and 0.311, respectively.

Before the simulations for the cure process were performed, the critical point for this uncured mixture is found by applying an important sampling technique.[12] The Metropolis sampling technique is used to sample states with the correct thermodynamic distribution proportional to $\exp(-E/kT)$, where E is the energy of each configuration. The number of nearest contacts (N_{PE}) between the epoxy prepolymer and thermoplastic polymer, which represents the energy state of the system, is computed over the time interval from 0 to 11000 mcs. Time evolutions of this quantity are represented in Figure 2, showing that the number of hetero-pair contacts decreases with increasing the Monte Carlo step. The figure shows that 6000 mcs is sufficient time for energy of each configuration to balance with its entropy. In order to sample the states in equilibrium, the numbers of hetero-pair contacts of the sample beyond 6000 mcs are averaged. When the number of hetero-pair contacts is plotted against kT/w in Figure 3, it reveals that the number of hetero-pair contacts in equilibrium decreases as the repulsive interaction energy increases and/or the temperature decreases. At the phase transition the number of hetero-pair contacts in a strict sense changes abruptly in the thermodynamic limit, $L \to \infty$, whereas this quantity has a smooth variation with temperature for finite L as in our case. However, as seen in Figure 3, a somewhat abrupt change seems to occur below 333 in kT/w which corresponds to 0.003 in w/kT. Therefore, the critical point for this finite system seems to be a value below 333 in kT/w though the critical point cannot be determined precisely since this is defined conventionally as an inflection point.[12-14]

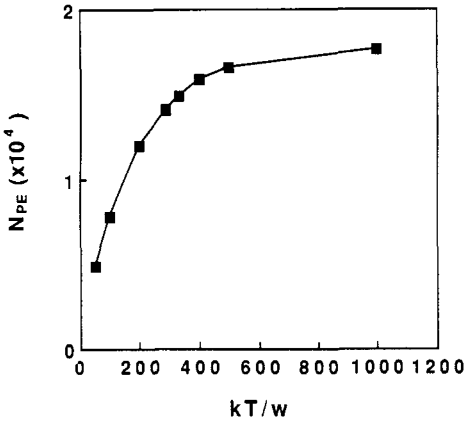

Figure 3. Transition curve showing the dependence of the number of hetero-pair contacts (N_{PE}) between the epoxy prepolymer and thermoplastic polymer on kT/w.

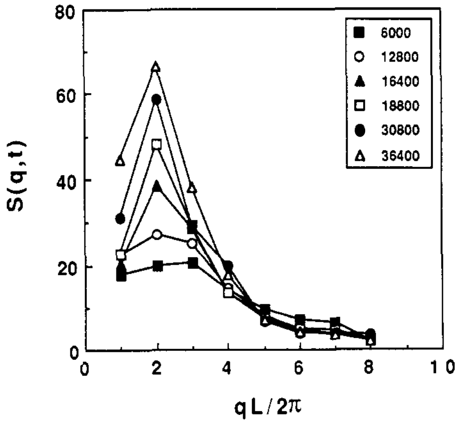

Figure 4. Typical time evolution of structure factor $S(q,t)$ plotted against shell number at various Monte Carlo steps as indicated in the legend. Monte Carlo step corresponds to the cure time of the mixture containing epoxy prepolymers. The simulation was carried out under the conditions that the reduced segmental interaction energy is 0.003 and the reactivity between an epoxide group and a curing agent is 0.0025. Since $S(q,t)$ is defined only for the discrete values $q = (2\pi/L)n$, the symbols are connected by straight lines in the figure for better visualization.

Since the initial mixture of epoxy prepolymers and thermoplastic polymers is structureless and homogeneous if the repulsive interactional energy between those is below the critical point, the simulations of the cure process were performed at values of the reduced segmental interaction energy w/kT below 0.003. Figure 4 shows some typical examples for the time evolution of the structure factor $S(q,t)$ plotted as a function of wave vector q. As a random mixture of thermoplastic polymer and epoxy prepolymers, which is initially structureless and homogeneous, is cured, the mixture starts to separate into an epoxy-rich phase and a thermoplastic-rich one. The cure process of the mixture of the epoxy resin and thermoplastic polymer can be explained in terms of the Flory–Huggins mixing free energy of the mixture (eq 3), where $\bar{V}_{1o}$ is the initial molar

$$\Delta G_M = (RT/\bar{V}_{1o})\left[\frac{\phi_1 \ln \phi_1}{n_1} + \frac{\phi_2 \ln \phi_2}{n_2} + \chi\phi_1\phi_2\right] \quad (3)$$

volume of the epoxy curing agent (component 1) and n_1 and n_2 are the ratios of the molar volumes of both components with respect to $\bar{V}_{1o}$. While n_2 remains constant during the curing process, n_1 increases with the epoxy conversion. As n_1 increases during the epoxy conversion, there is a decrease in the absolute value of the entropic contribution to the free energy of mixing. This leads to the demixing of the thermoplastic phase from a particular reaction extent. Thus the structure factor $S(q,t)$ increases with cure time. It is noteworthy that this growth is apparent at the second shell, which seems to be near a peak wave vector. Because of the wide spacing between the wave vectors, it is difficult to observe whether the peak wave vector shifts to the lower or not. The shift is apparently observable only when it has reached the lower

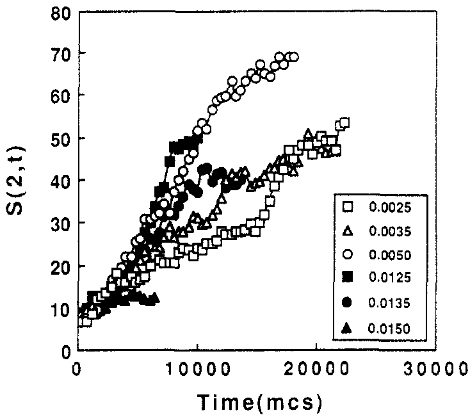

Figure 5. Growth of the structure factor at the second shell, $S(2,t)$, as a function of cure time in mcs at various reactivities as indicated in the legend. Data beyond 23 000 mcs are omitted for better visualization.

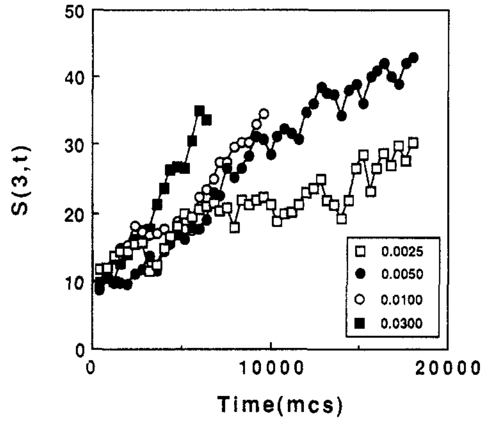

Figure 6. Growth of the structure factor at the third shell, $S(3,t)$, as a function of cure time in mcs at various reactivities as indicated in the legend.

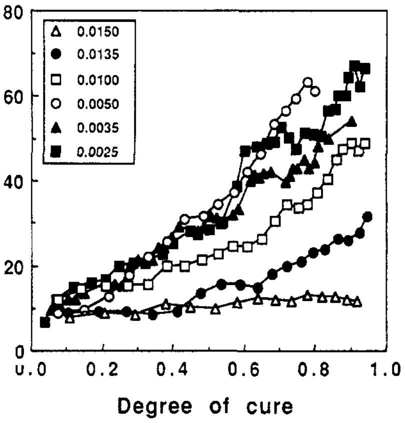

Figure 7. Plot of the structure factor at the second shell, $S(2,t)$, as a function of the degree of cure when the system is cured at various reactivities as indicated in the legend.

wave vector. This can be achieved by increasing the lattice size L since the spacing becomes narrower according to $q = (2\pi/L)n$. However, it would require an extraordinary amount of computer time.

Figure 5 is the structure factor at the second shell as a function of cure time. As epoxide groups are cross-linked by cross-linking agents, the molecular weight of the epoxy resin increases, reducing the degrees of freedom of the epoxy prepolymer. This means that the chance of the epoxy prepolymer's penetration into a thermoplastic-rich phase is aborted even though the other conditions except for the bond length criterion are satisfied. Phenomenologically, this explanation corresponds to the exclusion of thermoplastic polymers from the epoxy-rich phase. This is confirmed by the fact that the growth rate of the structure factor (the slope in Figure 5), especially at the second shell representing the long-range ordering, increases with the reactivity between an epoxide group and a cross-linking agent up to a value of 0.0125 as shown in Figure 5. This is caused by rapid phase demixing driven by the entropy loss due to the rapid increase in molecular weight of the epoxy resin as the cure proceeds. However, the initial growth rate of the structure factor at the second shell shows a maximum at the reactivity equal to 0.0125 and then decreases, as the reactivity increases further. This suggests that the structure development is suppressed at higher reactivity. In other words, the driving force for phase demixing due to the entropy effect increases, whereas the mobility of the system decreases, resulting in the retardation of phase demixing, as the molecular weight of the epoxy resin increases.

Even though the Cahn–Hilliard theory[15] was derived to describe the time dependence of the static structure factor after the system is quenched into the thermodynamically unstable region, the structure factor $S(q,t)$ follows an exponential growth as given by eq 4. The growth rate

$$S(q,t) = S(q,0)\exp(2R(q)\,t) \tag{4}$$

$R(q)$ is given as

$$R(q) = -Mq^2[(\partial^2\Delta G_M/\partial\phi^2)_0 + \kappa q^2] \tag{5}$$

where M is the mobility, $(\partial^2\Delta G_M/\partial\phi^2)_0$ is the second derivative of the free energy of mixing ΔG_M at the initial composition ϕ_0, and κ is a positive coefficient. For a certain wave vector q, the growth rate $R(q)$ is controlled by the mobility M and thermodynamic driving force, i.e., the second derivative of the mixing free energy, $(\partial^2\Delta G_M/\partial\phi^2)_0$. The magnitude of the slope of $S(q,t)$ vs cure time in Figure 5 (though the scale of the ordinate is not logarithmic) has the same meaning as the growth rate $R(q)$. As the reactivity between the epoxide group and cross-linking agent is higher, the thermodynamic driving force $(\partial^2\Delta G_M/\partial\phi^2)_0$ becomes greater than that in the case of curing with a curing agent of lower reactivity after the same cure time is elapsed. On the other hand, as the molecular weight increases, the mobility M decreases, resulting in the inversion of the growth rate $R(q)$.

Figure 6 is a plot of the structure factor at the third shell as a function of cure time. The scale in real space corresponding to the third shell is smaller than that corresponding to the second, and thus the structure factor at the third shell could be a good indicator for small-scale or short-time relaxation. As shown in Figure 6, the growth rate of the structure factor increases with increasing the reactivity in our simulation condition (reactivity below 0.03). This fact supports the suggestion that the increase in molecular weight of the epoxy resin is the origin of the driving force for the phase demixing. Comparing Figure 5 with Figure 6, it is realized that the phase demixing at the smaller scale corresponding to the third shell arises from the rapid increase in molecular weight due to high reactivity whereas the phase demixing at the larger scale corresponding to the second shell tends to cross over gradually from being driven to being resisted.

Figure 7 is a plot of the structure factor at the second shell as a function of the degree of cure, which is calculated in the manner that the number of reacted epoxide groups is counted. At the same degree of cure, the structure factor becomes larger as the reactivity decreases and then levels off in the range of reactivity below 0.005. This means that

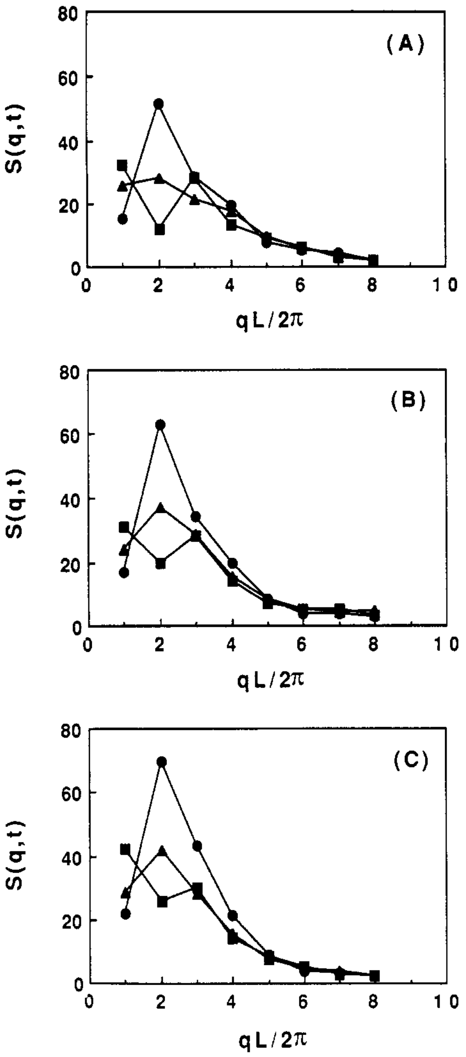

Figure 8. Profile of the structure factor for the system of various reduced segmental interaction energies. The symbols ●, ▲, and ■ denote the reduced segmental interaction energies 0.003 00, 0.002 75, and 0.002 50, respectively. The profiles of the systems cured for 10 000 (A), 14 000 (B), and 18 000 mcs (C) are plotted.

the systems which are cured with the cross-linking agent of reactivity below 0.005 have sufficient relaxation time for equilibration.

The effect of reactivity on the unrelaxated structure is as follows. At an equal degree of cure, the difference in the relative concentrations between the two phases decreases with increasing the reactivity. Although cross-linking induces the phase demixing due to the entropy loss, at the same time this also suppresses the mobility of both the epoxy prepolymers and thermoplastic polymers. As a result, the system has less time for relaxation of phase demixing as the reactivity increases, resulting in a similar difference in the relative concentration of two phases and the morphology of a smaller domain. However, there seems to be a critical reactivity. As can be seen in Figure 5, when the reactivity is higher than 0.015, the structure factor at the second shell does not increase with the degree of cure in our simulation conditions. Consequently, the two-phase structure cannot be observed at a large scale when a cross-linking agent of reactivity higher than 0.015 is used.

In order to investigate the effect of interaction energy between the epoxy prepolymer and thermoplastic polymer on the time evolution of the phase morphology, the structure factor $S(q,t)$ is computed for the system in which the reactivity between an epoxide group and a cross-linking agent is fixed at a value of 0.005. Figure 8 shows the profiles of structure factor versus wave vector at three different cure times, i.e., 10 000 (A), 14 000 (B), and 18 000 mcs (C). As considered previously, there is a decrease in the absolute value of the mixing free energy, ΔG_M, as the Flory–Huggins χ parameter increases. The degree of cure at the onset of phase separation (p_c) becomes lower as the χ parameter increases. Thus the time for phase separation to begin is shorter as conjectured in Figure 8. In our model, the Flory–Huggins χ parameter is directly proportional to the repulsive segmental interaction energy, w, although it cannot be simply estimated from the value of w. Recently there is a report[16] in which the relationship between the Flory–Huggins χ parameter and the segmental interaction energy is developed. It would be useful for future work if all users of this method would agree to this common version. Similiarly Figure 8 demonstrates that the maximum structure factor increases much faster with increasing the repulsive interaction energy. The thermodynamic driving force for phase demixing, $(\partial^2\Delta G_M/\partial\phi^2)_0$, is written as eq 6. As the χ parameter becomes larger, the thermodynamic driving force becomes more negative; thus, the growth rate $R(q)$ becomes larger (see eq 5). As seen in Figure 8, the structure factor grows much faster when the repulsive segmental interaction energy is larger. Particularly, the structure factor profile looks complicated at the lower reduced segmental interaction energy (0.0025). Note that the structure factor at the first shell results from the second reflection of the third shell. At the initial stage of curing the system has the structure composed of small domains, and at the later stage of curing the coarsening process begins to dominate as the cure time increases, resulting in the loss of periodicity.

$$(\partial^2\Delta G_M/\partial\phi^2)_0 = (RT/\bar{V}_{10})\left[\frac{1}{(1-\phi_0)z_1}+\frac{1}{\phi_0 z_2}-2\chi\right] \quad (6)$$

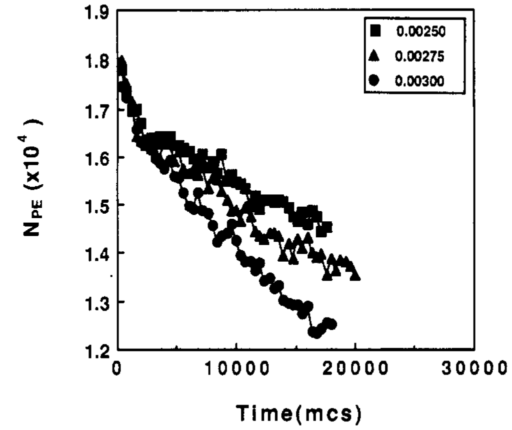

Figure 9. Time evolution of the number of hetero-pair contacts when the system is cured at various reduced segmental interaction energies as indicated in the legend.

Figure 9 shows that the number of hetero-pair contacts decreases as the cure time increases. The entropy loss of the system due to the increase in the molecular weight of the epoxy resin is compensated by lowering the number of the hetero-pair contacts in order for the system to be stabilized. Therefore, the number of hetero-pair contacts decreases as the cure time (the molecular weight of the epoxy prepolymer) increases. Figure 9 also shows that at a given cure time the number of hetero-pair contacts becomes smaller as the repulsive interaction energy becomes larger. The same cure time means that the molecular weight of the epoxy prepolymer is the same as long as the reactivity is constant as in our case, i.e., 0.005. Therefore, as the repulsive interaction energy becomes larger, the number of hetero-pair contacts decreases much faster. Consequently, the concentration difference between two developed phases becomes larger, and thus the maximum structure factor increases much faster.

Conclusions

Our analysis is similar in spirit to the experimental results of Meeks[17] and Rowe et al.[18] The former considered the effect of the reactivity between an epoxide group and a cross-linking agent on the phase morphology by varying the type of the cross-linking agent, and the latter investigated the effect of the difference in the solubility parameter between the rubber and the resin.

In this study we could simulate the phase demixing during the cross-linking of the epoxy prepolymer modified with thermoplastics using a Monte Carlo simulation. The effect of the reactivity between a cross-linking agent and an epoxy prepolymer on the phase structure was examined. As the reactivity increases, the rate of phase separation increases up to a critical value of reactivity and then decreases due to the loss of chain mobility. In other words, as the reactivity increases, the loss of entropy competes with the loss of chain mobility. It is also observed that the rate of phase separation increases with increasing the repulsive segmental interaction energy between an epoxy prepolymer and a thermoplastic polymer and thus the concentration difference between two phases increases much faster.

The numerical method in our paper uses a 3D version of the bond fluctuation method, in which one has to check for bond crossing. Recently there have appeared several papers[16,18–21] describing modifications which eliminate these checks and save computer time. It would be useful for future work if all users of the method would agree to one common version.

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