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Kinetic effect on the phase separation mechanism of a blend at different cure rates

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Introduction

In our previous papers1–5), a novel synthesized polyetherimide was used to toughen epoxy resin and good toughness was obtained considering the fracture energy. The formation of a thermoplastics continuous phase in the blend contributes to the good toughness, which is different from that of rubber modified epoxy resin. When the epoxy resin is modified with polyetherimide, the mixture is homogeneous at the initial stage, but the polyetherimide begins to separate from the epoxy-rich matrix after a period of cure reaction. The effects of the curing rate and the molecular weight of PEI on the structure formation were observed, and at the same time the process of morphology formation was traced by using time-resolved light scattering (TRLS) and scanning electron microscopy (SEM). It shows that in the system of epoxy resin modified with polyetherimide the phase separation takes place in accordance with the spinodal decomposition mechanism. It is in the control of thermodynamics of the system that cured samples display different morphologies such as dispersed particles of PEI, the co-continuous or the phase-inverted structure. At the same time, the kinetics affect the dimension of the phase structure. However, how these competitive effects between thermodynamics and kinetics works on the phase separation is not clear.

In recent years, polymerization-induced phase separation in thermostet-thermoplastic blends has raised much attention, because of the unusual equilibrium and nonequilibrium pattern formations6–10). Compared with the thermal induced phase separation, there are little studies done on the problem of phase separation induced by a certain reaction. In the polyetherimide modified system, two nonequilibrium phenomena – epoxy network formation and heterogenization (phase separation) – strongly affect the pattern formation. Jo et al. have applied a Monte Carlo simulation to study the effect of the reactivity on the phase separation behavior in an epoxy resin modified with a thermoplastic polymer11). In their conclusion, even though the phase separation behavior near the critical composition of the mixture shows the spinodal decomposition irrespective of the cure rate, the phase separation mechanism at the off-critical composition is changed with the cure rate. Furukawa has proposed the so-called nucleation-assisted spinodal decomposition mechanism12). The reaction first induces the nucleation and then pushes the reacted blends into the spinodal region, where the concentration fluctuation occurs around...
the stable nuclei. However, the computed results do not completely agree with the experimental data. Tran-Cong's and Harada's work shows that the elasticity effects need to be taken into account in a Cahn-Hilliard model for reacting blends\(^{13}\). In the system consisting of carboxyl terminated polybutadiene acrylonitrile/epoxy/methylene dianiline, Kyn and Lee\(^{15}\) predicted the “nucleation initiated spinodal decomposition” mechanism where the initial reductions of the length scale are triggered by nucleation. The different hypothesis is based on experimental results. So the understanding of the governing mechanism of reaction-induced phase separation is of great importance in controlling the pattern formation.

In the present paper, cross-link reaction induced phase separation has been investigated for a mixture of bisphenol-A diglycidyl ether (BADGB) epoxy/polyetherimide/4,4'-diaminodiphenyl sulfone (DDS). With the changes of cure temperature and the amount of cure agent, the reacted blends phase separation take place at different cure rates. The process of phase separation is traced by time-resolved light scattering (TRLS) and the final morphology is observed by scanning electron microscopy (SEM). The early stage of phase separation is analyzed using Cahn’s linearized theory, while the scaling postulate is tested in the late stage. The effect of the competition between thermodynamics and kinetics on the phase separation mechanism is discussed.

**Experimental part**

The epoxy oligomer used in this study was Dow DER 331 which has number-average relative molecular weight \(M_n\) of 380. The phenyl-terminated polyetherimide (PEI) was synthesized in our laboratory\(^1\), which had the inherent viscosity of 0.61dL/g. The cure agent 4,4'-diaminodiphenyl sulfone (DDS) (Shanghai Third Reagent Factory) was used without further purification.

An epoxy blend containing 25 phr of PEI was prepared by dissolving the PEI in DER 331 at 150°C. The mixture was cooled down to 130°C until a homogeneous, clear solution was obtained and an amount of cure agent was added while the mixture was stirred. After the cure agent was dissolved, a drop of the mixture was pressed between two pieces of glass to form a thin film. The film was completely transparent, suggesting miscibility at least at the length scale of the wavelength of light. The remaining blend for the use in DSC and in SEM was cooled rapidly to room temperature to avoid further curing reaction. The blend was designated as TaDb, where Ta stood for the cure temperature (a°C), Db for b phr of cure agent DDS.

A Setaram Differential Scanning Calorimetry (DSC92) instrument was used for the isothermal cure experiments and data analysis. The detailed analysis method was described elsewhere\(^1\).

The phase separation process during curing reaction was observed at real time and in situ on the self-made time resolved light scattering (TRLS) with a controllable hot chamber. The TRLS technique is described elsewhere\(^14\). The change of the light scattering profiles was recorded at appropriate time intervals during isothermal curing.

The morphology of the cured resins was observed under a Scanning Electron Microscope (SEM) (HITACHI S-520). The samples were fractured in liquid nitrogen.

**Results and discussion**

**Cure rate**

In this system, two ways were used to change the cure rates. One was that curing the system at different temperatures; the other, changing the amount of cure agent. The different cure temperatures were 140, 150, 160 and 170°C, respectively. The amount of cure agent altered from 20, 23 to 31 phr. All the plots of the degree of cure via curing time show the sigmoidal shapes, which are characteristic of the common autocatalysis mechanism (Fig. 1). The cure rate of different cure temperatures via time is shown in Fig. 2. It is obvious that the rate is increasing with increasing cure temperature. At the same time, the occurrence time of the maximum rate is hastened with the increase of the cure temperature. Fig. 3 depicts the cure rate via time of different amounts of cure agent blends. Naturally the cure rate is higher in the blend.

![Fig. 1. The cure degree at different cure temperatures via curing time](image1)

![Fig. 2. The cure rate of different cure temperatures via time](image2)
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Fig. 3. The cure rate via time of different amounts of cure agent blends

Fig. 4. \( q_m \) versus time for 31phrDDS composition at 140°C, 150°C, 160°C and 170°C

Phase separation

The phase separation processes of blends are traced by time-resolved light scattering. The typical time evolutions of scattered intensity versus scattering wave number \( q \) in different blends were obtained during cure reaction, where \( q \) is defined as \( q = (4 \pi / \lambda) \sin \theta / 2 \); \( \theta \) and \( \lambda \) are scattering angle and wavelength of light measured in the medium, respectively. In the blends T150D31 and T160D31, the scattering maximum \( (q_m) \) emerges first around a large angle, then moves to a shorter scattering angle which coincides with our understanding. However, with the others two scattering maxima \( (q_m) \) appear first and then develop to one scattering maximum or a broad peak. These phenomena are special and mean a complicated phase separation process.

Fig. 4 shows the plot of \( q_m \) versus time for 31phr DDS composition at various temperatures. The average length scale initially decreases and then the domains coarsen at a later stage at T170D31. This peculiar phenomenon has been explained in terms of a “domain insertion model” which suggests that newer domains are created in the interdomain regions of the preformed domains, leading to the shorter interdomain distances. Though the curing rate with more cure agent. However, the occurrence time of the maximum rate is not consistent with the change of the amount of cure agent. The works of many researchers have shown that there are more than one type of kinetic mechanism existing in an epoxy curing system, e.g., the mechanism in which the hydroxyl group in situ formed as a result of the reaction between the primary amine and epoxide group catalyzes the reaction between the secondary amine and an epoxide. The ratio of the rate constants (corresponding to primary amine and secondary amine reaction, respectively) will change with decreasing amount of cure agent. Moreover, this ratio is indeed supposed to have a strong effect on the cure process. So the occurrence time of maximum rate of the blend T150D23 is shorter than the other blends. Below we also display this effect on the phase separation process.

at 170°C is much faster than that at 160°C and 150°C in the early stage of phase separation and the reaction at higher temperatures moves more quickly from the metastable region to the unstable region. Phase separation at higher temperatures are also faster. If phase separation is faster than the cure reaction, phase decomposition may occur in the metastable region and the initial reduction of the length scale may be observed. This behavior accords with that of “nucleation initiated spinodal decomposition” mechanism suggested by Kyu and Lee. The same phenomena also occur in a short time of initial stage in the T160D31 blend. The two scattering maxima were obtained through separating peaks from the broad peaks in the plot of scattered intensity via scattering wave number \( (q_m) \) at 140°C (Fig. 5). But the initial reduction of the length scale is not observed and the domains coarsen at a later stage leading to a broad peak. In Fig. 6 with \( q_m \) vs curing time, two peaks increase in the average length scale with curing time. It seems that they all go through the spinodal decomposition mechanism.
However, the information given by T150D23 and T150D20 blends is even more difficult to comprehend. The maximum scattering appears around a small angle accompanied with another one developing in the large angle. It is very typical in the blend T150D23 depicted in Fig. 7. After 46 min of induction time, the scattering peak (peak 1) appears in $q_m = 1.5 \, \text{nm}^{-1}$ and moves to a short scattering angle with increasing scattering intensity. A new scattering peak (peak 2) is observed around $q_m = 2.5 \, \text{nm}^{-1}$ after about 50 min of curing. At 56 min of curing the peak 1 begins to decrease in scattering intensity while peak 2 increases. At last two peaks combine to form a broad peak from 0.30 to 3.5 $\, \text{nm}^{-1}$.

**Morphology**

The morphology of the cured blends is examined by SEM. Phase inverted structure displays in every blend with the epoxy particles dispersed in PEI-rich matrix. However, there are some difference between the blends. The blends T150D31, T160D31 and T170D31 (Fig. 8) show all full ball particles with surrounded white PEI threads. In the blends with a lower amount of cure agent or lower cure temperature the contrast between the two separated phases is not so clear and the sizes of particles vary greatly. This is because both the cure reaction and the phase separation process influence the final morphology.

**Discussion**

The components of PEI and epoxy are identical in our research systems and just cure rates are varied. So these systems are located on one line having the same volume fraction in the phase diagram. The phase diagram of PEI and epoxy was once obtained from the cloud point phase diagram without a curing agent. It is an upper critical solution temperature (UCST) curve with the critical volume fraction around 0.13\(^{18}\). In the case of the 25 phr PEI composition, the polymerization temperatures are located on the right side of the UCST peak. When the cure reaction occurs, the phase diagram will shift to higher temperature and to the right as epoxy molecular weight increases. The cure systems will move to meta-stable and unstable regions one after the other. In the blend T170D31 with the highest cure rate phase separa-
Study on the phase separation of a polyetherimide-modified epoxy resin. In the plot of $q_m$ vs cure time (Fig. 4a), the T170D31 blend shows the obvious NG (nuclear growth) character at an early stage. Then as the cure system moves to the unstable region, the blend goes through the SD mechanism. In the same way, the blend T160D31 also displays the NG character at an early stage but it is not as clear as that of the blend T170D31. The NG phase separation process can not be detected in the blend T150D31 though it also passes through the metastable region. This can be explained by stating that the components at the different cure temperatures have different diffusivity. The diffusivity of the components decreases with decreasing cure temperatures, which are determined from the Cahn’s plot, $R(q)/q^2$ vs $q^2$, listed in Tab. 1. Although the diffusivity is obtained from the early stage of SD mechanism, it is the character of the behavior of the components in the cure system at cure temperature. The blend T170D31 has such a high diffusivity that the phase separation is faster than the cure reaction. So the phase separation process in metastable region is detected in blend T170D31. As the diffusivity decreases with the cure temperature, the NG phase separation becomes difficult to be observed in blends T160D31 and T150D31. However, when the cure temperature decreases further than 140°C, the blend T140D31 only shows a broad peak on the plot of time evolution of scattering profiles (Fig. 8). The lower cure reaction leads to the slow evolution of the phase diagram and postponing the blend in the metastable region. The fact that no maximum is observed in the scattering profile and a great size range of epoxy-rich particles in the final morphology indicates the NG mechanism process. Although the blend will finally shift to the unstable region, the lower cure temperature and the vitrification of PEI-rich phases fix the size of the particles.

The change of the amount of cure agent only varies the cure rate but has no influence on the diffusion of the components. In other words, the decrease of the cure agent slows down the time evolution of the phase diagrams. For the blend T150D20 this means that in the early stage of phase separation it takes more time as in the metastable

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<th>Tab. 1. Apparent mutual diffusion coefficient of blends</th>
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<td>$D_{app} \times 10^4$ (cm$^2$/s)</td>
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<td>Time, in min</td>
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region and that causes a broad peak to appear in the plot of time evolution at the initial stage. When it shifts to the unstable region, the cure reaction will suppress the concentration fluctuations at large and short wavelengths except for the growth on the intermediate wavelength. Blend T150D23 shows special time evolution of the scattering profile in Fig. 7. There seems a process of phase dissipation existing in the intermediate stage of phase separation. This may be caused by the special cure behavior taking into account the specialty at the cure rate plot at 150°C. Keeping the same cure temperature the maximum cure rate occurs early compared to the other blends. The blend may stay in the metastable region for a shorter time than the blend T150D20 and a long time in the unstable region. While the upper critical solution temperature curve shifts to high temperature the phase separation still goes on in the unstable region. As the quench depth increases, the concentration fluctuation will occur around intermediate wavelength leading to the disappearance of the large particles in the blend. The SEM graphs may support the assumption (Fig. 9).

Fig. 9. Scanning electron micrographs of the cured blend T150D23 at different times: a) t = 55 min, b) t = 85 min


