

Structure Development via Reaction-Induced Phase Separation in Tetrafunctional Epoxy/Polysulfone Blends

TAESUNG YOON,¹ BONG SUP KIM,² DOO SUNG LEE³

¹Department of Textile Engineering, Sung Kyun Kwan University, Suwon 440-746, Korea

²Sunkyong Industries Ltd., R&D Center, Suwon 440-745, Korea

³Department of Polymer Science and Engineering, Sung Kyun Kwan University, Suwon 440-746, Korea

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ABSTRACT: For the cure process of tetrafunctional epoxy resin/polysulfone (EP/PSF) blends, we investigated the effect of cure temperature and blend composition on the phase separation behavior by light scattering and the structure development during cure by an optical microscope. The EP/PSF blend without the curing agent was shown to exhibit an LCST-type phase behavior (LCST = 241°C). At the early stage of curing, the EP/PSF blend was homogeneous at the cure temperature. As the cure reaction proceeded, the blend was thrust into a two-phase regime by the LCST depression caused by the increase in a molecular weight of the epoxy-rich phase, and the phase separation took place via a spinodal decomposition (SD) or nucleation and growth (NG) mode, depending on the blend composition and the cure temperature. When cured isothermally at 220°C, the blend exhibited a sea-island morphology formed via the NG mode below 5 wt % PSF content, while the SD mode prevailed above 20 wt % PSF content. At the intermediate composition range, combined morphology with both sea-island and cocontinuous structure was observed. On the other hand, by lowering the cure temperature and/or increasing the content of PSF component, a two-phase structure with a shorter periodic distance was obtained. It seems that the rate of the phase separation is considerable reduced, while that of the cure reaction is not as much. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **66**: 2233–2242, 1997

Key words: epoxy/polysulfone blend; reaction-induced phase separation; morphology; phase diagram

INTRODUCTION

Curing of epoxy resin involves chain extension, branching, and crosslinking. The chemical reac-

tion usually causes a change in the physical state, from a viscous liquid to a gel and then to a vitrified material. On the other hand, when thermoplastic polymers [e.g., poly(ether sulfone), polycarbonate, and poly(ether imide)] are incorporated to improve the toughness of epoxy resin,^{1–9} the cure process becomes much more complicated. In an epoxy/thermoplastic blend, starting from an homogeneous mixture, the system is thrust into a two-phase regime by the increase in molecular

Correspondence to: D. S. Lee.

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weight of the epoxy at the early stage of curing, and phase separation takes place to provide a phase-separated structure. The structure is fixed by gelation or vitrification of the epoxy-rich phase at the late stage of curing. Thus, the cure process of the epoxy/thermoplastic system involves various transformations: the sol-gel transition, the phase separation from single-phase to two-phase, and the vitrification by the increase of the glass transition temperature with an increase of the molecular weight of the epoxy-rich phase. Here, the phase separation can be progressed via two kinds of mechanism: the nucleation and growth (NG) mode, and the spinodal decomposition (SD) mode.¹⁰

Inoue et al.^{5,6,11} have reported the structure development via reaction-induced phase separation in epoxy/poly(ether sulfone) and epoxy/liquid rubber blends. They stated that the NG mode is not expected to take place in any case, mainly because of the fact that nucleation is recognized to be a very slow process and the sea-island morphology as well as cocontinuous morphology is developed by only the SD mode during cure. They explained for the structure development via the SD or NG mode during cure it is governed by two competitive progresses of the phase separation and the chemical reaction.

Lee et al.^{12,13} have reported about the curing, miscibility, and phase separation behavior of the tetrafunctional epoxy/polysulfone blend via thermal analysis, the rheological measurement, and the light-scattering method. These epoxy and polysulfones have very similar structures and their T_g s are very high due to containing aromatic rings.

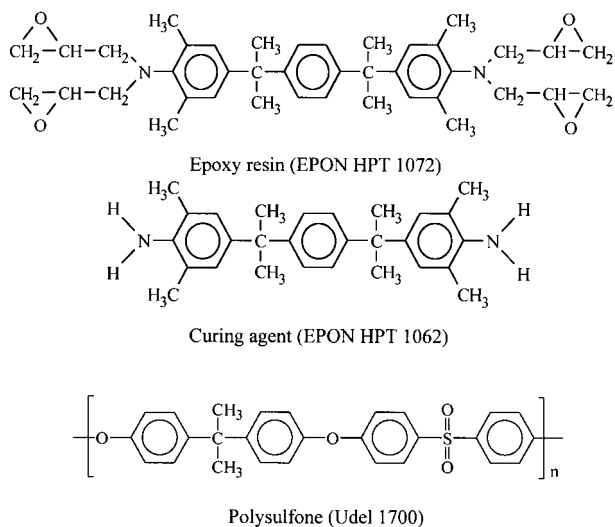
In this study, we deal with a tetrafunctional epoxy/polysulfone blend and investigate the effect of cure temperature and blend composition on the structure development during cure by an optical microscope and light scattering.

EXPERIMENTAL

Materials

A tetrafunctional epoxy resin, *N,N,N',N'*-tetraglycidyl- α,α' -bis(4-amino phenyl)-*p*-diisopropylbenzene, was supplied by Shell Chemical Co. (EPON HPT 1072). The curing agent was α,α' -bis(3,5-aminophenyl)-*p*-diisopropyl-

benzene (EPON HPT 1062). Polysulfone (PSF) (Amoco Co., Udel 1700, $M_w = 30.0 \times 10^3$) was used as a modifier. The structure form is shown below:



Sample Preparation

The epoxy and PSF were dissolved at 10 wt % of the total polymer in dichloromethane. The solution was cast onto a cover glass (for the microscopy). The cast films were dried under a vacuum

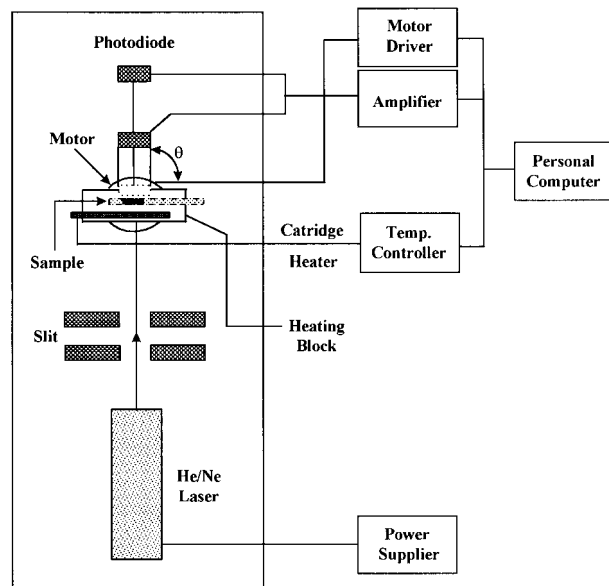


Figure 1 Light-scattering apparatus.

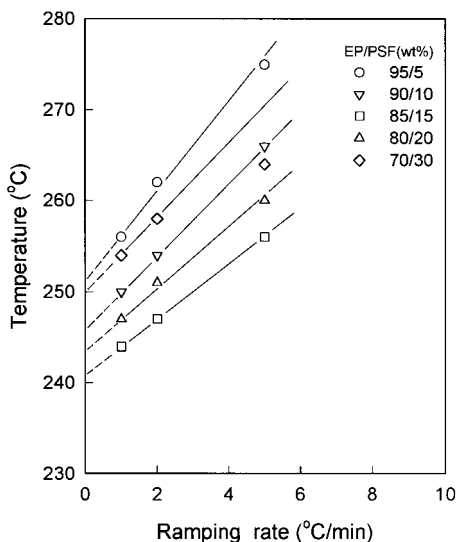


Figure 2 Cloud point as a function ramping rate for the EP/PSF blends.

of 10^{-4} mmHg for 20 h to remove a residual solvent.

Phase Diagram

The cast film of binary mixture onto the cover glass was inserted into a heating stage programmed to provide a linear rise in temperature at three different rates: 1, 2, and 5°C/min. During the linear tem-

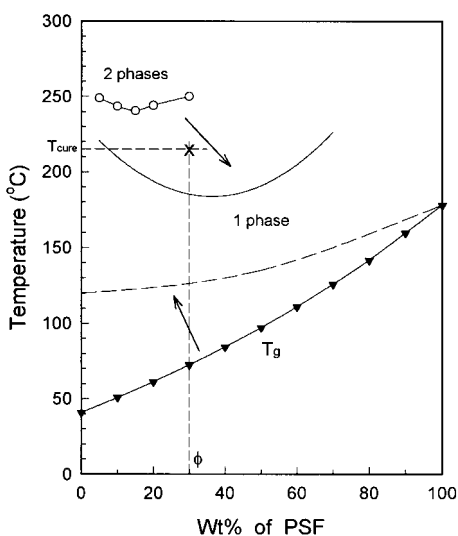


Figure 3 Phase diagram of a tetrafunctional epoxy/PSF blend.

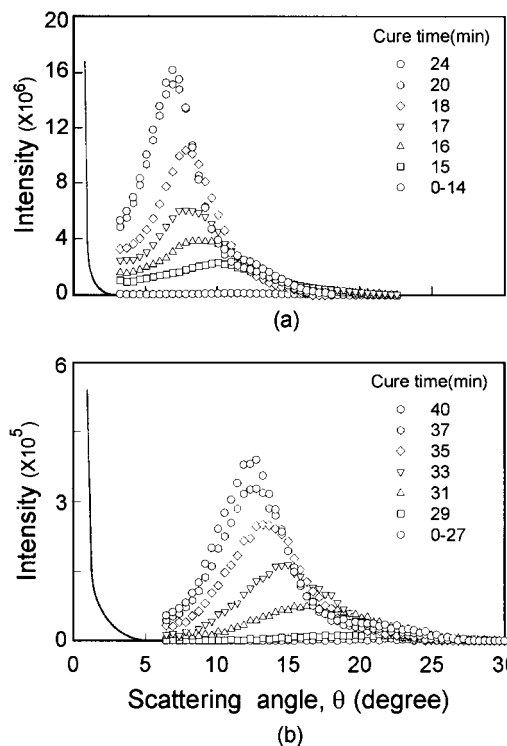


Figure 4 Change of the light scattering profiles of EP/PSF (70/30 wt %) during cure: (a) 230°C; (b) 210°C.

perature rise, we observed the onset of phase separation by the light-scattering apparatus. Based on this observation, we obtained the phase diagram of the epoxy/PSF mixture.

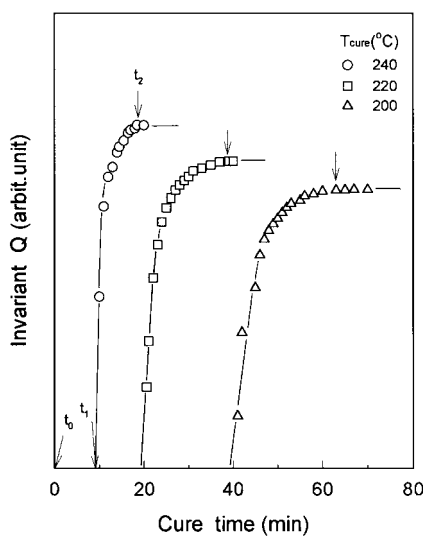


Figure 5 Time variation of invariant *Q* of EP/PSF (70/30 wt %) during cure at various cure temperatures.

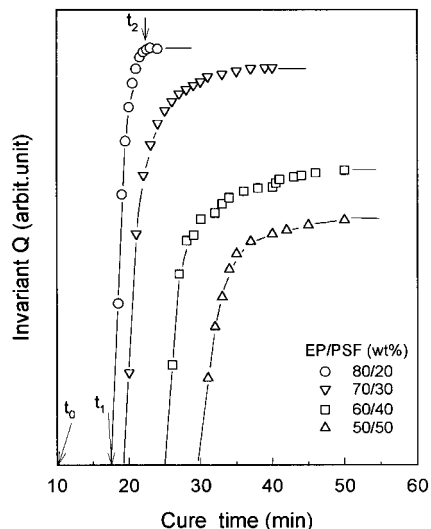


Figure 6 Time variation of invariant Q of various EP/PSF blend compositions during cure at 220°C.

Real-Time Light-Scattering and Microscope Observations

The ternary mixture (epoxy/curing agent/PSF, below EP/PSF) on the cover glass was annealed in the hot chamber set horizontally on the light scattering stage, as shown in Figure 1. Radiation of wavelength 632.8 nm from a He-Ne laser was applied vertically to the film. The intensity of scattered light from the film was measured under an optical alignment with parallel polarization. The angular distribution of scattered light intensity was detected by a one-dimensional photometer. The scattering profiles in a time of 1 min were recorded at appropriate intervals during isothermal annealing (curing) and were stored in a computer for further analysis. We also observed the structure development during cure by optical microscope (Nikon Co. model optiphot-2) with a VTR camera.

RESULTS AND DISCUSSIONS

The solution-cast film of the binary mixture of epoxy (w/o curing agent) and PSF was transparent and homogeneous under the optical microscope. During the linear temperature rise in the binary mixture, the onset of phase separation, T_s (spinodal temperature), was observed under the light-scattering apparatus. From the plot of the

T_s versus the heating rate, we obtained an intercept of T_s at which the heating rate is zero (Fig. 2).⁶ The intercept temperature may correspond to the binodal temperature, indicating lower critical solution temperature (LCST)-type phase behavior (LCST = 241°C). Figure 3 shows the phase diagram of epoxy/PSF blends and also shows the T_g curve, estimated by the Fox equation using the DSC data of epoxy and PSF.

On the basis of current understanding of polymer-polymer miscibility, the LCST in Figure 3 is expected to decrease, and the two-phase regime would prevail in the phase diagram as the molecular weight of epoxy increases with curing. The T_g of the mixture would be elevated when the molecular weight increases. These situations are demonstrated schematically in Figure 3. Figure 3 implies that the mixture of composition is initially at a single-phase regime at T_{cure} ; however, the system will be thrust into a two-phase regime as the curing reaction proceeds.

Figure 4 shows the change in the light-scattering profile of EP/PSF (70/30 wt %) blend during cure at 230°C (a) and 210°C (b). The epoxy/PSF

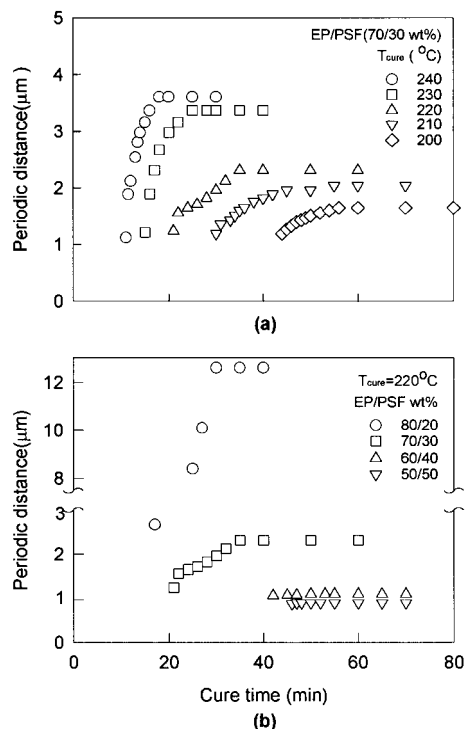


Figure 7 Time variation of periodic distance Λ_m during cure with varying temperatures and blend compositions.

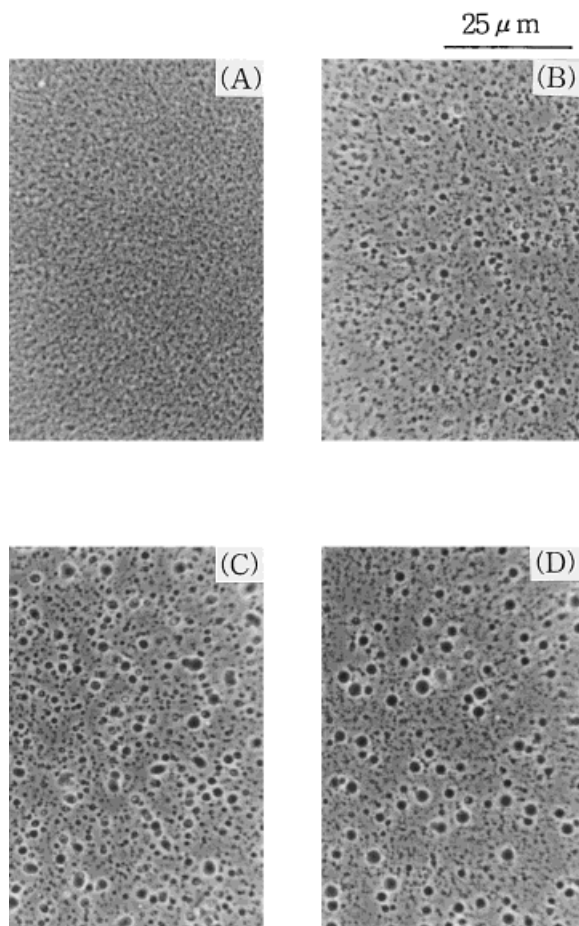


Figure 8 Morphological development of EP/PSF (95/5 wt. %) during cure at 220°C. Scale bar: 25 μm ; (A) 13 min; (B) 15 min; (C) 17 min; (D) 20 min.

mixture loaded by the curing agent was also a single-phase system at the two-cure temperatures, and no appreciable light scattering was detected from the mixture in the early stages of curing.¹³ After a time lag, the scattering profile appeared, as shown in Figure 4. As can be seen in the figure, the scattered intensity increases with cure time and the scattered angle at the maximum scattered intensity shifts to a smaller angle simultaneously. To easily understand the change in the scattering profile with cure time, it is convenient to employ the integrated scattering intensity, i.e., the invariant Q defined by

$$Q = \int I(q)q^2 dq$$

where q is the scattering vector, $q = (4\pi/\lambda)\sin(\theta_m/2)$, and $I(q)$ is the intensity of the scattered

light at q . Because the invariant Q from an optically isotropic system with concentration fluctuation is ascribed to the mean-square concentration fluctuation,¹³ it is more appropriate and a more sensitive quantity for the degree of phase separation than the profile itself. The Q values with varying cure temperatures are plotted in Figure 5. From the plot, one can determine the onset time of phase separation, t_1 , and the time at which phase separation ends, t_2 . All of cure conditions, the Q shows zero at the early stage of curing (t_0) and after an induction period, the Q starts (t_1) to increase with cure time and eventually levels off (t_2). The lower the cure temperature, the longer the time of t_1 and t_2 and the smaller the slope from t_1 to t_2 . Here, the slope means the growth rate of the concentration fluctuation. The time variation of Q of the various EP/PSF blend compositions during a cure at 220°C is also shown in

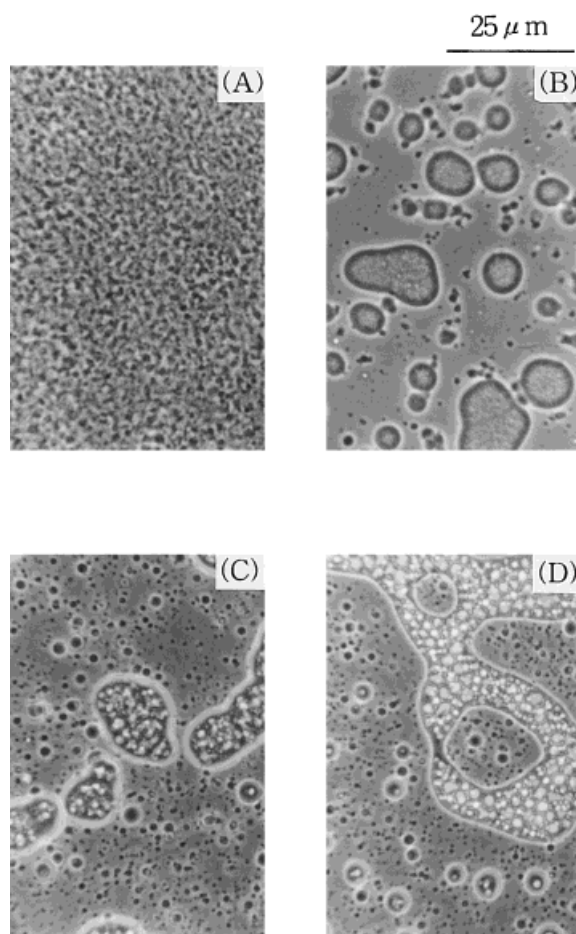


Figure 9 Morphological development of EP/PSF (90/10 wt %) during cure at 220°C. Scale bar: 25 μm ; (A) 13 min; (B) 15 min; (C) 17 min; (D) 20 min.

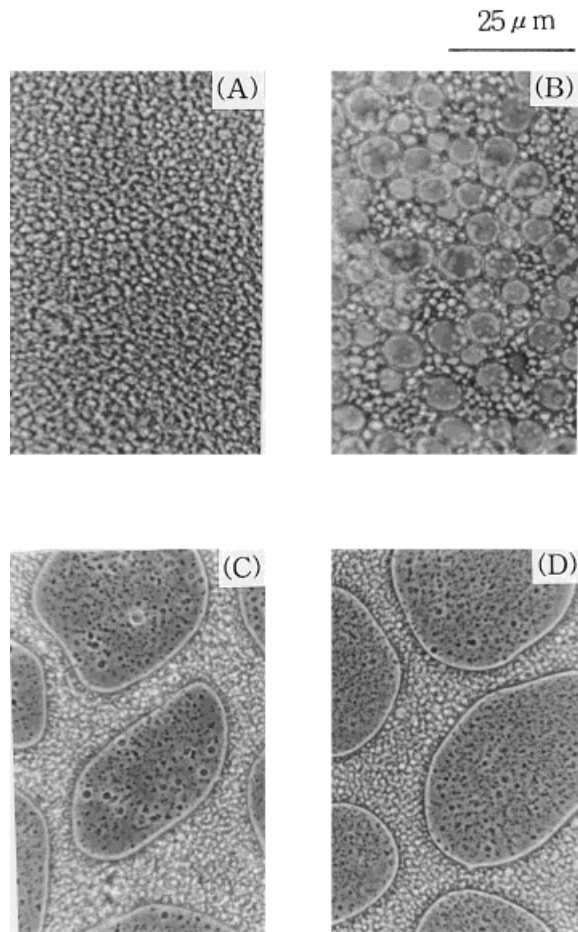


Figure 10 Morphological development of EP/PSF (85/15 wt %) during cure at 220°C. Scale bar: 25 μm ; (A) 15 min; (B) 17 min; (C) 20 min; (D) 25 min.

Figure 6. The more the content of PSF component, the longer the induction period of phase separation and the smaller the rate of phase separation. It seems that by lowering the cure temperature and increasing the PSF content, the rate of phase separation is considerably reduced, while that of the cure reaction is not so much. These two competing processes of phase separation and cure reaction are a controlling factor to determine the final morphology of the reaction-induced phase separation process.

To discuss a domain spacing of the phase-separated structure, we also estimate the periodic distance, Λ_m , in the phase-separated structure as a Bragg's spacing from the peak angle, θ_m , of the scattering profile in Figure 4. Λ_m is given by:

$$\Lambda_m = \lambda/2n \sin(\theta_m/2)$$

where λ is the wavelength of incident light in the medium and n is the refractive index. The plot of Λ_m versus time with varying cure temperatures and EP/PSF blend compositions are shown in Figure 7. For the change of cure temperature and blend composition, the Λ_m slightly increases with cure time and eventually levels off, suggesting that further growth of the structure is suppressed by gelation or vitrification of the epoxy-rich phase. In Figure 7(a), the values of Λ_m of the final morphology of the 70/30 (EP/PSF) composition are between 1–4 μm with varying cure temperatures from 200 to 240°C. The Λ_m of high cure temperature is larger than that of the lower one because the decrease of the medium viscosity with increasing cure temperature makes the phase separation easy. The values of Λ_m with varying blend compositions for the cure temperature of 220°C are decreased from 1 to 13 μm with increasing PSF con-

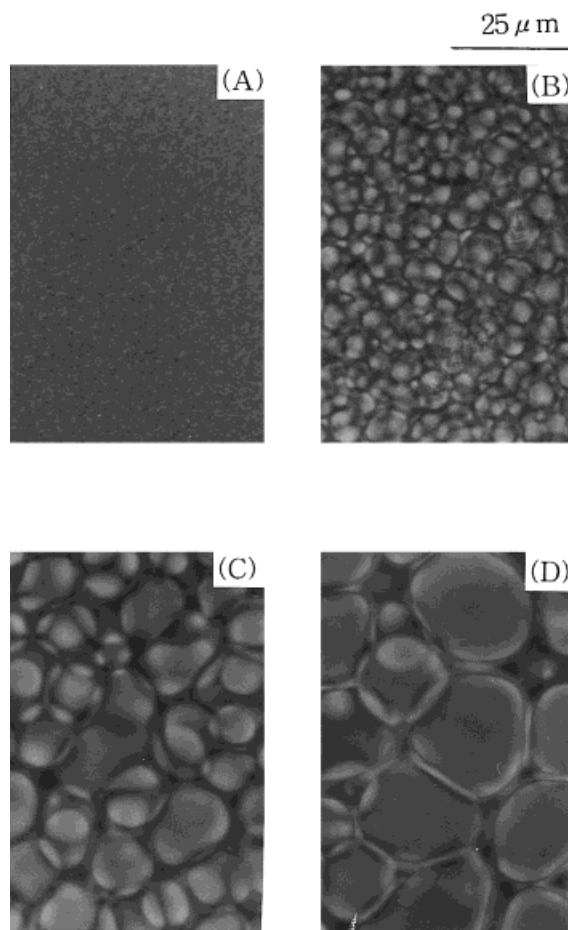


Figure 11 Morphological development of EP/PSF (80/20 wt %) during cure at 220°C. Scale bar: 25 μm ; (A) 15 min; (B) 20 min; (C) 23 min; (D) 25 min.

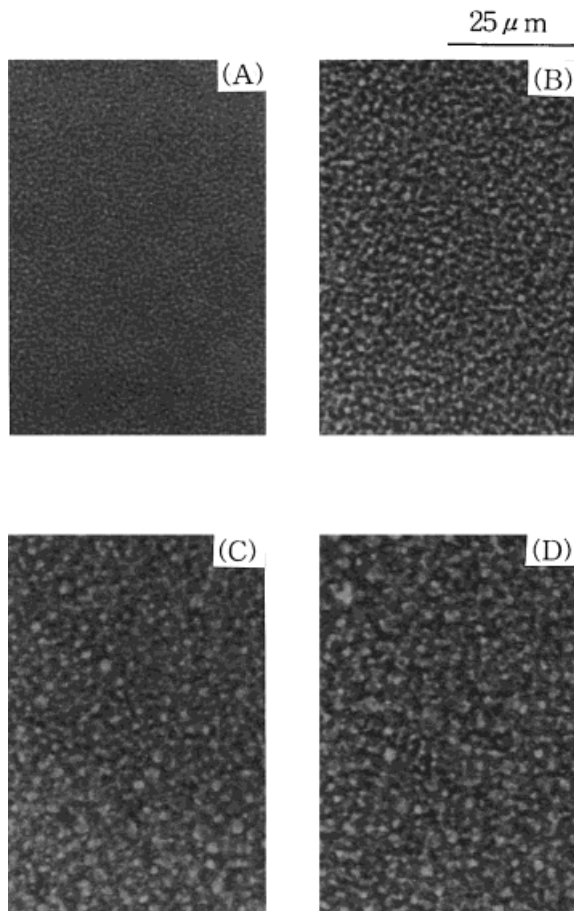


Figure 12 Morphological development of EP/PSF (60/40 wt %) during cure at 220°C. Scale bar: 25 μm ; (A) 25 min; (B) 28 min; (C) 30 min; (D) 35 min.

tent [Fig. 7(b)]. This implies that by increasing the PSF composition, the rate of phase separation is considerably reduced, while that of the curing reaction is not as much. Thus, the blend composition is the more significant factor on the phase domain size of the final morphology than the cure temperature in this system.

Figure 8 shows the optical micrographs of the EP/PSF (95/5 wt %) blend during cure at 220°C. As can be seen in figure, the phase separation starts ca. 13 min via the nucleation and growth (NG) mode. The spherical domains of PSF dispersed in the epoxy matrix are shown. With curing, the dispersed PSF domains grow in size without changing their loci. Finally, the structure is fixed by gelation or vitrification of the epoxy-rich phase at the late stage of curing.

Figure 9 shows the optical micrographs of the EP/PSF (90/10 wt %) blend during cure at 220°C.

The morphology at the early stage of phase separation is the same behavior as the EP/PSF (95/5 wt %) blend. However, as cure reaction proceeds, the combined structure is observed. It may be formed via the NG mode, subsequent rapid coalescence, and secondary phase separation within the PSF-rich phase. The secondary phase separation presumably occurred by the abrupt changes of equilibrium composition and viscosity during cure.

Figure 10 shows the optical micrographs of the EP/PSF (85/15 wt %) blend during cure at 220°C. Phase separation occurred via the SD mode at the early stage. This results in a spherical domain of the epoxy-rich phase dispersed quite regularly in the PSF-rich phase matrix. Like the EP/PSF (90/10 wt %) blend composition, combined structure is also seen, but the structure development with curing is quite different from that one. That is, for the EP/PSF (85/15 wt %) blend, the phase separation started in the SD mode and was followed by the NG mode, while in the EP/PSF (90/10 wt %) blend the phase separation took place via the NG mode and was followed by the SD mode.

Figure 11 shows the optical micrographs of the EP/PSF (80/20 wt %) blend during cure at 220°C. Phase separation started via the SD mode. Epoxy-rich globules with a uniform diameter of a few micrometers are dispersed in a PSF matrix. Note that the periodic distance between the globules in optical micrographs exactly correspond to those obtained by light scattering in Figure 4.

Figure 12 shows the optical micrographs of the

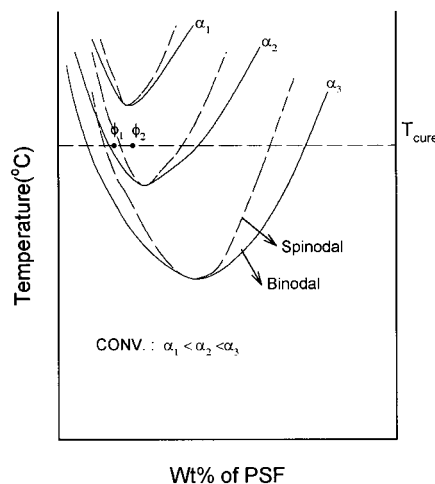


Figure 13 Schematic representation of LCST change in EP/PSF blends.

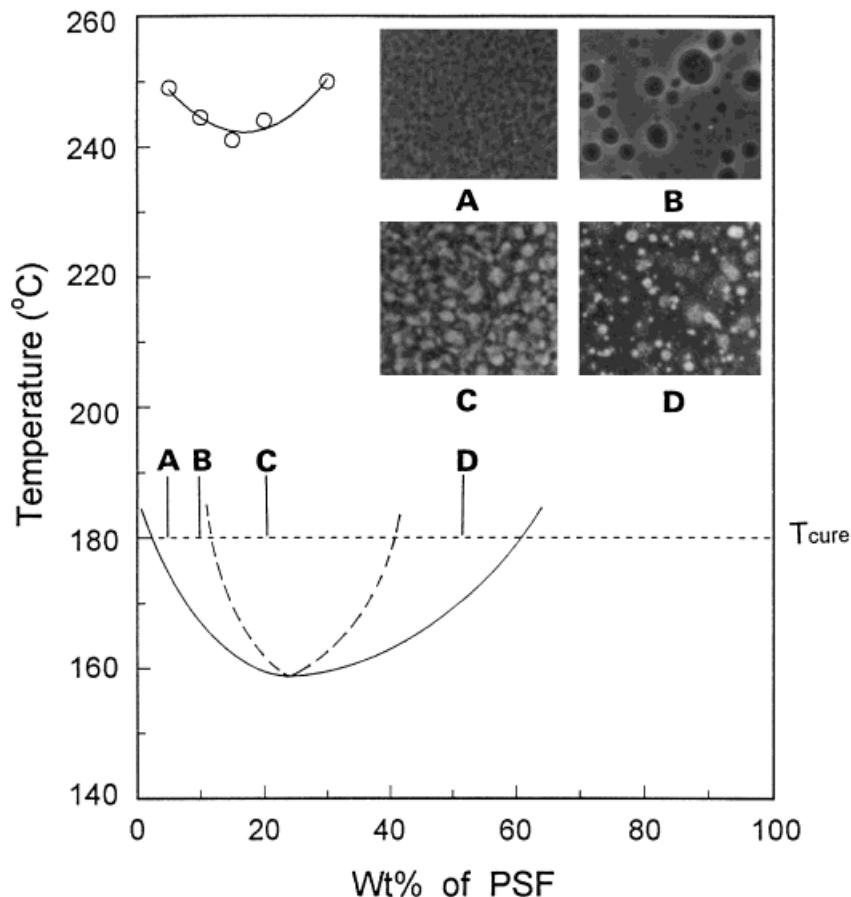


Figure 14 Phase diagram and final morphology of various EP/PSF (wt %) blends cured at 180°C. —; binodal - - - -; spinodal. (A) 95/5, (B) 90/10, (C) 80/20, (D) 50/50.

EP/PSF (60/40 wt %) blend during cure at 220°C. Like the 20% PSF content system, the phase separation started via the SD. However, the increase of the PSF content increased the viscosity of the system, thus reducing the rate of coalescence of the epoxy-rich globules in the late stage of the SD. Therefore, the smaller epoxy-rich globules dispersed in a PSF matrix is obtained.

From the results of Figures 8–12, one proposed a schematic change of a LCST-type phase diagram during cure at an isothermal cure condition, as shown in Figure 13. The mixture was homogeneous at the cure temperature at the early stage of curing. As the cure reaction proceeds, the system is thrust into a two-phase regime by the LCST depression caused by the increase in the molecular weight of the epoxy-rich phase. If the blend composition was located at φ_1 or φ_2 , when the conversion of the epoxy reaches α_1 , the system was homogeneous. As the reaction proceeds and the conversion is gradually increased to α_2 , the

systems are thrust into a heterogeneous phase. Here, if the blend composition is located at φ_1 , the phase separation took place via the NG mode and the phase separation started via the SD mode for φ_2 . In this region, any further phase separation will be stopped if the gelation or vitrification occurs. In such a case, phase separation via the NG mode will start and finish only in this metastable region. On the other hand, it is also possible that φ_1 will fall into the unstable region by passing the spinodal curve at the time of structural freeze-in by vitrification or by gelation. In such a situation, the phase separation actually takes place by two mechanisms in sequence; first, the NG and then the SD mode, while if the phase separation starts in the metastable region as in point φ_2 , the phase separation will proceed only by the SD mode. As the cure reaction further proceeds, when the conversion goes to α_3 , the phase separation takes place via the SD mode in both φ_1 and φ_2 . On the basis of the results of Figures

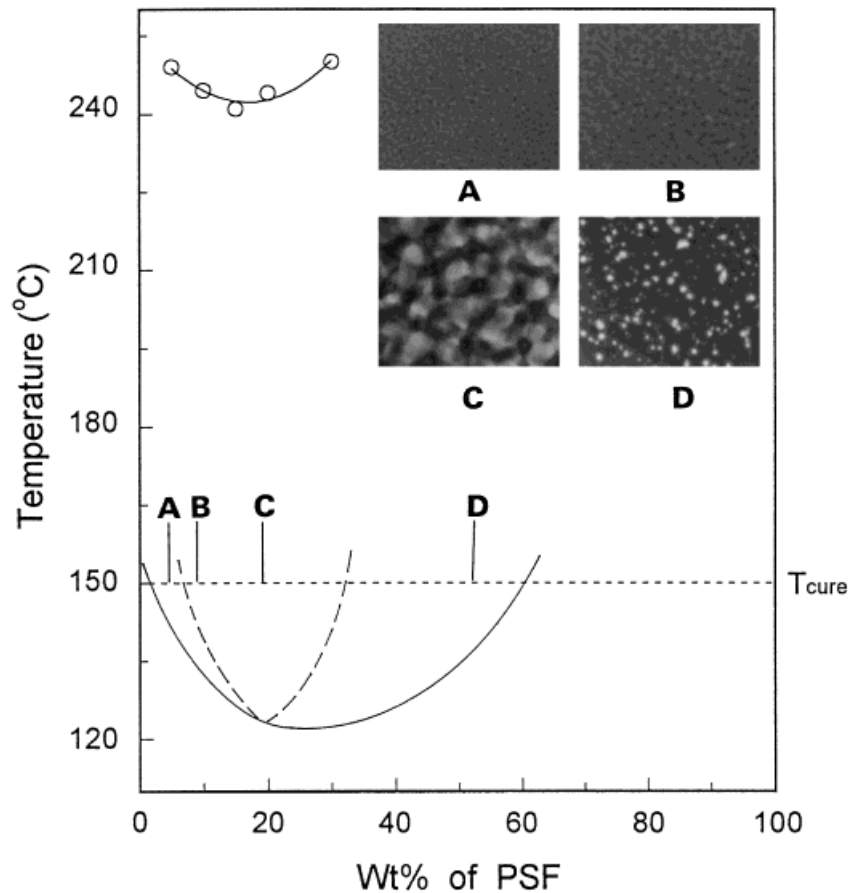


Figure 15 Phase diagram and final morphology of various EP/PSF (wt %) blends cured at 150°C. —; binodal - - - -; spinodal. (A) 95/5, (B) 90/10, (C) 80/20, (D) 50/50.

8–12, one describes the relationship between the possible phase diagram and morphology at the final stage of curing with various EP/PSF blend compositions.

When cured at 180°C (Fig. 14), sea-island morphology is observed below 10 wt % and above 50 wt % PSF contents, while for 20 wt % PSF content, interconnected structure is obtained. On the other hand, when cured at a relatively low temperature (150°C) (Fig. 15), the sea-island morphology is observed below 5 wt % and above 50 wt % PSF contents, while between 10 and 20 wt % PSF content, interconnected structure is obtained.

Figure 16 shows the relationship between the possible phase diagram and the phase separation mode at the final stage of curing with various cure temperatures and blend compositions. Here, open circles and closed circles indicate the SD and NG mode, respectively. Note that the SD and NG is judged by the optical microscope. As can be seen

in the figure, for 10 wt % PSF content, the lower the cure temperature, the NG mode changed into the SD mode. On the contrary, when cured at a high cure temperature for 30 wt % PSF content, the SD mode is obtained. That is, the rate of phase separation is much faster than that of the cure reaction so that the LCST passes quickly through the NG region and proceeds to the SD mode. On the other hand, for the low temperature curing (150°C), the cure reaction and the phase separation cannot be accomplished due to the vitrification of the polymer medium at a lower temperature than its T_g . This results in the NG mode. Thus, the phase separation mode of the PSF-modified epoxy was dependent on the PSF composition and cure temperature.

CONCLUSION

The structure development via reaction-induced phase separation in the EP/PSF blends was in-

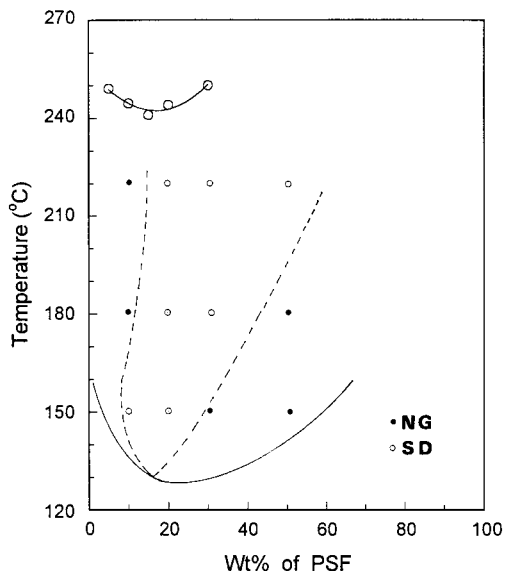


Figure 16 Phase diagram of EP/PSF blends with various cure temperatures and blend compositions. —; binodal - - - -; spinodal.

investigated by optical microscope and light scattering. The EP/PSF mixture was shown to exhibit the LCST-type phase behavior. Light scattering analysis revealed that the lower the cure temperature and the larger the content of the PSF, the smaller the periodic distance of the dispersed phase. When cured isothermally at 220°C, phase separation occurred via the NG mode and led to the spherical domains of the PSF dispersed in the EP-rich phase for the blends of 5 wt % PSF content. While for the blends above 20 wt % PSF content, the SD mode prevailed and led to the spherical domains of the EP dispersed in the PSF-

rich phase. At intermediate compositions (10, 15 wt % of PSF content), combined structure is observed. These morphology were formed via primary SD or NG and secondary phase separation within the dispersed and the matrix phases.

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