

# Cure Reaction and Phase Separation Behavior of Cyanate Ester-Cured Epoxy/Polyphenylene Oxide Blends

Shao-Jung Wu

Department of Chemical Engineering, Mingchi University of Technology, Taipei Hsien, 24301, Taiwan

Received 5 October 2005; accepted 18 January 2006

DOI 10.1002/app.24372

Published online in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** The cure reaction and phase separation mechanism of a cyanate ester-cured epoxy and its blends with polyphenylene oxide (PPO) were studied. An autocatalytic mechanism was observed for the epoxy and its blends. The reaction rate of the blends was higher than that of the neat epoxy at initial stage; however, the reached conversion decreased with PPO content. FTIR analysis revealed that the cyanate functional group reactions were accelerated by adding PPO and indicated that several coreactions have occurred. This was caused by the reaction of cyanate ester with the PPO reactive chain ends. But at a later stage of cure, the reaction could not progress further due to diffusional limitation of PPO. To understand the

relationship between the cure kinetics and phase separation of the blends, the morphology of the blends during cure was examined. When the homogeneous epoxy/PPO blends with low PPO content (10 phr) were cured isothermally, the blends were separated by nucleation and growth (NG) mechanism to form the PPO particle structure. But at high PPO content (30 phr), the phase separation took place via spinodal decomposition (SD). SD is favored near critical concentration and high cure rate system. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 1139–1145, 2006

**Key words:** blends; curing of polymers; Fourier transform infrared spectroscopy; phase separation; poly(phenylene oxide)

## INTRODUCTION

Applications of epoxy resins are extensive, because they are easy to process and have reasonable thermal and mechanical properties. However, the epoxy resins are generally brittle because of high crosslink densities. Toughening epoxy resins using rubbers has been known for a considerable time.<sup>1–4</sup> However, the rubber modification of epoxies becomes ineffective as the crosslink density of the epoxy matrix increases because of the inability of the rubber particles to deform by shear yielding or cavitation. Furthermore, the use of rubber as toughening agent results in a significant decrease in modulus,<sup>2,3</sup> yield strength, and glass transition temperature ( $T_g$ ) of the cured epoxy resins. Therefore, toughening of highly crosslinked thermosets was explored by blending with high modulus, high glass transition temperature thermoplastics.<sup>5–17</sup>

A classical example is polyphenylene oxide (PPO),<sup>9,10,15,16</sup> an amorphous thermoplastic with a low dielectric constant, a low dissipation factor, and high glass transition temperature. Thermoplastics addition to thermosets is expected to not only alter the morphology but also the cure kinetics. Phase separation took place either by nucleation and growth

(NG) or by spinodal decomposition (SD) mechanism, and a heterogeneous morphology formed if the thermoplastic and the crosslinked thermoset were not miscible during cure. In addition, phase separation during cure progress is also expected to significantly influence the properties of cured epoxy blends.<sup>15</sup> An efficient use of the reaction-induced phase separation in thermoplastic modified thermoset needs knowledge of factors that control the morphologies generated and their relationships with required properties. In this study, the effects of the PPO additives on the cure kinetics and the phase separation behavior of cyanate ester-cured epoxy/PPO blends were investigated by differential scanning calorimetry (DSC), Fourier transform infrared spectroscopy (FTIR), nuclear magnetic resonance (NMR), and optical microscopy (OM).

## EXPERIMENTAL

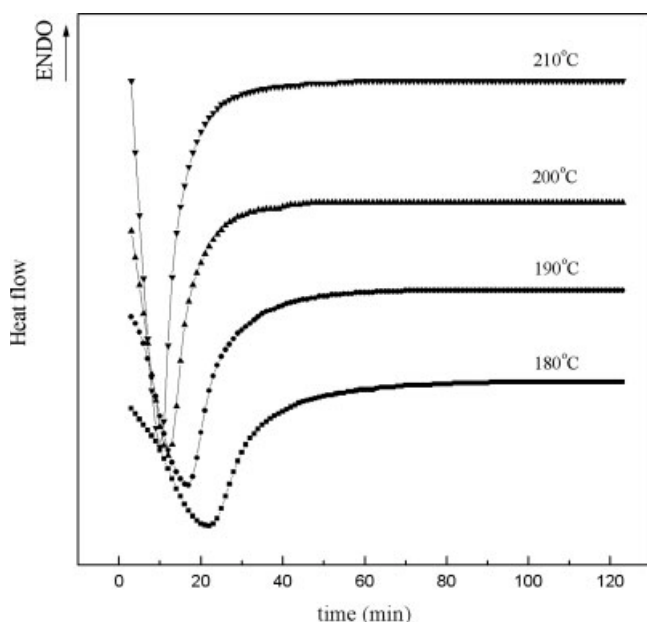
### Materials

The epoxy resin used in this work was a commercial diglycidyl-type resin (Epon 828, Shell) and the curing agent was multifunctional cyanate ester (PT-30, Lonza). The thermoplastic polymer used was poly(2,6-dimethyl-1,4-phenylene oxide) (PPO, GE) with an intrinsic viscosity of 0.4 dL g<sup>-1</sup> measured in chloroform at 25°C.

### Blend preparation

Epoxy/PPO blended mixtures with 10 phr, 30 phr, and 50 phr of PPO, were prepared (phr represents

Correspondence to: S.-J. Wu (sjwu@ccsun.mit.edu.tw).



**Figure 1** Isothermal DSC thermograms of cyanate ester-cured epoxy/PPO (30 phr) mixture samples.

the number of parts of PPO per hundred parts of the epoxy resin). First, PPO was weighted and dissolved completely in dichloromethane. The resulting polymer solution was then mixed with the epoxy resin and 20 phr cyanate ester at room temperature. The solvent in the mixture was vaporized in a circulation oven at 50°C for 1 h, followed by removal of the residual solvent in a vacuum oven at 50°C for 12 h.

#### Differential scanning calorimetry

The cure reaction of the epoxy resin and its blend was followed by DSC (Perkin-Elmer DSC 7). The temperature scale and the energy output of the calorimeter were calibrated using indium and zinc standards. Dry nitrogen was used as purge gas. Samples (5–10 mg) were placed in DSC aluminum pans. The isothermal cure reaction was considered complete when the signal returned to the baseline. The conversions of neat epoxy and epoxy/PPO blends were estimated from the relationship  $(_i(t) = \Delta H_i(t)/\Delta H_T$ , where the value of  $(_i(t)$  is determined by measuring the partial heat of reaction up to time  $t$  ( $\Delta H_i(t)$ ) and dividing by the total heat of the reaction ( $\Delta H_T$ ), which can be estimated from a nonisothermal temperature scan (10°C/min).<sup>18</sup>

#### Fourier transform infrared spectroscopy

Fourier transform infrared (FTIR, BIORAD FTS-40) absorption spectra were obtained at 8 cm<sup>-1</sup> resolution and the number of scans was 16. The recorded wavenumber range was 400–4000 cm<sup>-1</sup>.

The measurements were carried out on thin films cast onto a potassium bromide (KBr) disk. Samples were prepared by dissolving appropriate amounts of the components in dichloromethane to yield 2 wt % solution. Thin films for FTIR studies were obtained by casting the epoxy resin or epoxy/PPO solutions onto KBr disks at room temperature, followed by rapidly evaporating the solvent by placing the sample in a vacuum oven at 50°C for 2 h.

#### Solid-state NMR

High-resolution solid-state <sup>13</sup>C NMR experiments were carried out at room temperature, using a Bruker DSX-400 spectrometer operated at a resonance frequency of 100.46 MHz. The <sup>13</sup>C CP/MAS spectra were measured with 4.7 μs 90° pulse, with 1.5-s pulse delay time, acquisition time of 0.0246 s, and 4000 scans. A magic angle sample spinning (MAS) rate of 6 kHz was used to eliminate resonance broadening attributed to the anisotropy of the chemical shift tensors.

#### Optical microscopy

A drop of the mixture was placed between glass slides. A set of these samples was cured in an oven at 180°C. Partially-cured specimens were extracted at different times for observation with an optical microscopy (OM, Nikon model SN).

## RESULTS AND DISCUSSION

#### Cure reaction

Figure 1 shows the isothermal DSC thermograms of the blend system containing 30 phr PPO at various cure temperature. The maximum exothermic peaks were found after the start of the reaction, and the peaks shifted to shorter time with increasing temperature. These results are shown in Table I. All isothermal DSC curves showed that the reaction was

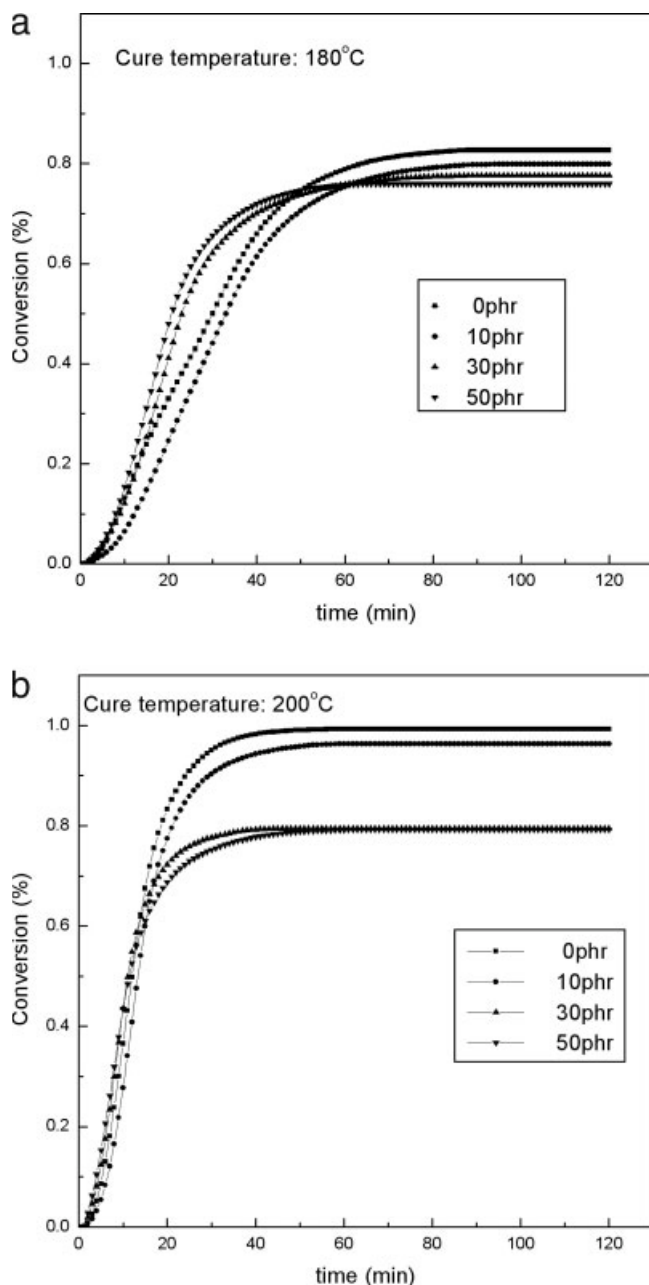
**TABLE I**  
Isothermal Cure Reaction for Epoxy/PPO Blends with 30 phr PPO

Isothermal temperature (°C)	tp (min) <sup>a</sup>	$\Delta H_i$ (J/g) <sup>b</sup>	$\Delta H_T$ (J/g) <sup>c</sup>	$\alpha$ (%)
180	24.8	215	277	77.6
190	17.1	218	277	78.7
200	12.3	220	277	79.4
210	10.5	235	277	84.8

<sup>a</sup> tp: the exothermic peak times.

<sup>b</sup>  $\Delta H_i$ : heat of reaction at isothermal temperature.

<sup>c</sup>  $\Delta H_T$ : heat of reaction from a non-isothermal temperature scan.

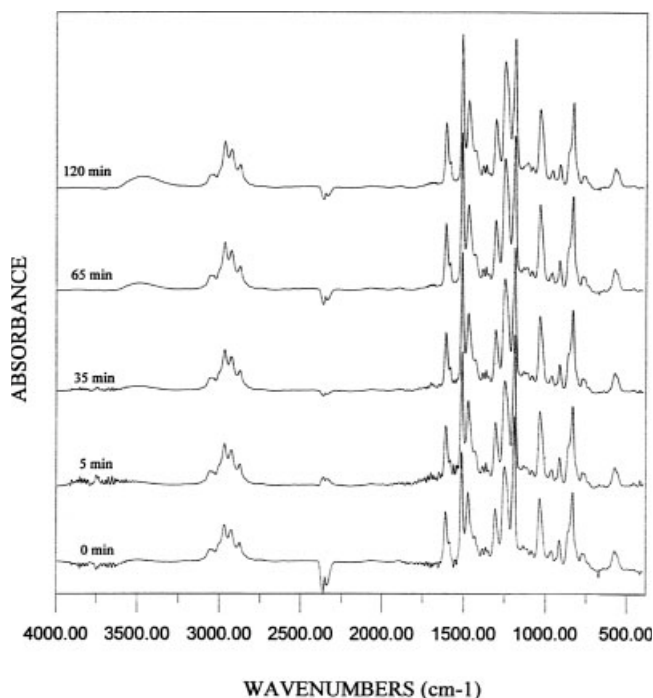


**Figure 2** (a) Plots of the conversion versus time for cyanate ester-cured epoxy/PPO mixture samples at 180°C. (b) Plots of the conversion versus time for cyanate-ester cured epoxy/PPO mixture samples at 200°C.

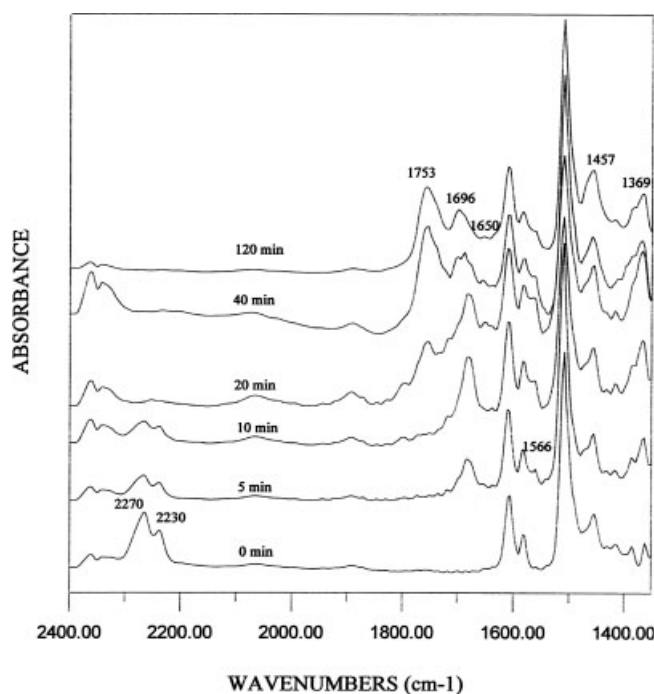
accelerated with cure time at the early stage of reaction. Conversion versus time curves are shown in Figure 2 for the neat epoxy and the blends with PPO at different temperatures. The maximum heat evolutions of the cyanate ester-cured epoxy and its blends did not occur in the initial isothermal DSC signal. The results are characteristics of autocatalytic reaction. Therefore, the plots of conversion ( $\alpha$ ) as a function of time were obtained from the relationship  $(\alpha(t) = \Delta H_I(t)/\Delta H_T$  and all the curves showed s-shape. Furthermore, plots of reaction rate  $d\alpha/dt$  versus time

will show a maximum reaction rate at time greater than zero. These results also mean that the cure reaction followed the autocatalytic mechanism. It was also found that the conversion of the epoxy/PPO blend at the initial stage was higher than that of the neat epoxy. This means that the PPO acts as a catalyst for the cyanate ester cured epoxy system. However, the maximum conversion decreased with the increment of PPO content. The incomplete cure reaction obtained in isothermal conditions could be explained in terms of the structural changes produced by polymerization reactions associated with an increase of  $T_g$  of the reaction system. Moreover, the decrease in the final conversion in the blend could be ascribed to an increase in viscosity of the reacting medium that hinders the mobility of the reacting species at increasing PPO contents.

The effects of PPO content on the cure behavior in the cyanate ester-cured epoxy were also investigated with FTIR. Figure 3 shows the change in FTIR spectrum at 180°C in the epoxy/PPO (30 phr) system without cyanate ester. As the process proceeds after 35 min, an epoxy band at  $906\text{ cm}^{-1}$  decreases slightly and a hydroxyl band at  $3200\text{--}3600\text{ cm}^{-1}$  increases with the time. This may be due to the etherification between epoxy and water in environment or PPO reactive chain ends. Note that the epoxy group exists for 120 min at 180°C. Figure 4 shows the change in FTIR spectrum with isothermal cure at 180°C in the cyanate ester-cured epoxy. With cure,



**Figure 3** Changes in the FTIR spectrum with cure at 180°C in the epoxy/PPO (30 phr) system without cyanate ester.



**Figure 4** Changes in the FTIR spectrum with cure at 180°C in the epoxy/cyanate ester system.

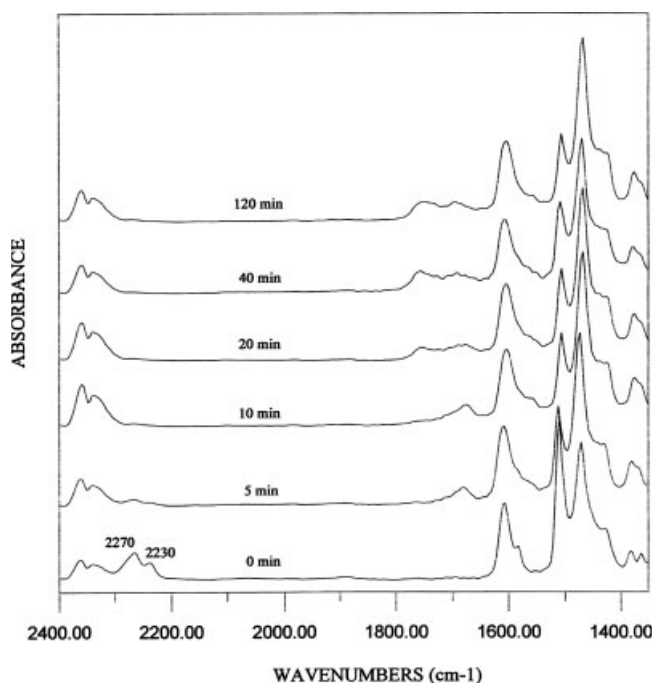
the cyanate bands at 2270 and 2230  $\text{cm}^{-1}$  decrease gradually and finally disappear at 20 min. The polymerization mechanism of epoxy-cyanate system is very complex. The main reaction is the trimerization reaction of the cyanate monomers to form a triazine at 1566  $\text{cm}^{-1}$  or aryl cyanurate at 1369  $\text{cm}^{-1}$ , which is initiated by water or impurities. Then the aryl cyanurate can react with epoxy groups to form alkyl cyanurate. Subsequently, the isomerization of alkyl cyanurates into alkyl isocyanurates occurs (1457 and 1696  $\text{cm}^{-1}$ ). Finally, the reaction of glycidyl ether with alkyl isocyanurate forms oxazolidinone at 1753  $\text{cm}^{-1}$ .<sup>19-21</sup> The second is the reaction of the cyanate ester and epoxy monomer, which leads to a structure containing an oxazoline cycle at 1650  $\text{cm}^{-1}$ . The other reaction includes the etherification of epoxy and hydroxyl groups.

Figure 5 shows the change in FTIR spectrum with cure at 180°C for times up to 120 min in cyanate ester-cured epoxy with 50 phr PPO. As the cure reaction proceeds, the cyanate bands at 2270 and 2230  $\text{cm}^{-1}$  quickly decrease and then disappear within 10 min. It can be seen that the rate of cyanate groups reaction in the blend is faster than that in the system without PPO. In our previous study, the reactions' rates for the epoxy/PPO blends were found to be higher than that of the neat epoxy.<sup>15,22</sup> The acceleration is increased upon increasing the PPO content. It is suggested that the presence of the PPO reactive chain ends, resulting in a fast cure rate in a polymerization at early stage. It is interesting to

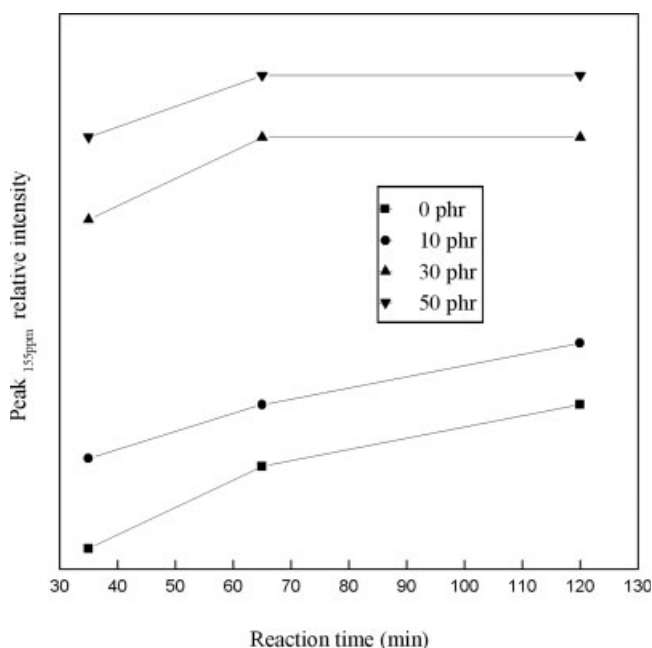
find that the oxazolidinone absorption band is not obvious after cure in the blend system. Although the consumption of cyanate groups is rapid, the subsequent reaction cannot progress further. This is an indication that the steric and diffusional limitations were imposed by PPO on the formation of oxazolidinone at later stage of cure. For this reason, the formation of oxazolidinone has been equally identified by solid-phase  $^{13}\text{C}$  NMR. Figure 6 shows the oxazolidinone group ( $\text{C}=\text{O}$ , 155 ppm) peak relative intensity ( $\text{CH}_3$  is used as the internal standard) versus time for the cyanate ester-cured epoxy system blends with PPO at cure temperature 180°C. At high PPO content, the oxazolidinone peak relative intensity does not change further after 65 min of cure. But at low PPO content or without PPO, the oxazolidinone peak relative intensity increases continuously at later stage of cure. The cure rate at initial stage increases because of the catalytic role of PPO, although at a later stage the reaction cannot progress further because of the diffusion control of formed PPO domains. The result is similar to DSC analysis.

### Phase separation

At the early stage of cure, the solution-cast film of cyanate ester-cured epoxy with 10 and 30 phr PPO was transparent and homogeneous under the optical microscope. As the cure reaction proceeds, phase separation in amorphous PPO/cyanate ester-cured epoxy blending system is induced by cure reaction, i.e., reaction-induced phase separation. Figures 7 and 8



**Figure 5** Changes in the FTIR spectrum with cure at 180°C in the cyanate ester-cured epoxy/PPO (50 phr) system.



**Figure 6** Plots of the oxazolidinone group peak relative intensity versus time for cyanate ester-cured epoxy/PPO blends system at a curing temperature of 180°C.

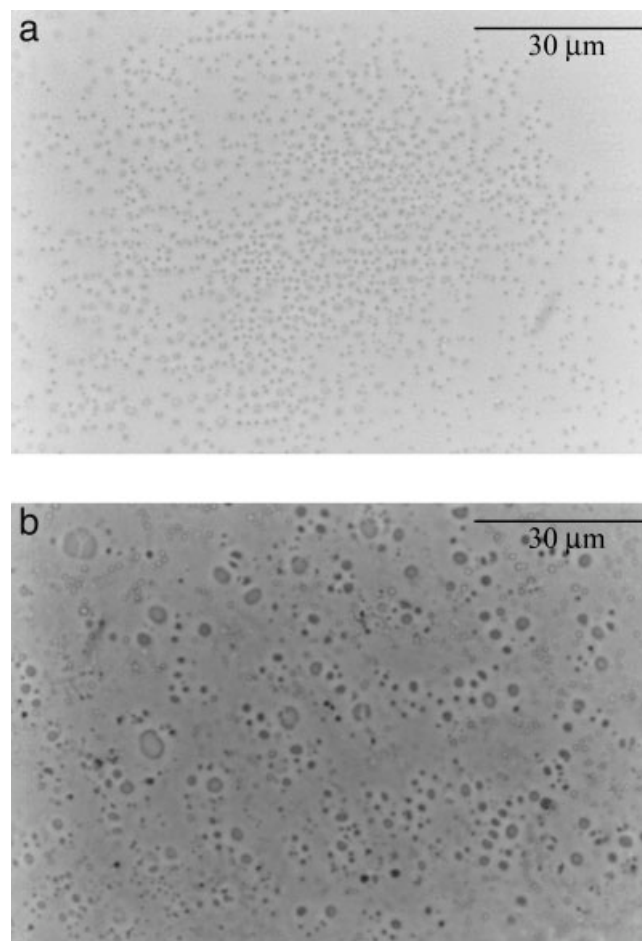
display OM micrographs of two different compositions, which illustrate the phase separation process. The micrographs in Figure 7 show the phase separation process of 10 phr PPO blend, heated at 180°C with respect to time. As can be seen in Figure 7, the phase separation starts at 10 min via the nucleation and growth (NG) mode. The spherical domains of PPO dispersed in the epoxy matrix. The dispersed PPO domains grow in size with cure. Finally, the structure is fixed by gelation of the cyanate ester-cured epoxy phase at later stage of cure.

Changes in morphology for the 30 phr PPO containing blend system during cure are presented in Figure 8. Phase separation occurs via spinodal decomposition (SD) mode at the early stage, resulting in the development of a bicontinuous structure. The separation takes place by a continuous and spontaneous process by an uphill diffusion with negative diffusion coefficient. As phase separation proceeds, the development of regularly phase-separated or modulated structure is followed by coarsening. At the time of 20 min, phase connectivity will be interrupted by the increase in interfacial tension, resulting in a dispersed-droplet morphology. In our blending system, the blends were separated by NG mechanism with low PPO content. But at high PPO content, the phase separation took place via SD. When the thermoplastic modifier concentrations was close to or higher than the critical concentration, SD has been observed.<sup>23</sup> Further, the cure rate was accelerated by the PPO, and the epoxy conversion is increased and jumps over the binodal curve to a

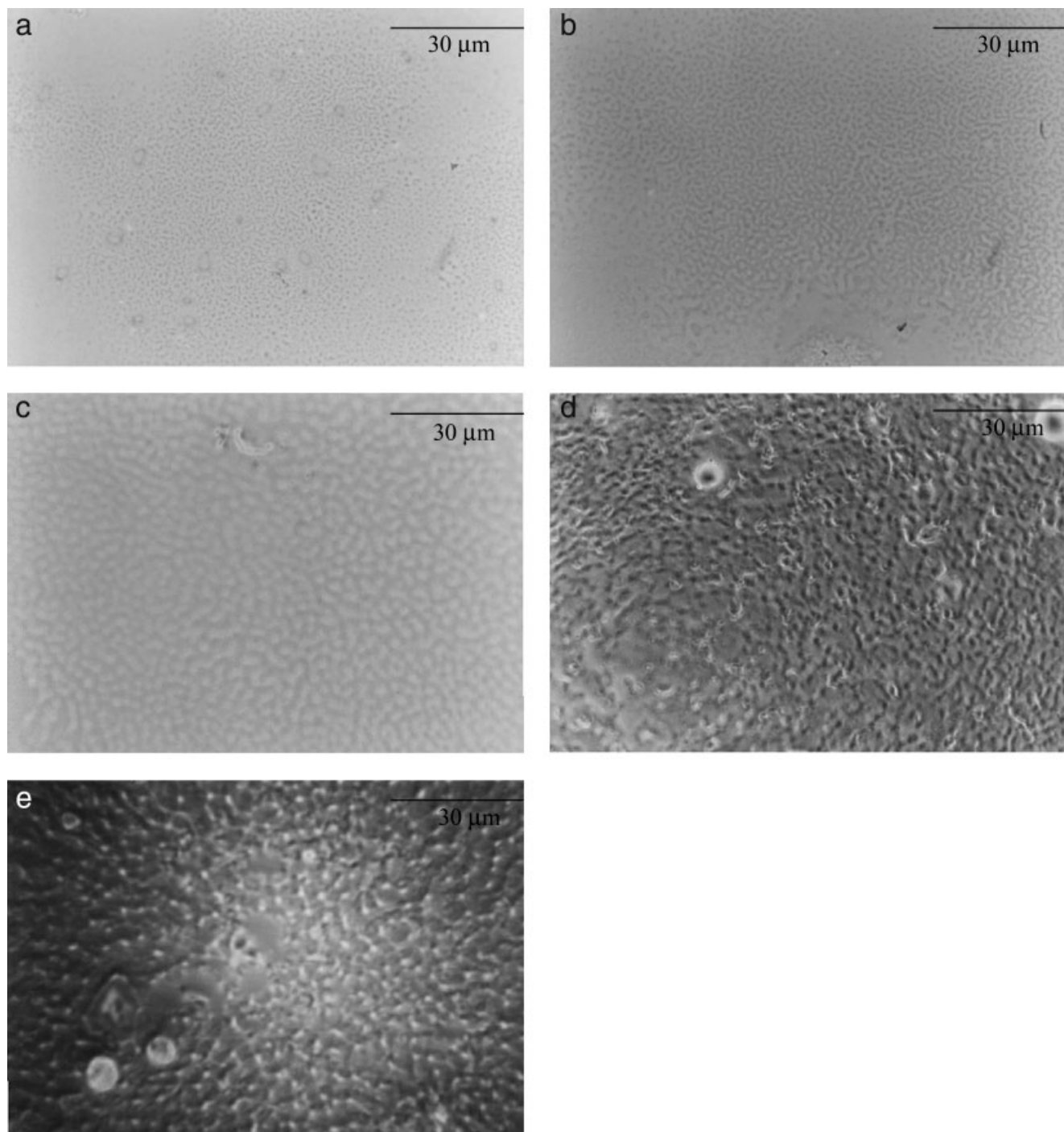
point at spinodal curve. Then the phase separation initiates via SD mechanism.

## CONCLUSIONS

An autocatalytic mechanism was observed for a cyanate ester-cured epoxy and its blends with PPO. With the increment of PPO content, the cure rate at the initial stage increased because of the PPO reactive chain ends, while ultimate conversion decreased because of the diffusional limitation of formed PPO domains. FTIR analysis of cyanate ester-cured epoxy system revealed that all cyanate groups have reacted and were accelerated by PPO. Several coreactions have occurred in this system, which we have mentioned earlier. But at later stage of cure, the reaction cannot progress further because of diffusion control of PPO. The possibility of starting phase separation process is determined by the ratio between the intrinsic rate of phase separation process (thermodynamic factor) and the rate of cure (kinetic factor). SD mechanism has been observed in 30 phr PPO blend, because the PPO concentration is close to critical



**Figure 7** Optical micrographs of cyanate ester-cured epoxy/PPO (10 phr) cured for different times at 180°C; (a) 10 min; (b) 20 min.



**Figure 8** Optical micrographs of cyanate ester-cured epoxy/PPO (30 phr) cured for different times at 180°C; (a) 2 min; (b) 5 min; (c) 10 min; (d) 15 min; (e) 20 min.

concentration and the initial cure rate is high in this composition. In 10 phr PPO blend (PPO concentration lower than critical composition), many tiny spots appeared after a certain reaction via NG mechanism.

## References

1. Sultan, J. N.; McGarry, F. J *Polym Eng Sci* 1973, 13, 29.
2. Meeks, C. *Polymer* 1974, 15, 675.
3. Kunz, S. C.; Sayre, J. A.; Assink, R. A. *Polymer* 1982, 23, 1897.
4. Chen, T. K.; Jan, Y. H. *J Mater Sci* 1991, 26, 5848.
5. Bucknall, C. B.; Partridge, I. K. *Polymer* 1983, 24, 639.
6. Cecere, J. A.; McGrath, J. E. *Polym Prepr (Am Chem Soc Div Polym Chem)* 1986, 27, 299.
7. Partridge, I. K. *Polym Eng Sci* 1986, 26, 54.
8. Bucknall, C. B.; Gilbert, A. H. *Polymer* 1989, 30, 213.
9. Pearson, R. A.; Yee, A. F. *J Appl Polym Sci* 1993, 48, 1051.
10. Pearson, R. A.; Yee, A. F. *Polymer* 1993, 34, 3658.

11. Akay, M.; Cracknell, J. G. *J Appl Polym Sci* 1994, 52, 663.
12. Kim, B. S.; Chiba, T.; Inoue, T. *Polymer* 1995, 36, 43.
13. Teng, K. C.; Chang, F. C. *Polymer* 1996, 37, 2385.
14. Hwang, J. W.; Cho, K.; Yoon, T. H.; Park, C. E. *J Appl Polym Sci* 2000, 77, 921.
15. Wu, S. J.; Lin, T. K.; Shyu, S. S. *J Appl Polym Sci* 2000, 75, 26.
16. Wu, S. J.; Tung, N. P.; Lin, T. K.; Shyu, S. S. *Polym Int* 2000, 49, 1452.
17. Mimura, K.; Ito, H.; Fujioka, H. *Polymer* 2001, 42, 9223.
18. Halley, P. J.; Mackay, M. E. *Polym Eng Sci* 1996, 36, 593.
19. Grenier-Loustalot, M. F.; Grenier, P.; Bente, M. P. *Eur Polym Mater* 1992, 28, 987.
20. Bauer, M.; Bauer, J.; Ruhmann, R.; Kühn, G. *Acta Polym* 1989, 40, 397.
21. Shimp, D. A.; Wentworth, J. E. *Int Sampe Symp* 1992, 37, 293.
22. Wu, S. J.; Lin, T. K.; Zhang, J. X.; Shyu, S. S. *J Adhes Sci Technol* 2000, 14, 1423.
23. Borrajo, J.; Riccardi, C. C.; Williams, R. R. J.; Cao, Z. Q.; Pascault, J. P. *Polymer* 1995, 36, 3541.