

# Study on the Phase Separation of Thermoplastic-Modified Epoxy Systems by Time-Resolved Small-Angle Laser Light Scattering

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**ABSTRACT:** Reaction-induced phase-separation behavior of an epoxy (E-51) system modified by thermoplastics, namely, polyetherimide (PEI) and polycarbonate (PC), isothermally cured with 4,4'-diaminodiphenylsulfone (DDS) at various temperatures, was investigated by the time-resolved small-angle laser light-scattering (SALLS) technique. It was found that the morphology evolution of this E-51 curing system was controlled by the competition between the curing reaction and the phase separation. It was verified that the phase separation of these systems followed the spinodal decomposition mechanism through analyzing the scattering pattern evolution and the cocontinuous morphology observed by optical microscopy. The curing temperatures and compositions of these epoxy systems were considered to be the determining factors for the domain size and the phase-separation behavior. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 85: 950–956, 2002

**Key words:** time-resolved small-angle laser light-scattering; reaction-induced phase separation; epoxy; polyetherimide; polycarbonate

## INTRODUCTION

High-performance epoxy resins are some of the most important thermosetting polymeric materials and have been extensively used as adhesives, electric encapsulants, and advanced structural matrices because of their high thermal resistance, high tensile strength and modulus, and good chemical resistance.<sup>1–3</sup> Unfortunately, the intrinsic drawback of brittleness has severely limited their applications. So, for decades, great effort has been made concerning the modification of ep-

oxy resins both theoretically and in applications.<sup>4–7</sup>

In contrast to the conventionally rubber-toughened epoxy resins, high-performance engineering thermoplastic-modified epoxies are novel materials avoiding the usual shortcomings of rubber modification (i.e., reduction of glass transition temperature, yield strength, and elastic modulus) and having improved impact strength and fracture toughness.<sup>8,9</sup>

Concerning multicomponent polymers, there exist some systems in which chemical reactions take place together with spinodal decomposition.<sup>10–12</sup> The so-called reaction-induced phase separation is a process through which an initially homogeneous viscous mixture of modifiers and epoxy monomers becomes a multiphase polymer system exhibiting special morphology and formation of phase separation. On the basis of these

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characteristics, people have attempted to design new materials. Nowadays, reaction-induced phase separation of a curing epoxy system has attracted extensive attention because of its significant influence on the structures, and so on the mechanical property optimization, of the resulting epoxy composites.<sup>13–15</sup>

Since the 1980s, the small-angle laser light-scattering (SALLS) technique has been used to study thermally induced phase separation of polymer blends.<sup>16,17</sup> Compared with the commonly used optical microscope, the SALLS apparatus is more sensitive to the weak concentration fluctuation and the fine-domain development at the very early stages of phase separation. Thereafter, the kinetics of spinodal decomposition for multi-component polymers, especially for those consisting of thermoplastic components, was widely investigated.<sup>18–20</sup> However, the influence of temperature and composition on the phase separation of reaction-induced curing systems has not been investigated to date.

This study was concerned with the influence of temperature and composition on the early stage of the reaction, namely, the polymerization-induced phase separation of the polyetherimide (PEI)- and polycarbonate (PC)-modified epoxy (E-51) curing system. The mechanism and phase behaviors in the curing process are interpreted through examining the phase separation induced by the molecular weight increase of the epoxy during the curing reaction.

## EXPERIMENTAL

The epoxy resin used was E-51, a commercial-grade product based on diglycidyl ether of bisphenol-A (DGEBA), with an  $M_n^- = 392$ , produced by the Hangzhou Chemical Plant (China). The thermoplastics were a PC based on bisphenol-A, with an  $M_n^- = 23,345$ , and PEI, with an  $M_n^- = 18,000$ , products of the Idenitsu Kosan Co. (Japan) and the General Electric Co., respectively. The curing agent was 4,4'-diaminodiphenylsulfone (DDS),  $M_n^- = 243.31$ , obtained from the 3rd Chemical Agent Co. (Shanghai, China).

Before dissolving, all the materials were each dehydrated at 120°C under a vacuum for at least 24 h to ensure that no residual solvent existed. PC and PEI were dissolved in dichloromethane ( $\text{CH}_2\text{Cl}_2$ ), forming a clear, homogeneous solution. The solution was degassed in a vacuum oven at room temperature. Then, the solution was mixed

with E-51 and heated slowly to 140°C to drive off most of the  $\text{CH}_2\text{Cl}_2$  and cooled to 100°C. At this stage, the solution was a clear, homogeneous, viscous liquid. The curing agent DDS was added stoichiometrically to the epoxy–thermoplastic mixture and stirred to ensure that it was fully dispersed (dispersing time should be less than 20 min to avoid curing). A drop of the mixture was put on a small glass plate preheated at 100°C, carefully covered by another glass plate to avoid air bubbles, and then quenched on a film cooled by the ice to avoid rapid curing. The transparency of all samples used for the SALLS test indicated no phase separation at this time.

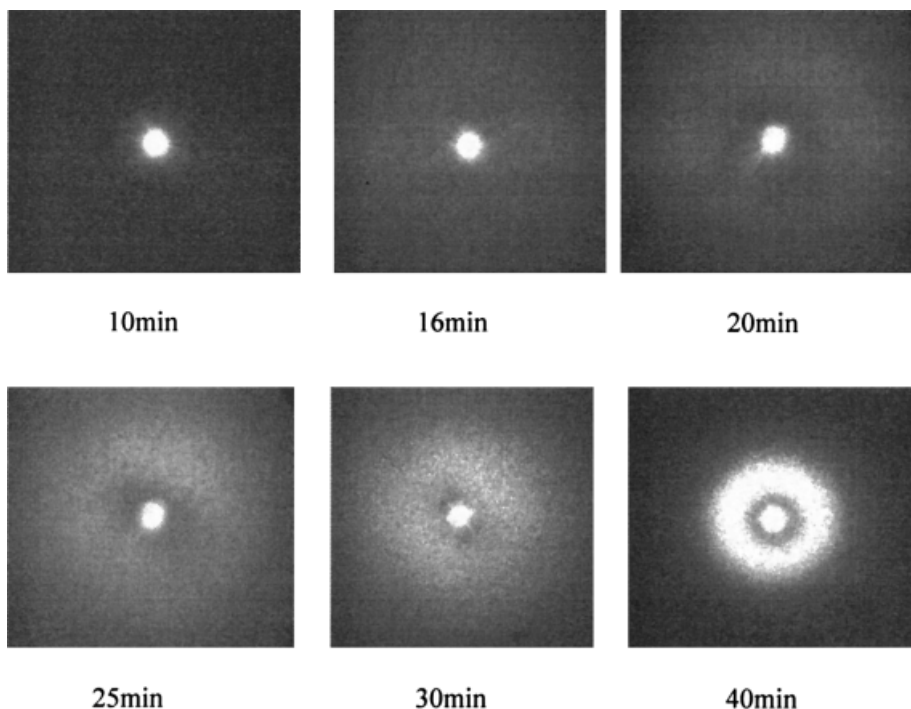
The time-resolved SALLS apparatus used here was similar to that described in many earlier articles of our group<sup>21</sup> except for some improvements. The glass plates loaded with E-51, thermoplastics, and DDS mixtures were placed on the hot stage and isothermally cured in the temperature range from 150 to 210°C. For isothermal curing, the hot stage, with a power of 100 W, was controlled by an intelligent controller. The temperature of the hot stage usually recovered to equilibrium within 10–40 s after the samples were placed on it, depending on the temperature of the hot stage.

We did not begin recording until the temperature was stable as set. The accuracy of the temperature control was on the order of  $\pm 0.2^\circ\text{C}$ . On-line circular averaging of each radius symmetric scattering pattern was performed to obtain the intensity distribution, namely, the relationship between the intensity and the scattering angle. The intensity at the beginning of the examination was subtracted from the intensity measured at a later times as background to avoid the negative effects of parasitic light, thermal fluctuation in the homogeneous samples, and the dark current of a charge coupling digital (CCD) camera. The recording intervals were set or altered before testing according to different needs, such as the composition of the sample, the phase separation speed, and the experiment temperature.

## RESULTS AND DISCUSSION

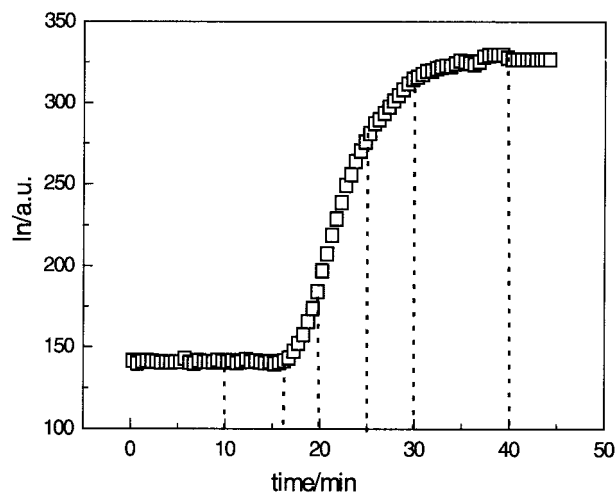
### Mechanism of Phase Separation

Figure 1 gives the scattering pattern evolution of the E-51/PEI/PC/DDS curing system. No appreciable light scattering was detected in the early stage of curing, indicating the existence of a ho-



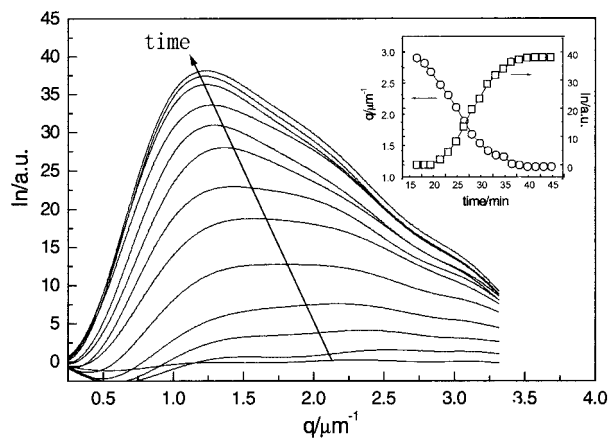
**Figure 1** Evolution of typical light-scattering patterns with time for E-51/PEI/PC (100/10/10) system isothermally cured with DDS (30 phr) at 150°C.

mogeneous phase. A weak scattering appeared after the induction period of 15 min; then, the scattering pattern became brighter while its diameter decreased with further curing. The plot of the corresponding integrated intensity  $I_n$  evolution versus the curing time is shown in Figure 2. It can be found that  $I_n$  grows dramatically to

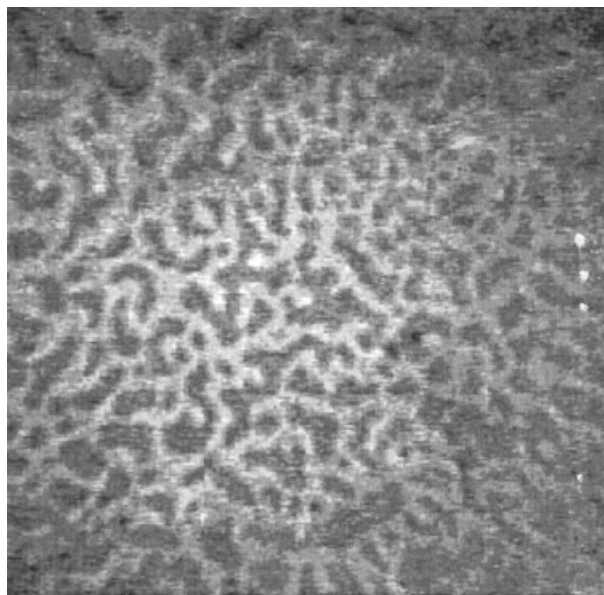


**Figure 2** Relationship between  $I_n$  and curing time for various E-51/PEI/PC (100/10/10) systems isothermally cured with DDS (30 phr) at 150°C.

reach its maximum, then eventually levels off after a period of induction. Figure 3 shows that, after a short delay of 14 min,  $I_n$  peaks appear. With further curing,  $I_n$  increases and approaches the maximum, and the scattering vector  $q$  shifts exponentially toward a smaller value. Then,  $q$  remains unchanged, although  $I_n$  continues to increase, as clearly shown in the inlays. We believe



**Figure 3** Change of  $I_n$  and  $q$  with curing time for E-51/PEI/PC (100/10/10) system isothermally cured with DDS (30 phr) at 180°C. The inlay is change of  $I_n$  and  $q$  with curing time.



**Figure 4** Optical microscopy photograph of E-51/PEI/PC (100/10/10) system isothermally cured with DDS (30 phr) at 180°C for 30 min.

that this process is related to the domain-size development and morphology fixation in the curing system.

The typical scattering pattern evolution process in Figure 1, together with the following optical microscopy photograph of cocontinuous morphology that we observed, as shown in Figure 4, indicates that the phase-separation mechanism of the E-51/PEI/PC/DDS curing system is a typical spinodal decomposition, which is in agreement with the results by other researchers.<sup>12,22</sup> Furthermore, we also predict that during the induction period the reaction-induced curing system may also undergo metastable nuclear growth, but the process is too slow and the domain sizes are too small to be detected by our SALLS apparatus.

#### Temperature Dependence of Phase-separation Behavior and Domain Sizes

The curing process of epoxy resins involves chain diffusion, branching, and crosslinking of the epoxy monomer. According to the Arrhenius expression

$$\eta = A \exp(-\Delta E_{\eta}/RT) \quad (1)$$

where  $\eta$ ,  $\Delta E_{\eta}$ ,  $A$ ,  $R$ , and  $T$  are the viscosity of the E-51 monomers, the viscosity activation energy, the exponent factor, the gas constant, and the

absolute temperature, respectively, and the Stokes–Einstein theory,<sup>23</sup>

$$D_{AB} = kT/6\pi R_A \eta_B \quad (2)$$

where  $D_{AB}$ ,  $R_A$ ,  $\eta_B$ , and  $k$  are the diffusion coefficient, domain size of thermoplastics, viscosity of E-51, and Boltzman constant, respectively, the elevated curing temperature  $T$  lowers the viscosity  $\eta$ , and, at the same time, increases the diffusion coefficient  $D_{AB}$ . As a result, the mobility of E-51 monomers will be greatly enhanced.

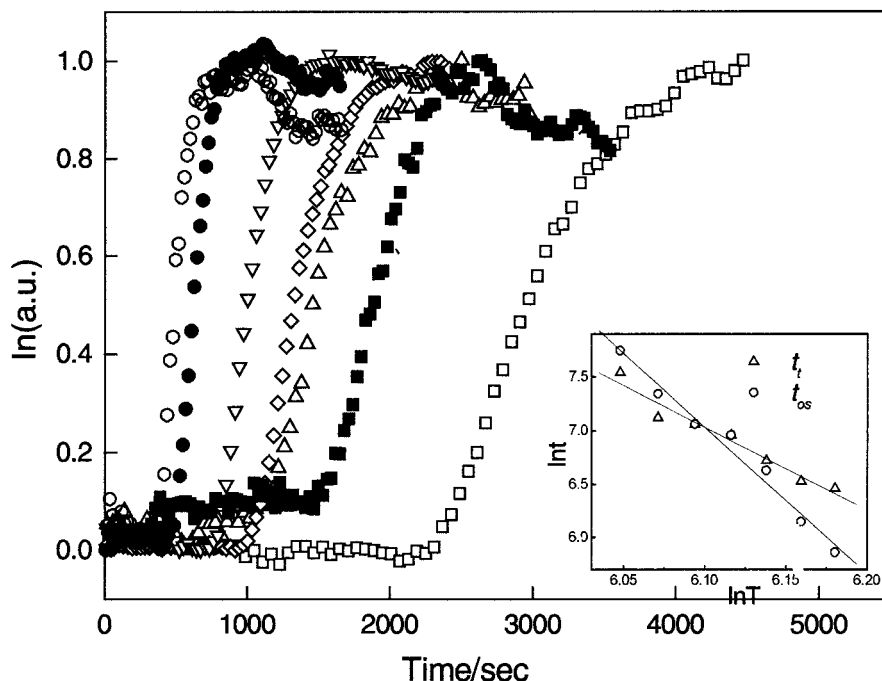
It is noted that reaction-induced phase separation is a competitive process between the curing reaction and phase separation. There exists a relationship

$$K = K_{sp}/K_c \quad (3)$$

where  $K_{sp}$ ,  $K_c$ , and  $K$  are the phase-separation rate, curing reaction rate, and ratio of  $K_c$  to  $K_{sp}$ . When  $K \rightarrow \infty$ , equilibrium is instantaneously reached, and if  $K \rightarrow 0$ , no phase separation can be observed.<sup>11</sup> The actual  $K$  value, which is located within these two critical values depends on whether phase separation or curing prevails.

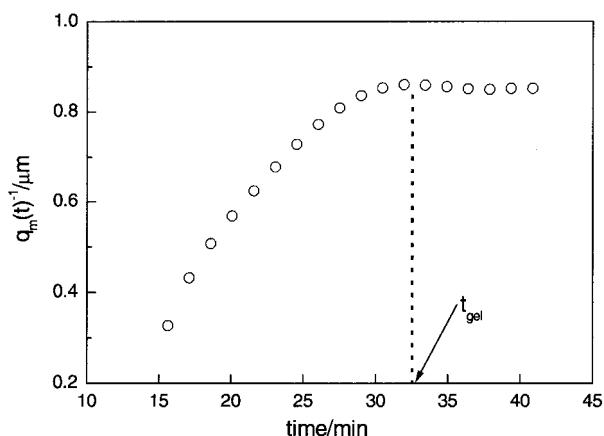
Figure 5 shows that under the experimental temperature range from 150 to 210°C the light-scattering intensity increases exponentially with curing and finally approaches a maximum after different induction periods. With increase of  $T$ , the curing proceeds rapidly and phase separation occurs earlier. Here, we define  $t_{on}$  and  $t_{ed}$  as the start and the end of the time for phase separation, respectively. Consequently, the time period of phase separation  $t_t$  is given as  $t_t = t_{ed} - t_{on}$ . The inlay shows that both  $t_{on}$  (the line with the circle symbol) and  $t_t$  (the line with the square symbol) decrease linearly with the curing temperature and  $t_t$  decreases more slowly. The reason for different  $t_{on}$  can be ascribed to the viscosity effect on the mobility of the epoxy monomer since no phase separation occurs at that time. But, at higher temperature, the greatly enhanced mobility of epoxy chains simultaneously speeds up the curing reaction of epoxy and the phase separation, and then the curing reaction prevails over the phase separation, resulting in a more slowly decreasing  $t_t$ .

Figure 6 gives the relationship between the domain size and the curing time for E-51/PEI/PC (100/10/10) isothermally cured at 180°C with DDS (30 phr) as a curing agent. The fact that



**Figure 5** Time dependence of  $I_n$  for E-51/PEI/PC (100/10/10) system isothermally cured with DDS (30 phr) at various temperature of ( $\square$ ) 150, ( $\blacksquare$ ) 160, ( $\triangle$ ) 170, ( $\diamond$ ) 180, ( $\nabla$ ) 190, ( $\bullet$ ) 200, and ( $\circ$ ) 210°C. The inlay is temperature-dependent on  $t_{on}$  and  $t_t$ .

during curing the domain size continually increases, approaches the maximum, then remains almost unchanged suggests that further domain growth was suppressed by the curing. Here, as shown in Figure 6, we define the  $t_{gel}$  as the gelation time at which the curing system changes from a viscous liquid into a stagnant gel and then the structure of the system is nearly fixed. After  $t_{gel}$ , the curing proceeds further with a slight

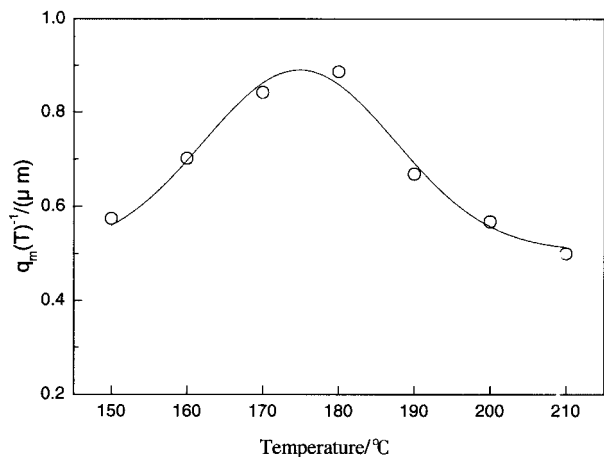


**Figure 6** Time dependence of domain size for E-51/PEI/PC (100/10/10). System was isothermally cured with DDS at 180°C.

change in the composition between thermoplastic-rich and E-51-rich regions until equilibrium morphology is reached. According to phase-transition theory,<sup>24</sup> the domain size is controlled by the thermodynamics and meets the relationship given by  $R_m \propto q_m(t)^{-1}$ , in which  $R_m$  is the typical domain size of the curing system. Therefore, we can qualitatively characterize the domain size with  $q_m(t)^{-1}$ . The temperature dependence of domain sizes, as shown in Figure 7, reveals that when the temperature is lower than 180°C the domain size increases with the curing temperature, but at higher than 180°C, the domain sizes decrease. This can be attributed to the different temperature sensitivity of the diffusion rate  $D_{AB}$  and the curing reaction rate  $K_c$ . When the curing temperature is lower than 180°C,  $D_{AB}$  is more sensitive to increase of the temperature, resulting in an increasing domain size. Above 180°C,  $K_c$  is more sensitive to the change of temperature. As a result, the domain sizes appeared smaller because further domain growth was suppressed under rapid curing.

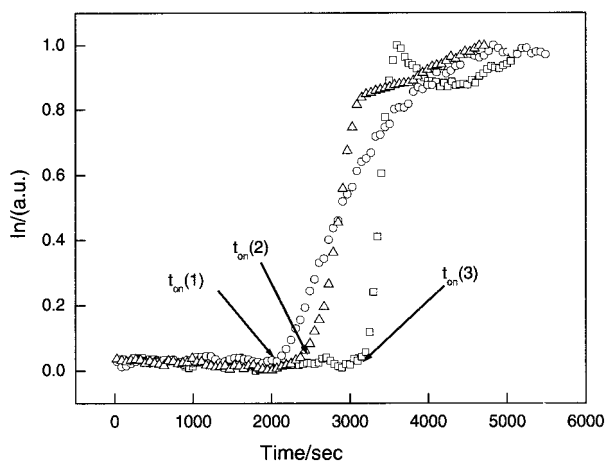
#### Composition Influence on Phase Separation

The engineering thermoplastics at various contents have different influence on the phase separation.

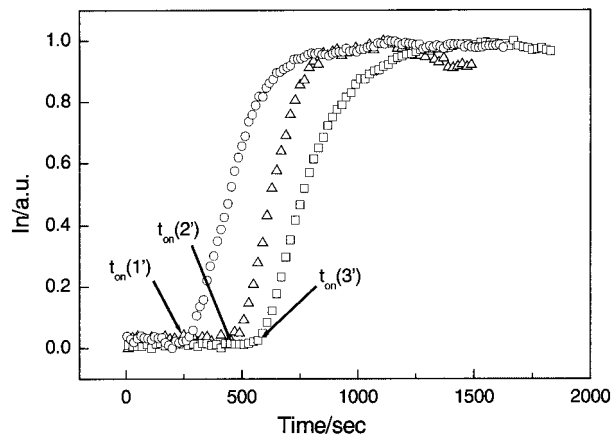


**Figure 7** Temperature dependence of typical domain size for E-51/PEI/PC (100/10/10) system isothermally cured with DDS (30 phr).

ration of the E-51 curing systems. Figure 8 gives the relationship of  $I_n$  and the curing time for the systems with various contents of PEI, isothermally cured at 150°C. It was found that the delay of  $t_{on}$ , caused by the increase of PEI content, is due to the concentration dilution of E-51 monomers and DDS. Even though the addition of PEI also increased the viscosity of the system,  $D_{AB}$  is still believed to be the dominant factor leading to the ranking of  $t_{on}(1) < t_{on}(2) < t_{on}(3)$  as compared with  $K_c$ . On the other hand, it is emphasized that this process speeds up with increase of the PEI content. Additionally, when examining the influence of PC incorporation into E-51/PEI/DDS on  $I_n$



**Figure 8** Relationship between  $I_n$  and curing time for various E-51/PEI systems isothermally cured with DDS (30 phr) at 150°C: (○) 100/10; (△) 100/20; (□) 100/30.



**Figure 9** Relationship between  $I_n$  and curing time for various E-51/PEI/PC systems isothermally cured with DDS (30 phr) at 150°C: (○) 100/10/0; (△) 100/10/5; (□) 100/10/10.

and  $t_{on}$ , we found that  $t_{on}$  appears earlier with increase of the PC content in the case where the content of E-51 and PEI remained constant, resulting in the rank of  $t_{on}(1') < t_{on}(2') < t_{on}(3')$ , as shown in Figure 9. The reason for this is that at lower incorporation (<20 phr) PC usually has a promoting effect on the curing reaction of the E-51 monomers<sup>2</sup> and can interact with E-51 or the curing agent DDS or else the newly formed network through hydrogen bonding following a special mode, that is, an *in situ* curing mechanism. According to this mechanism, we believe that the reaction between epoxide and amine groups takes place along the PC chains. Therefore, the curing reaction is accelerated and results in earlier phase separation.

## CONCLUSIONS

It was proved experimentally that the reaction-induced phase-separation mechanism and morphology evolution in the curing thermoplastic (PEI and PC)-modified E-51 system can be interpreted in terms of the phase-separation behavior through SALLS measurement. In the reaction-induced curing system, there exists a complicated competition between the phase separation and curing reaction of the E-51 matrix, which determines the morphology and final properties of the matrix networks. For a given thermosetting system incorporated within the thermoplastic component, two main factors control the final morphology of the blends, that is, thermodynamics

and the kinetics of phase separation and the curing reaction. Through controlling the curing temperature and compositions, we can regulate the  $\eta_B$  and  $D_{AB}$  for the purpose of controlling  $K_{sp}$  and  $K_c$ .

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