

## Rheological behavior during the phase separation of thermoset epoxy/thermoplastic polymer blends

Hongkyeong Kim and Kookheon Char\*

*School of Chemical Engineering, Seoul National University  
San56-1, Shinlim-dong, Kwanak-gu, Seoul 151-742, KOREA*

(Received January 20, 2000; final revision received May 19, 2000)

### Abstract

Rheological behavior of thermoset/thermoplastic blends of epoxy/polyethersulphone (PES) was monitored during curing of the epoxy resin. During the isothermal curing of the mixture, a fluctuation in viscosity just before the abrupt viscosity increase was observed. This fluctuation is found to be due to the phase separation of PES from the matrix epoxy resin during the curing. The experimentally observed viscosity fluctuation is simulated with a simple two phase suspension model in terms of the increase in domain size. The viscosity profiles obtained experimentally at different isothermal curing temperatures are in good agreement with the predictions from the simple model taking into account the viscosity change due to the growth of PES domain and the network formation of the epoxy matrix.

**Keywords:** epoxy/polyethersulphone/reaction induced phase separation/suspension model/rheology

Studies on the mechanism of simultaneous curing and phase separation have been a topic of interest for many years (Riew and Kinloch, 1992) due to the fact that toughened thermosets have been widely used in many applications but the mechanism is still not well understood due to the complexity of the system. Many studies on the toughened thermosets have mainly focused on the structure-property relationship and the toughening mechanism by Riew and Kinloch (1992) and by Kiefer and coworkers (1996), and some on the phase separation kinetics by Kiefer and coworkers (1996), by Kim and Kim (1991), by Lee and Kyu (1990), and by Kim and coworkers (1993). Present study focuses on the effect of phase separation on rheological properties of thermoplastic toughened epoxy system before gelation.

The toughened epoxy system employed in this study consisted of an epoxy (diglycidyl ether of bisphenol A (DGEBA), YD128, Kukdo Chemical Co.), a curing agent (4, 4'-diaminodiphenylmethane (DDM), Aldrich), and a thermoplastic modifier (polyethersulphone (PES), Ultrason E6020, BASF). The epoxy equivalent weight of YD128 was 184 ~ 190. The amounts of YD128 and DDM were determined to assure stoichiometric mixture. PES was purified by reprecipitation before use, and its weight average molecular weight was 58,000.

The change of complex viscosity of the mixtures during isothermal curing was monitored by rheometrics mechani-

cal spectroscopy (RMS 800, Rheometrics Inc.) with disposable parallel stainless steel plates of 10 mm diameter, and the gap height between parallel plates was set at 0.5 mm. To obtain the Newtonian region of initial mixtures, preliminary frequency and strain sweeps were carried out. The curing experiments were performed at a frequency of 20 rad/sec and a strain of 25%, and the initial mixtures showed the Newtonian behavior with this condition. Fig. 1 shows the time change of complex viscosity of DGEBA/DDM stoichiometric mixtures with 10 wt% PES at several isothermal curing temperatures. It is typical in the viscosity profile during the isothermal curing of toughened epoxy system that initially low viscosity increases with curing reaction (Riew and Kinloch, 1992). We note, however, from Fig. 1 that there exist fluctuations in viscosity just before the abrupt viscosity increase, which is believed to be due to the phase separation of the toughened epoxy mixture induced by the curing reaction. This type of viscosity behavior has also been noticed in prior works by Riew and Kinloch (1992) and Kim and Kim (1991), but was not addressed in detail.

The phase separation induced by the curing reaction was observed by using both small angle light scattering (SALS) and scanning electron microscopy (SEM). A 30 mW He-Ne laser with wavelength  $\lambda = 632.8$  nm was used as the incident light source for SALS experiment. The scattered light intensity was measured with the photomultiplied tube (PMT) connected to the optical fiber which was rotated with a stepping motor at the measuring angle from 1° to 40° within 10 seconds. The incident and transmitted light inten-

\*Corresponding author: khchar@plaza.snu.ac.kr  
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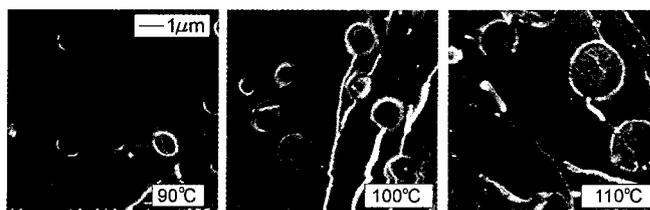
sities were measured with photodiodes to correct the observed scattered light intensity. Fig. 2(a) shows the SEM photographs of epoxy/PES (90/10 by weight) mixtures fully cured at three different temperatures mentioned in Fig. 1, and Fig. 2(b) represents one example of a sample isothermally cured at 110°C. In this figure, the correlation length,  $\Lambda$ , which is determined from the maximum scattering wave vector  $q_m$  as  $\Lambda = 2\pi/q_m$ , is known to be proportional to the domain size as reported by Kim and Kim (1991), by Lee and Kyu (1990), and by Kim and coworkers (1993), and the domain size is corrected from SEM photograph of a sample in fully cured state as shown in Fig. 2(a). At an isothermal curing temperature of 110°C, as shown in Fig. 2(b), the complex viscosity gradually increases with time due to the increase in molecular weight of epoxy matrix and it suddenly decreases when the PES domain size grows larger than a critical value. It is also worthwhile to note that the start and the end points of domain growth completely embraces the viscosity fluctuation implying that the domain growth due to phase separation has a profound effect on the viscosity of the mixture. The viscosity then abruptly increases due to the extensive network formation of the epoxy matrix. During the curing of toughened epoxy system, the initially homogeneous epoxy/PES mixture usually separates into two phases, epoxy rich and epoxy lean phases, due to the increase in the epoxy molecular weight. We believe that the curing of the DGEBA/DDM/PES system goes through three steps as indicated in Fig. 2(b); first, epoxy molecules combine one another (curing) in a homogeneous mixture (step I) before the onset of phase separation due to the molecular weight increase of the matrix epoxy (step II). After completion of the phase sep-

aration, the epoxy molecules still grow to an infinite network (step III).

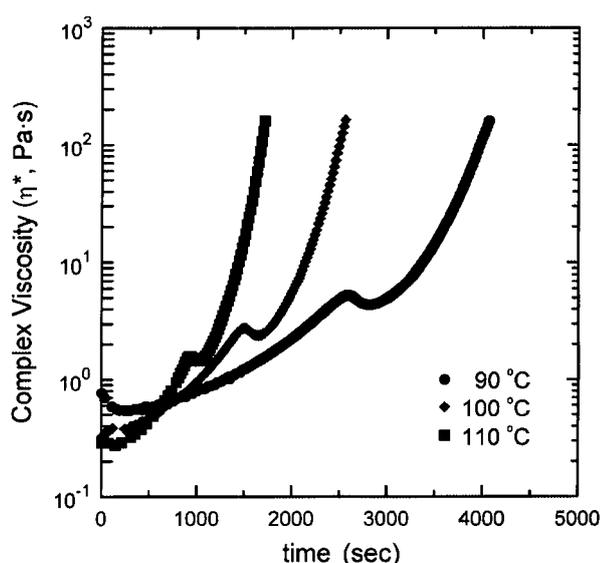
The domain phase separation will affect rheological properties of the toughened epoxy system because the mixture evolves from a homogeneous state to a heterogeneous one. The observed viscosity fluctuation can be explained in terms of the increase in domain size during phase separation. In order to estimate the viscosity of a heterogeneous system, many models have been suggested by Choi and Schowalter (1975), by Russel and coworkers (1989), by Yanovsky (1993), by Graebling and coworkers (1993), and by Lee and Park (1994). In this study, an empirical equation reported by Yanovsky (1993) for a homogeneous polymer mixture (equation (1)) before phase separation and a simple two phase suspension model (equation (2)), which is proposed by Graebling and coworkers (1993), applicable after phase separation were employed to estimate the mixture viscosity:

$$\ln \eta_{med} = W_{epoxy} \ln \eta_{epoxy} + W_{PES} \ln \eta_{PES} \quad (1)$$

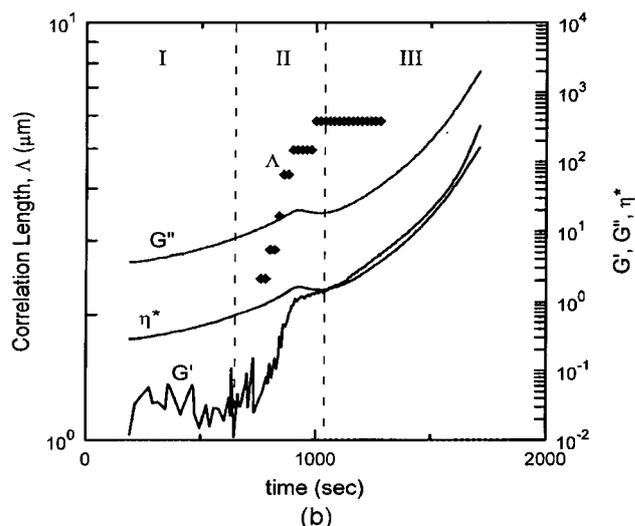
$$G^*(\omega) = G_{med}^*(\omega) \frac{1+3\phi H(\omega)}{1-2\phi H(\omega)} = i\omega \eta^*(\omega) \quad (2)$$



(a)



**Fig. 1.** Semi-log plot of complex viscosity profiles of DGEBA/DDM stoichiometric mixtures with 10 wt% PES at different isothermal curing temperatures.



(b)

**Fig. 2.** (a) Scanning electron micrographs of phase-separated mixtures fully cured at 90, 100, and 110°C and (b) Change of domain correlation length and rheological properties of DGEBA/DDM/PES mixture with 10 wt% PES isothermally cured at 110°C as a function of time.

where

$$H = \frac{4\left(\frac{\alpha}{R}\right)(2G_{\text{med}}^* + 5G_{\text{PES}}^*) + (G_{\text{PES}}^* - G_{\text{med}}^*)(16G_{\text{med}}^* + 19G_{\text{PES}}^*)}{40\left(\frac{\alpha}{R}\right)(G_{\text{med}}^* + G_{\text{PES}}^*) + (2G_{\text{PES}}^* + 3G_{\text{med}}^*)(16G_{\text{med}}^* + 19G_{\text{PES}}^*)}$$

where  $w_{\text{epoxy}}$  and  $w_{\text{PES}}$  are the weight fractions of epoxy and PES in homogeneous medium, and  $\eta_{\text{epoxy}}$  and  $\eta_{\text{PES}}$  are the viscosities of epoxy at each cured state and PES, respectively.  $\phi$  is the total volume fraction of domain in the phase separated mixture,  $\eta_{\text{med}}$  is the viscosity of the homogeneous medium, and  $\alpha$  is the interfacial tension between epoxy rich matrix and PES rich domain which is assumed to be independent of local shear and interfacial area change. Typical values of the interfacial tension are  $10^{-3} \sim 10^{-2}$  N/m for blends of molten polymers as reported by Graebing and coworkers (1993). Since the interaction parameter between epoxy and PES and the molecular weight of epoxy are hardly obtainable at each cured states, the compositions in the phase separated domains and matrix were calculated with an assumption that the phase separated domains are pure PES, and thus  $\eta_{\text{domain}}$  was substituted with  $\eta_{\text{PES}}$ . The viscosity of epoxy rich phase (medium,  $\eta_{\text{med}}$ ) after phase separation was also estimated in equation (1) with increasing  $\eta_{\text{epoxy}}$ . Since the viscosity of PES cannot be measured at the experimental temperatures which are far below the glass transition temperature of PES, we estimate  $\eta_{\text{PES}}$  from equation (1) with various compositions at uncured state. The equation (1) is a simple empirical equation which will be valid only a limited range of composition. The valid composition range of the equation (1) can be obtained through estimated  $\eta_{\text{PES}}$ : The estimated value of  $\eta_{\text{PES}}$  stays nearly constant as  $3 \times 10^{11}$  Pa·s at 110°C until the weight fraction of PES in DGEBA/DDM matrix reaches 0.1. When the PES weight fraction in DGEBA/DDM exceeds 0.1,  $\eta_{\text{PES}}$  deviates from the constant value and shows the increase in  $\eta_{\text{PES}}$ , presumably due to the elastic effect of long PES chains. In this case, the empirical equation (1) is no longer valid. We, however, believe that this empirical equation is still valid in estimating the viscosity of the homogeneous mixture since the concentration of PES in the homogeneous medium throughout phase separation does not exceed 10 wt% and, at the same time, the viscosity of DGEBA/DDM remains fairly low when the viscosity fluctuation is observed.

Information on phase separation kinetics such as domain size growth and the number of domains was obtained from both SALS and SEM during phase separation as shown, for one example, in Fig. 2, and used to calculate  $\phi$  in equation (2) with the assumption of uniform spherical PES domains. Since the matrix epoxy resin initially shows the Newtonian behavior with low viscosity at a given experimental condition and the elastic effect on rheological properties of the

medium is smaller than the viscous effect before gelation which is generally determined from the crossover between storage modulus ( $G'$ ) and loss modulus ( $G''$ ), we assume that the elastic effect on rheological properties of the medium is negligible and that only PES domains show the viscoelastic behavior which is described by a simple Maxwell model:

$$G_{\text{med}}^* = i\omega\eta_{\text{med}} \quad (3)$$

$$G_{\text{PES}}^* = \frac{i\omega\eta_{\text{PES}}}{1 + i\omega\tau_{\text{PES}}}$$

where  $\tau_{\text{PES}}$  is the characteristic relaxation time for PES domain,  $\omega$  is the angular frequency of oscillatory shear, and  $i$  is  $\sqrt{-1}$ . Fig. 3 shows the estimated viscosity profiles calculated from equations (1) through (3) at zero-shear state ( $\omega = 0$ ) and no interfacial tension ( $\alpha = 0$ ). In this Figure, the viscosity of matrix (or, in step I, the homogeneous mixture) was obtained by using equation (1) during the whole curing procedure while the viscosity of the mixture was estimated by using equation (2) with the viscosity of matrix obtained from equation (1). This figure is in good agreement with the experimental viscosity behavior of DGEBA/DDM/PES mixtures during the simultaneous isothermal curing and phase separation before gelation. We also note that these calculated results agree with a viscoelastic model of immiscible blends proposed by Choi and Schowalter (1975) if the elastic effect is negligible, and a model proposed by Lee and Park (1994) with small values of interfacial tension. Shear and interfacial tension effect on the complex viscosity were also tested with a few oscillatory

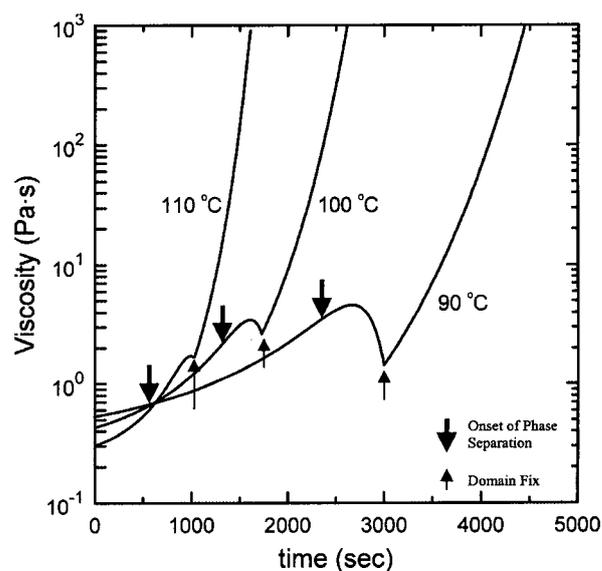
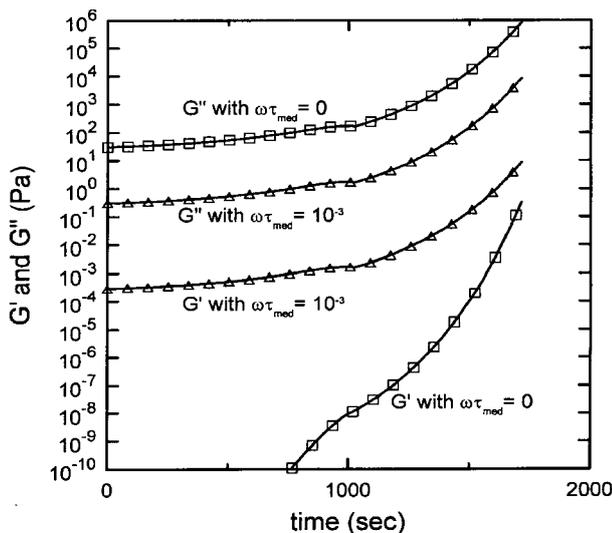


Fig. 3. Viscosity profiles of DGEBA/DDM stoichiometric mixtures with 10 wt% PES calculated using a suspension model (equations (1) through (3) in the text) at different isothermal curing temperatures.

frequencies ( $\omega = 0, 10^2$ , and  $\infty$ ) and three values of interfacial tension ( $\alpha = 0, 10^{-3}$ , and  $1 \text{ N/m}$ ), and it was noted that the complex viscosity profiles calculated with different frequencies and interfacial tensions are almost overlapped with the profiles shown in Fig. 3: the complex viscosity at  $\omega = \infty$  is slightly lower than that with  $\omega = 0$  in the viscosity fluctuation region and the complex viscosity after completion of the phase separation slightly decreases with increasing interfacial tension. From these calculations, we are convinced that the complex viscosity is hardly affected by applied oscillatory shear as well as interfacial tension since the matrix viscosity is so lower than that of PES domains that the shear and interfacial tension effects from the phase separated PES domains has little effect on the rheological properties in the viscosity fluctuation region of the epoxy/PES blend.

We noticed, however, from the calculations that storage and loss moduli depend on shear; they increase as increasing  $\omega\tau_{\text{PES}}$ . The storage modulus is, however, still lower than the loss modulus with all the frequencies. Curves with square symbols in Fig. 4 are the calculated storage and loss moduli at  $\omega\tau_{\text{PES}} = 10^2$ ,  $\alpha = 0.1$ , and  $\omega\tau_{\text{med}} = 0$ . Although the order of magnitude of the storage modulus is much lower than the experimental value given in Fig. 2(b), the estimated storage and loss moduli qualitatively explain the experimental results fairly well in that the loss modulus shows a fluctuation during the phase separation of PES and the initially low storage modulus of the mixture increases abruptly at the time of phase separation. The huge difference between the estimated and the experimental storage moduli is thought to be due to the assumption that the matrix is a purely viscous liquid. In order to take into



**Fig. 4.** Time dependent dynamic moduli ( $G'$  and  $G''$ ) of epoxy/PES (90/10 by weight) mixtures calculated using the Palierne model at  $110^\circ\text{C}$ ;  $\alpha = 0.1$ ,  $\omega\tau_{\text{PES}} = 10^2$ , and  $\omega\tau_{\text{med}} = 0$  (square) and  $10^{-3}$  (triangle).

account the viscoelastic effect of the matrix, a simple Maxwell model is required:

$$G_{\text{med}}^* = \frac{i\omega\eta_{\text{med}}}{1 + i\omega\tau_{\text{med}}} \quad (4)$$

where  $\tau_{\text{med}}$  is the characteristic relaxation time of the matrix. Since the matrix epoxy contains a reactive component,  $\tau_{\text{med}}$  is not a constant but a function of curing time. It is difficult to obtain  $\tau_{\text{med}}(t)$  experimentally since curing reaction is generally too fast for frequency sweep to obtain  $\tau_{\text{med}}$  accurately. In this situation, the order of magnitude of the storage modulus can only be analyzed at the time of phase separation by using a few fixed  $\tau_{\text{med}}$  values. If  $\tau_{\text{med}}$  is assumed to be zero, the matrix is a purely viscous fluid, and the estimated dynamic moduli are the curves with square symbols in Fig. 4. We note from Fig. 4 that the storage modulus increases with increasing  $\tau_{\text{med}}$  (i.e., increasing elasticity). The curves with triangle symbols in Fig. 4 are the dynamic moduli estimated with  $\omega\tau_{\text{med}} = 10^{-3}$ . We note that the difference in the order of magnitude between  $G''$  and  $G'$  is remarkably reduced and comparable to the experimental results shown in Fig. 2(b) even though the overall shape of the curve is not so important since a constant value of  $\tau_{\text{med}}$  is assumed. It should, however, be reminded that there is an abrupt change in the storage modulus at the beginning of phase separation as shown in Fig. 2(b), although  $G'$  value still remains much lower than  $G''$  value during the phase separation.

In summary, the viscosity fluctuation upon phase separation of a thermoplastic polymer, PES, from an epoxy matrix is identified and shown to be dependent on isothermal curing temperature. The viscosity profiles experimentally obtained at different isothermal curing temperatures are in good agreement with the predictions from a simple rheological model taking into account the viscosity change due to the domain phase separation. The storage and loss moduli calculated from the model, however, cannot estimate the experimental results fairly well because of difficulty in accurately estimating the matrix relaxation time as a function of curing time at a given temperature.

### Acknowledgment

This work was supported by the Korea Science and Engineering Foundation (KOSEF) under Grant 97-0502-0901-5. Financial aid from the Korean Ministry of Education through the Brain Korea 21 Program is also gratefully acknowledged.

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