

# Cure Kinetics and Mechanical Properties of the Blend System of Epoxy/Diaminodiphenyl Sulfone and Amine Terminated Polyetherimide-Carboxyl Terminated Poly(butadiene-co-acrylonitrile) Block Copolymer

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**Abstract**—The cure kinetics of blends of epoxy resin (4,4'-tetraglycidyl diaminodiphenyl methane; TGDDM)/curing agent (diaminodiphenyl sulfone; DDS) with ATPEI (amine terminated poly-etherimide) - CTBN (carboxyl terminated poly (butadiene-co-acrylonitrile)) block copolymer (AB type) were studied using differential scanning calorimetry under isothermal conditions to determine the reaction kinetic parameters such as activation energy and reaction constants. Final cure conversion decreased with increasing amount of AB in the blends. A diffusion controlled reaction was observed as the cure conversion increased, and the curing reaction was successfully analyzed by incorporating the diffusion control term in the rate equation for the epoxy/DDS/AB blends. The fracture toughness was improved to about 350% compared to that of the unmodified resin at 30% of AB block copolymer. This is attributed to the formation of co-continuous morphology between the epoxy phase and AB block copolymer phase. By increasing the amount of AB, the modulus of the cured blends decreased, which was due to the presence of CTBN rubbery phases.

Key words: Epoxy, Amine, AB Block Copolymer, Kinetics, Toughness

## INTRODUCTION

In recent years, to improve the toughness of epoxy resin in order to meet highly qualified structural and mechanical component applications, significant works on epoxy resin modification with both functionalized and non-functionalized thermoplastics have been undertaken. Epoxy/polyetherimide (PEI; Ultem 1000) and epoxy/polyethersulfone (PES; Udel) blends have been used to investigate mechanical properties of modified epoxy resin especially in toughness, while retaining high mechanical strength [Bucknall and Gilbert, 1989; Hourston et al., 1992; Alig and Jenniger, 1998]. In these cases, the increase of toughness was not significant. Much work [Wise et al., 2000; Chen et al., 1994] has been done on morphologies of the separated phases in the epoxy/carboxyl terminated poly(butadiene-co-acrylonitrile) (CTBN) and epoxy/amine terminated poly(butadiene-co-acrylonitrile) (ATBN) blends. Impact strength of these cured blends increased significantly, but mechanical properties such as modulus and tensile strength decreased by the presence of rubbery phases. Most of the studies on thermoset/thermoplastic blends have dealt with thermoplastics, such as commercial grades of PEI, PES, polysulfone, nylon 610, polyimide, etc., as a modifier, which is incompatible with the epoxy resin in cured blends [Oyanguren et al., 1998; Su and Woo, 1995; Bonnet et al., 1996, 1999; Zhong and Guo, 1999; Agag and Takeichi, 1999]. It has been reported that complete miscibility is not desired for increasing the toughness in cured thermoset/thermoplastic blends.

In most studies of epoxy/PEI blends, amine curing agents have been used to study the cure kinetics and morphologies [Varley et al., 2000; Mimura et al., 2000; Rajagopalan et al., 2000]. Most studies of cure kinetics of thermoset/thermoplastics blends have been per-

formed by differential scanning calorimetry (DSC), and in some studies, Fourier-transform infrared spectroscopy with attenuated total reflectance (ATR-FTIR) has been used to estimate the reaction parameters [Girard-Reydet et al., 1999]. Kinetics models for cure reactions and the equations proposed for kinetics models are commonly based on the general rate equation of the *n*th order [Rayn and Dutta, 1979]. In DSC analysis, both the isothermal and the dynamic heating experimental modes have been used extensively to determine the cure kinetic models and their parameters for the neat epoxy and epoxy/thermoplastic blends, which are mostly cured with an amine curing agent. In the epoxy system, the cure reactions based on 4,4'-tetraglycidyl diaminodiphenyl methane (TGDDM) are typically characterized by an initial accelerated reaction, due to autocatalysis in the early stages of the reaction, while in the latter stages a decrease in the reaction rate is shown by the onset of gelation and crosslinking, due to the cure reactions becoming diffusion controlled [Lopez et al., 2001].

For the purpose of improving fracture toughness of epoxy resin with minimized reduction of the modulus, a functionalized thermoplastic-rubber diblock copolymer modifier was blended. In this study, the cure kinetics of an epoxy system containing 4,4'-tetraglycidyl diaminodiphenyl methane (TGDDM) and diamino diphenyl sulfone (DDS) as the curing agent, and their blends with amine terminated polyetherimide (ATPEI) - CTBN (AB type) block copolymer, i.e., named in this paper as a AB block copolymer, were studied. The amount of AB block copolymer was 10, 20, 30 wt% on the basis of the added amount of TGDDM and AB block copolymer. The contribution of diffusion to the cure kinetics was also considered.

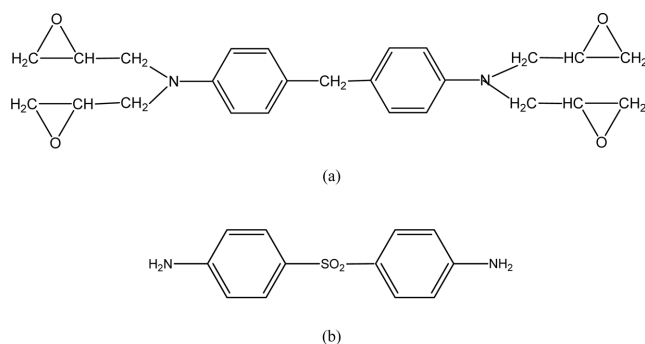
## EXPERIMENTAL

### 1. Materials

The epoxy system was based on commercial grade TGDDM

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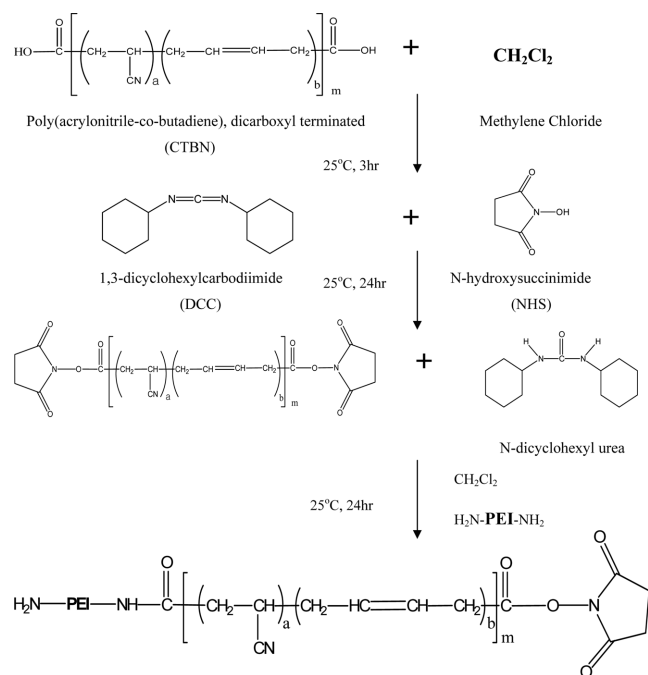


**Fig. 1.** Chemical structures of 4,4'-tetraglycidyl diaminodiphenyl methane (a) and diaminodiphenyl sulfone (b).

(Grade: LER-430, LG Chemical Co, Korea) with an average epoxy equivalent weight of 129.87 g/eq. The epoxy blends with AB block copolymer were cured with a curing agent, DDS, supplied by Aldrich Co. Methylene chloride was used as a solvent for AB block copolymer. The chemical structures of materials are shown in Fig. 1.

## 2. Synthesis of AB Block Copolymer

CTBN (Mn=3,500, CN=18%) was dissolved in methylene chloride and stirred in a flask. After that, for activating the carboxyl groups of CTBN, 1,3-dicyclohexylcarbodiimide (DCC) and N-hydroxysuccinimide (NHS) were added with a quantity of twice that of CTBN, stoichiometrically, at 0 °C. After one hour, when the precipitated matter was observed, laboratory synthesized ATPEI [Kim et al., 2003] dissolved in methylene chloride was added in the flask and stirred for 24 hr, and then, a brown and viscous solution was obtained. This solution was refined with a process of soxhleting and drying, and then, ATPEI-CTBN (AB block) copolymer could be obtained. The synthesis scheme of AB block copolymer is shown in Fig. 2.



**Fig. 2.** Synthesis of ATPEI-CTBN diblock copolymer.

## 3. Preparation of Blends and Curing Schedule for Specimens

Epoxy/AB block copolymer blended resin mixtures with 10, 20, and 30 wt% of AB block copolymer were prepared. First, AB block copolymer was weighed and dissolved completely in methylene chloride and the resulting polymer solution was then mixed with the epoxy resin at room temperature. The solvent in the mixture was vaporized in a circulation oven with an exhaust fan at room temperature, followed by removing the residual solvent in a hot vacuum oven for 2 days at 100 °C. Subsequently, 35 phr of DDS (=0.67 stoichiometric equivalent of epoxy) was slowly added, with continuous stirring, to the resin-AB block copolymer mixture in an oil bath at 180 °C. The mixture was poured into an aluminum mold and degassed under vacuum at 120 °C to remove air bubbles, and then, cured isothermally in an air circulating oven. The cure schedules for specimens employed in this study were as follows: 160 °C/3 hr+175 °C/2 hr+190 °C/3 hr+220 °C/6 hr.

## 4. Differential Scanning Calorimetry

A differential scanning calorimeter (Mettler Toledo DSC 822e, equipped with an intra-cooler and a DEC computer for data acquisition/analysis) was used for the isothermal cure experiments and data analysis. Prior to the DSC runs, the temperature and heats of reaction were calibrated by using indium and zinc standards. Isothermal cure reaction was conducted at three temperatures (160, 175, and 190 °C). The reaction was considered complete when the isothermal DSC thermo-gram leveled off to the baseline, which generally took approximately 3 hrs. The total area under the exothermal curve, which was based on the extrapolated baseline at the end of the reaction, was used to calculate the isothermal heat of cure,  $\Delta H_{iso}$ . After the cure reaction was completed in the calorimeter, the sample was cooled to -50 °C. To determine the residual heat of reaction,  $\Delta H_R$ , the samples after curing were scanned at 10 °C/min from -50 °C to 350 °C. The sum of both the isothermal heat ( $\Delta H_{iso}$ ) and residual heat ( $\Delta H_R$ ) of reaction was taken to represent the total heat of cure ( $\Delta H_T$ ). The degree of cure,  $\alpha$  (i.e., cure conversion), was determined on the basis of the following equation:

$$\alpha = \frac{\Delta H_{iso}}{\Delta H_T} \quad (1)$$

The cure reaction rates were obtained from the cure conversion data as a function of time by taking the derivative of  $\alpha$  with respect to time, i.e.,  $d\alpha/dt$ .

## 5. Morphology and Mechanical Properties

The morphology of specimens according to the compositions (10-30 wt%) was observed by SEM. Fractured sample was immersed in methylene chloride and sonicated in a bath for 1 hr, then dried completely before sputtering.

The critical stress intensity factor,  $K_{IC}$ , was obtained from three point bending tests performed on single edge notched bending specimens (SENB). A UTM (universal testing machine, INSTRON 4485) was used. The procedure proposed by ASTM D 5045 was strictly followed with a cross-head speed of 1.2 mm/min.  $K_{IC}$  was calculated as the mean values of at least five test samples.

## RESULTS AND DISCUSSION

### 1. Cure Conversion

The typical cure conversion is shown in Fig. 3(a), and the plot of

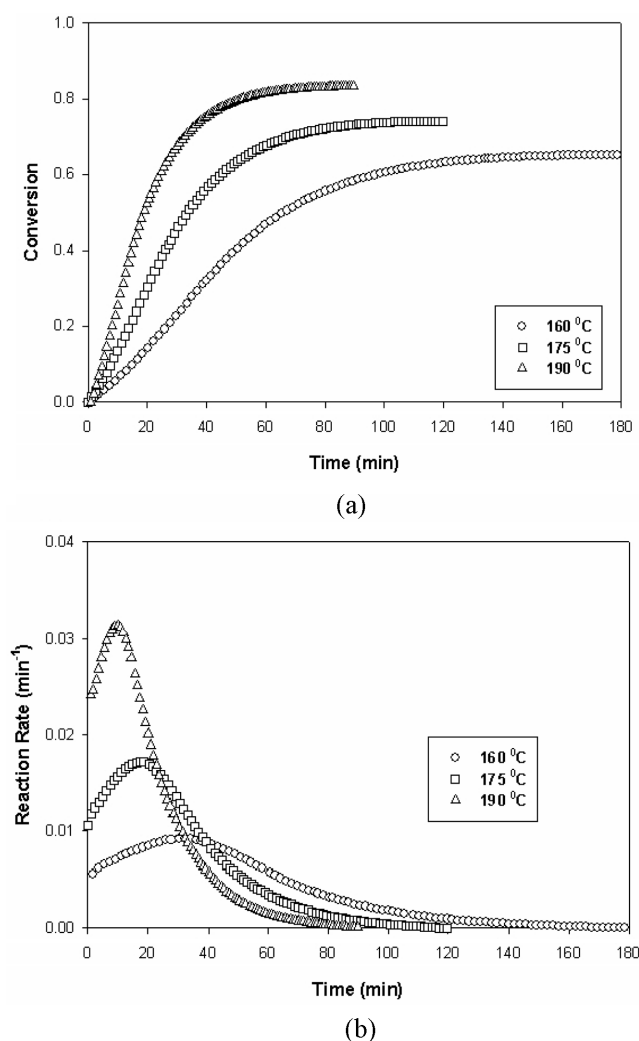


Fig. 3. Conversion vs. time curves (a) and conversion rate vs. time curves (b) for the epoxy/DDS/AB systems (AB 20 wt%).

the conversion rate versus time is shown in Fig. 3(b). After a strong increase in conversion in the early stages of the cure reaction, a retardation of the conversion gradually occurred as the blends matrix became vitrified and the cure reaction rapidly became diffusion controlled, as shown in Fig. 3(a). The rate curves shown in Fig. 3(b) were autocatalytic in nature, with the maximum rate of conversion occurring at the early stage of reaction, which is similar in behavior to that of other epoxy systems [Su and Woo, 1995; Varley et al., 2000; Lopez et al., 2001]. By increasing the curing temperature, the position of the maximum rate of conversion was shifted to the start of the reaction. As AB content increased, the final values of conversion decreased at the same cure temperature, indicating that diffusion control should be considered at lower values of conversion, comparable to that of the neat epoxy resin. As the cure temperature increased, the final conversion increased in all of the compositions of AB in the blend, as shown in Table 1.

As mentioned by Varley et al. [2000] this decrease in the final epoxy conversion with increasing thermoplastic content can be explained by the partitioning of epoxy resin in both the epoxy-rich phase and the thermoplastic-rich phase in the blends. Another possible way of explanation is the partitioning of the curing agent in both of the separated phases.

## 2. Isothermal Kinetics: The Autocatalytic Model with a Diffusion Control Factor

To consider the autocatalytic reaction where initial reaction rate of an autocatalytic reaction is not zero, Sourour and Kamal [1976] proposed the generalized expression Eq. (2).

$$\frac{d\alpha}{dt} = (k_1 + k_2 \alpha^m)(1 - \alpha)^n \quad (2)$$

where  $\alpha$  is the conversion,  $k_1$  and  $k_2$  are the rate constants,  $m$  and  $n$  are the kinetic exponents of the reactions, and  $m+n$  is the overall reaction order. The constant  $k_1$  was graphically calculated as the initial reaction rate at time zero, given by the intercept of plots of conversion rate versus time. The kinetic rate constants,  $k_1$  and  $k_2$

Table 1. Heats of reaction and final conversion of neat epoxy and with various contents of AB

Temperature (°C)	Isothermal enthalpy $\Delta H_{ISO}$ (kJ/mol)	Residual enthalpy $\Delta H_R$ (kJ/mol)	Total enthalpy $\Delta H_T$ (kJ/mol)	Final conversion $\alpha_f$
Epoxy/AB (0 wt%)				
160	397.62	171.98	552.86	0.6889
175	410.08	129.46	539.54	0.7601
190	485.05	91.65	576.70	0.8411
Epoxy/AB (10 wt%)				
160	330.32	169.13	499.45	0.6614
175	346.43	113.03	459.46	0.7539
190	382.93	69.36	452.29	0.8466
Epoxy/AB (20 wt%)				
160	306.70	163.87	470.57	0.6517
175	375.96	131.17	507.13	0.7413
190	384.20	77.27	461.47	0.8326
Epoxy/AB (30 wt%)				
160	265.60	149.27	414.87	0.6402
175	296.41	108.24	404.65	0.7325
190	315.00	72.24	387.24	0.8134

**Table 2. Kinetic constants of the autocatalytic model for epoxy/DDS/AB blend systems**

Temp. (°C)	m	n	m+n	k <sub>1</sub> (min <sup>-1</sup> )	k <sub>2</sub> (min <sup>-1</sup> )
Epoxy/AB (0 wt%)					
160	1.0110	2.5410	3.5520	0.0070	0.0563
175	1.0213	2.3883	3.4096	0.0183	0.1241
190	1.0012	2.0346	3.0358	0.0274	0.1688
Epoxy/AB (10 wt%)					
160	1.0179	3.1792	4.1971	0.0069	0.0834
175	1.4494	2.8137	4.0610	0.0208	0.2027
190	1.4115	2.3171	3.7286	0.0366	0.2611
Epoxy/AB (20 wt%)					
160	1.0100	3.4210	4.4310	0.0042	0.0995
175	1.3213	3.0072	4.3285	0.0120	0.2288
190	1.2194	2.4750	3.6944	0.0245	0.2404
Epoxy/AB (30 wt%)					
160	1.0898	3.7662	4.8560	0.0050	0.1052
175	1.5328	3.1938	4.7266	0.0173	0.2432
190	1.4628	2.5251	3.9879	0.0287	0.3605

are assumed to be constant at given temperature and to follow an Arrhenius temperature dependence.

To calculate the parameters in Eq. (2) from isothermal curve data, several methods have been proposed previously [Ryan and Dutta, 1979; Keenan, 1987]. In the present study, the reaction orders and the rate constants were calculated simultaneously by using a regression Wizard method in the program of Sigma Plot 2001, and the results are shown in Table 2. Activation energies and the frequency factors are determined by using the Arrhenius equation, for the dependence of the rate constants on the temperature.

Due to the vitrification of epoxy resin, the later stage of the reaction is virtually subjected to diffusion control. A rate equation with a diffusion control factor [Chem and Poehlein, 1987] is a semi-empirical equation based on free-volume considerations and has been proposed to explain the retardation of cure reaction in the later stage of the reaction. The diffusion control factor  $f(\alpha)$  can be expressed as follows:

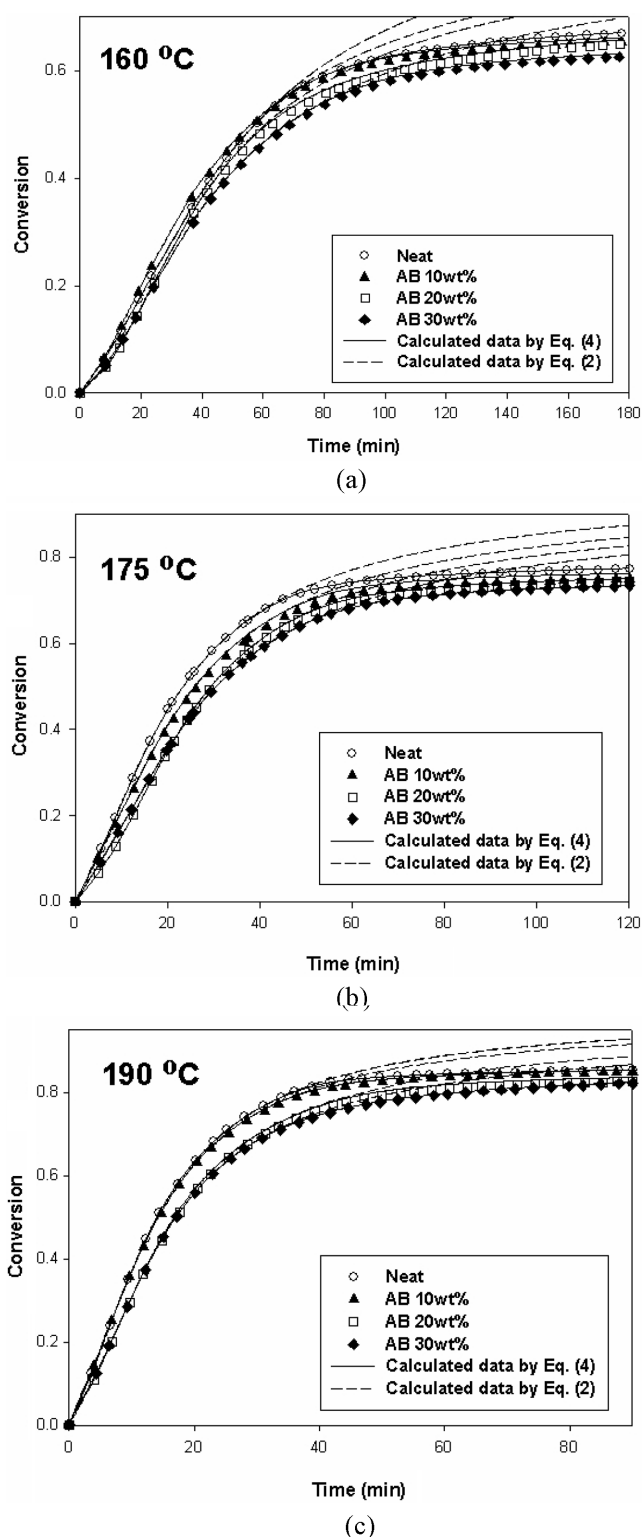
$$f(\alpha) = \frac{1}{1 + \exp[C(\alpha - \alpha_c)]} \quad (3)$$

Where  $C$  is a parameter of diffusion control and  $\alpha_c$  is a critical value of cure conversion. As  $\alpha$  reaches to  $\alpha_c$ , the cure reaction becomes controlled by diffusion. The final rate equation can be written as follows:

$$\frac{d\alpha}{dt} = \frac{(k_1 + k_2 \alpha^n)(1 - \alpha)^n}{1 + \exp[C(\alpha - \alpha_c)]} \quad (4)$$

In the present study, the conversion versus reaction time at 160, 175, and 190 °C of the epoxy/AB blends with various compositions of AB in the blends is shown in Fig. 4. The calculated solid and dashed lines were obtained from Eqs. (4) and (2), i.e., with and without the diffusion control factor, respectively. The calculated lines are compared with the experimental data. The % confidence of experimental data to Eq. (4) was in the range of 97.6–99.9%.

The autocatalytic nature of epoxy resin curing reaction, charac-



**Fig. 4. Degree of conversion vs. time plot for the cure process of epoxy/DDS/AB systems: experimental data (symbols) and calculated data (lines) at various isothermal conditions; at 160 °C (a), 175 °C (b), and 190 °C (c).**

terized by the maximum cure rate at the early stage of the reaction, is clearly evident even in the presence of AB in the blends. As cure conversion approaches to the final conversion, differences between

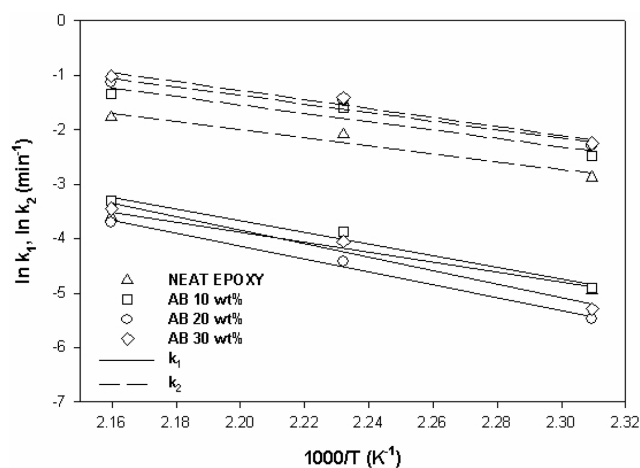
the model predictions without the diffusion control factor and the experimental data became pronounced, indicating that, at the later

**Table 3. Values of critical conversion and diffusion control parameter at different curing temperature for epoxy/DDS/AB systems**

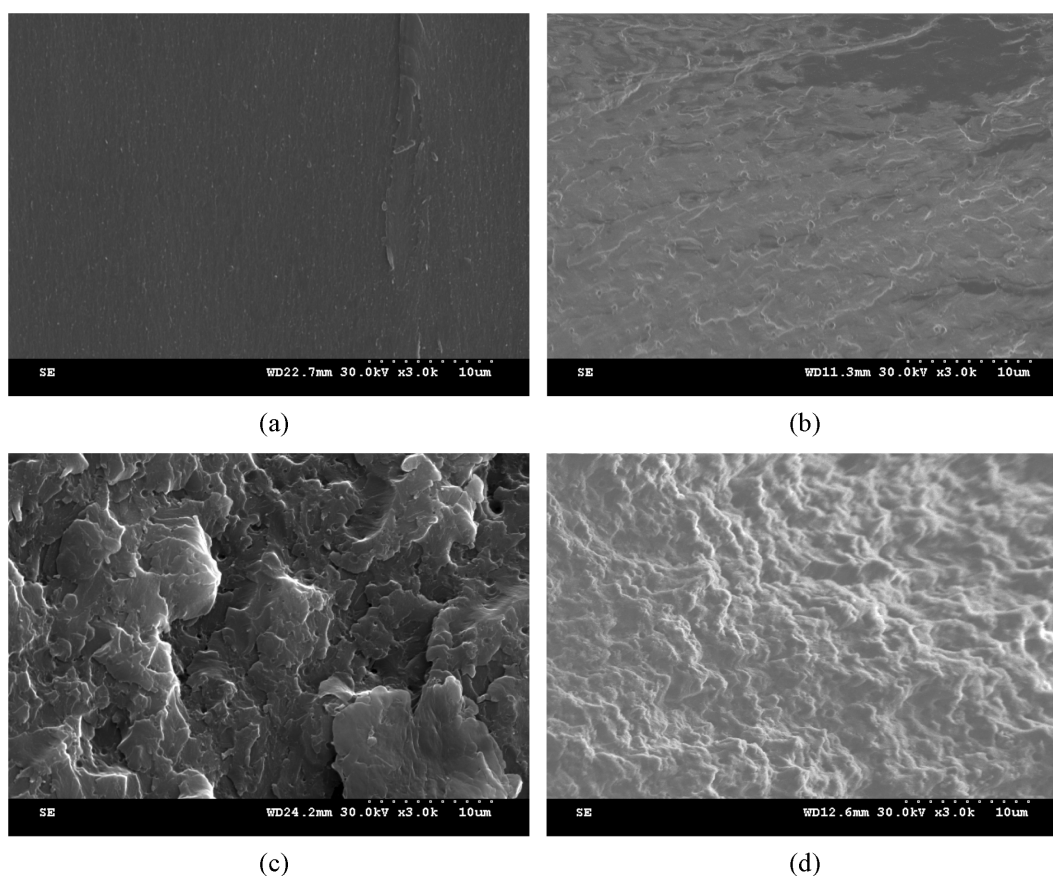
Temp. (°C)	$\alpha_c$	C	$\ln A_1$	$\ln A_2$	$E_{a1}$ (kJ/mol)	$E_{a2}$ (kJ/mol)
Epoxy/AB (0 wt%)						
160	0.6025	29.4179				
175	0.7295	55.8380	16.28	14.22	76.19	61.32
190	0.8247	96.8610				
Epoxy/AB (10 wt%)						
160	0.6162	43.2449				
175	0.7273	67.0958	20.00	15.33	88.22	62.91
190	0.8220	67.7762				
Epoxy/AB (20 wt%)						
160	0.6041	22.3260				
175	0.7122	53.2980	21.80	15.89	96.67	64.36
190	0.8087	65.2680				
Epoxy/AB (30 wt%)						
160	0.5965	44.0334				
175	0.6988	55.5426	23.27	16.89	101.07	67.74
190	0.7930	31.8300				

stage of reaction, the diffusion control factor in the rate expression should be considered as shown in Eq. (4). The differences also became pronounced when the curing temperature decreased.

All parameters in Eq. (4) can be obtained simultaneously by applying a non-linear regression method, and the calculated results are in Table 2. The overall reaction order,  $m+n$ , is in the range of 3.0-4.8 for the amine cured epoxy/AB blends with  $m$  fluctuating around 1.0 and  $n$  ranging from 2.0-3.7. In a previous study [Lopez



**Fig. 5. Arrhenius plot of the rate constants for isothermal runs.**



**Fig. 6. Scanning electron micrographs of the epoxy/DDS/AB systems (x3 K); neat epoxy (a), epoxy/DDS/AB 10 wt% (b), epoxy/DDS/AB 20 wt% (c) and epoxy/DDS/AB 30 wt% (d).**

et al., 2001], the values of  $m+n$ ,  $m$ , and  $n$  ranged from 2.2 to 4.5, about 1.0, and 1.3-3.5, respectively, for the TGDDM/DDS/poly(styrene-co-acrylonitrile) system. In the present study, values of  $n$  depend strongly on the curing temperature and the contents of AB. The values of  $n$  increased as the reaction rate decreased, which indicates that for the epoxy blends the reaction may be hindered by the phase separation. The term  $k_2\alpha''$  in Eq. (2) represents the initial autocatalytic reaction. As a result, the values of  $m$  are approximately 1.0 even though the AB content is increased, which indicates that neither the curing reaction nor the vitrification affects the initial autocatalytic reaction.

Levels of activation energy,  $E_{a,1}$  and  $E_{a,2}$ , can be calculated from the Arrhenius plot, which is shown in Fig. 5. The values of  $E_{a,1}$  and  $E_{a,2}$  obtained in this study for the neat amine-cured TGDDM epoxy were 76.19 and 61.32 kJ/mol, respectively, which agreed well with those reported in the literature [Su and Woo, 1995; Lopez et al., 2001]. The values of  $E_{a,1}$  and  $E_{a,2}$  increased significantly with the increased content of AB. This means that AB hinders the cure reaction.

### 3. Morphology

Fig. 6 shows SEM photographs of the epoxy-AB block copolymer matrix according to AB contents of (a) 0 wt%, (b) 10 wt%, (c) 20 wt%, and (d) 30 wt%. These micrographs are the fractured (after that etched with methylene chloride) surface of the epoxy/AB block copolymer. For the case of neat epoxy, the surface is smooth, but for epoxy/DDS/AB blends, sea island structure was obtained at 10 wt% and co-continuous structures at 20 wt% and 30 wt%. These may be due to the presence of CTBN rubbery phases and high molecular weight of the AB block copolymer.

### 4. Fracture Toughness and Mechanical Properties

In the case of introducing thermoplastics into the epoxy resin as the second phase, fracture toughness can be improved without sacrificing thermal properties and mechanical strength. It is well known that the degree of improvement of fracture toughness is strongly dependent on the morphology of the second phase. Fig. 7 shows the fracture toughness and modulus of the epoxy-AB block copolymer matrix according to AB content. The fracture toughness increased compared to neat epoxy resin. The value was  $2.21 \text{ MPa m}^{0.5}$  at AB 30 wt%, which is improved to about 350% compared to that of the neat epoxy.

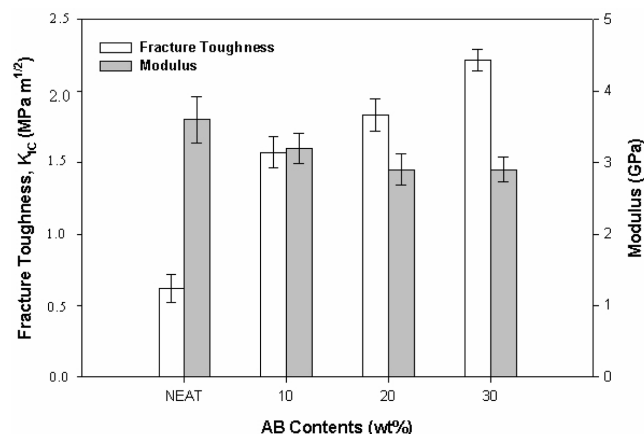


Fig. 7. Fracture toughness and modulus of the epoxy/DDS/AB systems.

The modulus was a little decreased according to the content of AB. This is due to the presence of CTBN rubbery phases.

### 5. Conclusion

An autocatalytic mechanism was observed for epoxy/DDS/AB block copolymer blends over a range of composition. A change in the reaction mechanism may affect the total heat of a reaction and the final cure conversions. By increasing the content of AB block copolymer in the epoxy system, a decrease in the total heat of the reaction and final cure conversion was observed.

A diffusion-incorporated autocatalytic model well fits the experimental data in both the early and the later stages of the reaction, since the diffusion control factor has been introduced into the autocatalytic model to correct the change in the reaction mechanism range of conversion near vitrification. At the same cure temperature, as the content of AB block copolymer increases, the diffusion-controlled reaction region occurs as much earlier stages of the reaction. The overall reaction order,  $m+n$ , is in the range 3.0-4.8 for the amine cured epoxy/AB blends with  $m$  fluctuating around 1.0, and  $n$  was 2.0-3.7. With increasing AB block copolymer compositions, the  $K_{IC}$  of the blend increased. This is due to the formation of connected globular morphology. By increasing the content of AB in the epoxy blends, the modulus of cured blends decreased slightly. Though the CTBN is copolymerized with ATPEI as an AB block copolymer, the rubbery phase reduced the modulus of the cured blends.

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### REFERENCES

- Agag, T. and Takeichi, T., "Synthesis and Characterization of Epoxy Film Cured with Reactive Polyimide," *Polymer*, **40**, 6557 (1999).
- Aling, I. and Jenniger, W. F., "Curing Kinetics of Phase Separating Epoxy Thermosets Studied by Dielectric and Calorimetric Investigations; A Simple Model for the Complex Dielectric Permittivity," *Polymer*, **36**, 246 (1998).
- Bonnet, A., Pascault, J. P., Sautereau, H., Taha, M. and Camberlin, Y., "Epoxy-diamine Thermoset/Thermoplastic Blends. 1. Rates of Reactions Before and After Phase Separation," *Macromolecules*, **32**, 8517 (1999).
- Bonnet, A., Pascault, J. P., Sautereau, H. and Camberlin, Y., "Epoxy-Diamine Thermoset/Thermoplastic Blends. 2 Rheological Behavior Before and After Phase Separation," *Macromolecules*, **32**, 8524 (1999).
- Bucknall, C. B. and Gilbert, A. H., "Toughening Tetrafunctional Epoxy Resins using Polyetherimide," *Polymer*, **30**, 213 (1989).
- Chen, D., Pascault, J. P., Bersch, R. S. and Sieboert, A. R., "Synthesis, Characterization and Properties of Reactive Liquid Rubbers Based on Butadiene-acrylonitrile Copolymers," *J. Appl. Polym. Sci.*, **51**, 1959 (1994).
- Chem, C. S. and Poehlein, G. W., "Kinetic Model for Curing Reactions of Epoxides with Amines," *Polym. Engng. Sci.*, **27**, 782 (1987).
- Girard-Reydet, E., Sautereau, H. and Pascault, J. P., "Polyetherimide-

- Modified Epoxy Networks: Influence of Cure Conditions on Morphology and Mechanical Properties," *Polymer*, **40**, 1677 (1999).
- Hourston, D. J. and Lane, J. M., "The Toughening of Epoxy Resins with Thermoplastics. 1. Trifunctional Epoxy Resin-polyetherimide Blends," *Polymer*, **33**, 1379 (1992).
- Keenan, M. R., "Auto Catalytic Cure Kinetics from DSC Measurements: Zero Initial Cure Rate," *J. Appl. Polym. Sci.*, **33**, 1725 (1987).
- Kim, M., Kim, W., Choe, Y., Ahn, B., Kim, D.-S. and Park, J.-M., "Modeling of Multi-Autocatalytic Cure Reactions of an Epoxy/Amine Terminated Polyetherimide/NMA System," *Polymer Bulletin*, **51**, 167 (2003).
- Lopez, J., Lopez-Bueno, I., Nogueira, P., Ramirez, C., Abad, M. J., Baral, L. and Cano, J., "Effect of Poly(styrene-co-acrylonitrile) on the Curing of an Epoxy/amine Resin," *Polymer* **42**, 1669 (2001).
- Mimura, K., Ito, H. and Fujioka, H., "Improvement of Thermal and Mechanical Properties by Control of Morphologies in PES-Modified Epoxy Resins," *Polymer*, **41**, 4451 (2000).
- Oyanguren, P. A., Riccardi, C. C., Williams, R. J. J. and Mondragom, I., "Phase Separation Induced by a Chain Polymerization: Polysulfone-Modified Epoxy/Anhydride Systems," *Polymer*, **36**, 1349 (1998).
- Rahagopalan, G., Immaordino, K. M., Gillespie, J. W. and McKnight, S. H., "Diffusion and Reaction of Epoxy and Amine in Polysulfone Studied using Fourier Transform Infrared Spectroscopy: Experimental Results," *Polymer*, **41**, 2591 (2000).
- Ryan, M. E. and Dutta, A., "Kinetics of Epoxy Cure: A Rapid Technique for Kinetic Parameter Estimation," *Polymer*, **20**, 203 (1979).
- Sourour, S. and Kamal, M. R., "Differential Scanning Calorimetry of Epoxy Cure: Isothermal Cure Kinetics," *Thermochim Acta*, **14**, 41 (1976).
- Su, C. C. and Woo, E. M., "Cure Kinetics and Morphology of Amine-cured Tetraglycidyl-4,4'-diaminodiphenylmethane Epoxy Blends with Poly(ether imide)," *Polymer*, **36**, 2883 (1995).
- Varley, R. J., Hodgkin, J. H., Hawthorne, D. G., Simon, G. P. and Maculloch, D., "Toughening of a Trifunctional Epoxy System Part III; Kinetic and Morphological Study of the Thermoplastic Modified Cure Process," *Polymer*, **41**, 3425 (2000).
- Wise, C. W., Cook, W. D. and Goodwin, A. A., "CTBN Rubber Phase Precipitation in Model Epoxy Resins," *Polymer*, **41**, 4625 (2000).