

Cure Reactions of Epoxy/Anhydride/(Polyamide Copolymer) Blends

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Abstract : The cure kinetics of blends of epoxy (DGEBA, diglycidyl ether of bisphenol A)/anhydride resin with polyamide copolymer, poly(dimmer acid-co-alkyl polyamine), were studied using differential scanning calorimetry (DSC) under isothermal condition. On increasing the amount of polyamide copolymer in the blends, the reaction rate was increased and the final cure conversion was decreased. Lower values of final cure conversions in the epoxy/(polyamide copolymer) blends indicate that polyamide hinders the cure reaction between the epoxy and the curing agent. The value of the reaction order, m , for the initial autocatalytic reaction was not affected by blending polyamide copolymer with epoxy resin, and the value was approximately 1.3, whereas the reaction order, n , for the general n -th order of reaction was increased by increasing the amount of polyamide copolymer in the blends, and the value increased from 1.6 to 4.0. A diffusion-controlled reaction was observed as the cure conversion increased and the rate equation was successfully analyzed by incorporating the diffusion control term for the epoxy/anhydride/(polyamide copolymer) blends. Complete miscibility was observed in the uncured blends of epoxy/(polyamide copolymer) up to 120 °C, but phase separations occurred in the early stages of the curing process at higher temperatures than 120 °C. During the curing process, the cure reaction involving the functional group in polyamide copolymer was detected on a DSC thermogram.

Keywords : cure kinetics, epoxy, polyamide copolymer, diffusion control.

Introduction

Polymer modification has been an important subject in recent years to improve the mechanical properties of engineering plastics and thermoset resins in order to meet highly qualified structural and mechanical component applications. A number of works on epoxy resin modification with both functionalized and non-functionalized thermoplastics have been undertaken till now.¹⁻⁵ Epoxy/polyetherimide (PEI: Ultem 1000) and epoxy/polyethersulfone (PES: Udel) blends have been investigated as typical examples of those modified epoxy resins, and the toughness of epoxy was significantly improved by adding PEI or PES, with retaining high glass transition temperature and high mechanical strength.¹⁻³ 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.⁶⁻¹⁴

Cure kinetics of thermoset/thermoplastic blends can be examined by differential scanning calorimetry(DSC), although a fourier transform infrared spectroscopy - attenuated total

reflectance (ATR-FTIR) has been also used to estimate the reaction parameters.¹⁵ Kinetic models for cure reactions are commonly based on the general rate equation of the n -th order.^{16,17} In DSC analysis, both the isothermal and the dynamic heating 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 based on diglycidylether of bisphenol A (DGEBA), the cure reactions 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 exhibited by the onset of gelation and crosslinking due to the cure reactions becoming diffusion controlled.

In the present study, a polyamide copolymer, poly(dimmer acid-co-alkyl polyamine), was used as a modifier because the polyamine-containing polyamide copolymer could be participated in cure reaction at the interface between epoxy and the copolymer, which could provide increased interfacial interaction. The cure kinetics of an epoxy system containing the DGEBA and anhydride curing agent, and their blends with polyamide of 0, 5, and 10 phr of contents were studied. The contribution of diffusion to the cure kinetics was also discussed.

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Experimental

Materials. The epoxy system was based on a commercial grade of DGEBA (KUKDO Chemicals Co., Korea) with an average epoxy equivalent weight of 187.5 g/eq. The epoxy blends with a polyamide copolymer, poly(dimmer acid-co-alkyl polyamine) (Aldrich), were cured with an anhydride curing agent, nadic methyl anhydride (KUKDO Chemicals Co.), in the present of a catalyst, 2,4,6-tris(dimethylaminomethyl)phenol, (KUKDO Chemicals Co.). The chemical structures of materials are shown in Figure 1.

Preparation of Blends. The polyamide copolymer solution in methylene dichloride was mixed with the epoxy prepolymer under high-speed stirring for 2 h. Then the solvent was removed in a rotary vacuum evaporator at 80°C for 24 h. A stoichiometrically balanced amount of curing agent (or 120% excess) and a catalyst (5-10 phr) were blended with the epoxy/polyamide copolymer mixture in a three-roll mill at room temperature for 1 h.

Differential Scanning Calorimetry. The cure reaction rate and the degree of conversion as a function of time can be obtained using differential scanning calorimetry (DSC), which is operated isothermally at 110, 120 and 130°C to

find the parameters of the cure kinetics of the reactive epoxy/(polyamide copolymer) blends. The calculated parameters were the reaction order (n) and the rate constant (k).

The degree of cure, α (i.e., cure conversion), was determined based on the following equation:

$$\alpha = \frac{\Delta H_t}{\Delta H_\infty} \quad (1)$$

where ΔH_t is the partial heat of reaction at time t and ΔH_∞ is the average total heat of the reaction. The cure reaction rate, r , was obtained from the cure conversion data as a function of time by taking the derivative of α with respect to time:

$$r = \frac{d\alpha}{dt} \quad (2)$$

Results and Discussion

Miscibility of Epoxy/(Polyamide Copolymer) Blends.

Multiple glass transitions indicate that the thermoset/thermoplastic blends are immiscible, whereas single glass transition indicates that the blends are miscible. Typically, most binary blends of engineering thermoplastics, PEI, PES, and polyamide, with the DGEBA-based epoxy resin, exhibited single glass transition, indicating complete miscibility over a given or an entire composition range. The glass transition temperature of neat epoxy resin was -25°C. As expected, in this study, a single glass transition temperature of epoxy/(polyamide copolymer) blends has been shown (i.e. approximately -9°C for 10 phr of polyamide composition), which indicates that the epoxy/(polyamide copolymer) blend is miscible.

As an alternative way to investigate miscibility of multi-component blends, simple optical tests of clarity has been widely employed. A visual observation indicated that the epoxy/(polyamide copolymer) blend without amine, up to 120°C, was to be homogeneous and optically clear. In comparison, with amine or anhydride, the blends became gradually turbid as cure reaction proceeded at elevated temperatures of about 120°C or higher.

Monitoring the Onset of Phase Separation. As the cure reaction occurs, the molecular weight increases and an average molecular weight is reached where a homogeneous mixture is no longer favored and consequently the thermoplastic-reacting thermoset blend system separates into two phases. At this point as a result of both phase separation and advancement of the epoxy-anhydride reaction, the viscosity increases rapidly because the epoxy-anhydride cure reaction rate is readily increased in the polyamide-free phase. At the onset of phase separation, therefore, the viscosity begins to increase. This advancement of the epoxy-anhydride reaction can be detected by the viscosity measurements. The time-temperature history of both the onset of phase separation and reaction advance-

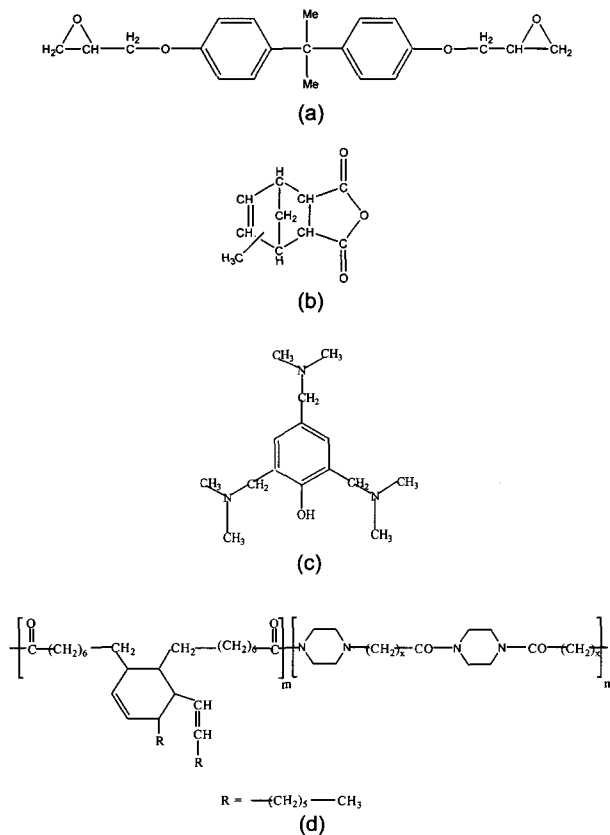


Figure 1. Chemical structures of diglycidyl ether of bisphenol A (a), nadic methyl anhydride (b), 2,4,6-tris(dimethylaminomethyl)phenol (c), and poly(dimmer acid-co-alkyl polyamide) (d).

ment is important in knowing and controlling the morphology. In some works,^{18,19} dynamic mechanical measurements were used to describe the onset of phase separation in the thermoplastic/thermoset blends. A rheological detection of the onset of phase separation in the epoxy/(polyamide copolymer) blend is shown in Figure 2. In the Figure, at the onset of phase separation, the increase in viscosity was observed, which is an evidence for the advancement of the epoxy-anhydride reaction. After the onset of phase separation, the viscosity once decreased and then gradually increased. The transmitted and polarized light microscope equipped with a heating stage was used to detect the onset of phase separation and monitor phase separation through the cure reaction. The scanning electron microscope also proves the phase separation after the onset of phase separation, near the gel point, as shown in the inset of Figure 2.

Cure Conversion. The typical cure conversion is shown in Figure 3, and the plot of the conversion rate vs. time is shown in Figure 4.

The conversion drastically increased as time increased, as was also seen in some works on cure kinetics of epoxy/thermoplastics blends.^{7, 12, 20-22} After a drastic 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 Figure 3. Although 10 phr of polyamide copolymer was blended with epoxy resins, the rate curves shown in Figure 4 were autocatalytic in nature, with the maximum rate of conversion at the early stage of reaction, which is similar in behavior with that of other epoxy systems. On increasing the curing temperature, the position of the maximum rate of conversion was shifted to the smaller time, i.e. the start of the reaction. Table I shows the effect of

polyamide copolymer content on the maximum rate of conversion and final conversion. As polyamide copolymer content increased, the final conversion decreased at the same cure temperature, indicating that diffusion control should be considered at lower values of conversion compared to that of the neat epoxy resin. As cure temperature increased the final conversion increased for all compositions of polyamide copolymer in the blend.

As mentioned by Varley *et al.*,¹² 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. As another possible way to explain the low final epoxy conversion, the partitioning of the curing agent in both of the separated phases in the blends may cause this decrease in the final epoxy conversion. Preliminary studies to investigate the effect of the partitioning of the curing

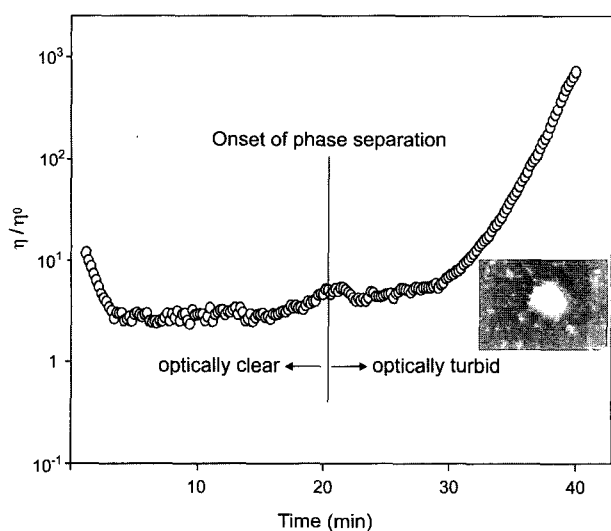


Figure 2. Typical onset of phase separation (η_0 : reference viscosity).

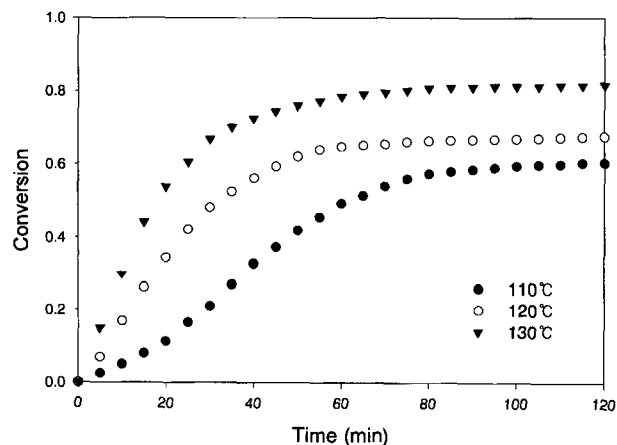


Figure 3. Typical cure conversions for the epoxy/anhydride/(polyamide copolymer) system (polyamide copolymer: 10 phr).

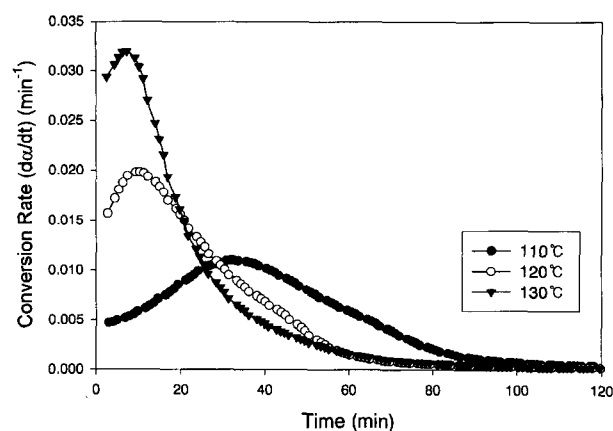


Figure 4. Plot of conversion rate vs. reaction time for the epoxy/anhydride/(polyamide copolymer) system (polyamide copolymer: 10 phr).

Table I. Maximum Conversion Rate and Final Conversion of Neat Epoxy and Blends of Various Contents of Polyamide Copolymer

Samples	Isothermal Temperature(°C)	Maximum Conversion Rate (min ⁻¹)	Final Conversion α_f
Neat Epoxy	110	0.0213	0.8049
	120	0.0266	0.8814
	130	0.0461	0.9500
Polyamide Copolymer, 5 phr	110	0.0149	0.7024
	120	0.0240	0.7699
	130	0.0391	0.9247
Polyamide Copolymer, 10 phr	110	0.0110	0.6047
	120	0.0198	0.6767
	130	0.0320	0.8174

agent in both of the separated phases in the blends showed that when the 20% excess of curing agent was added to the blends, evidently 10 to 15% increase in the final conversion was observed.

Isothermal Kinetics: the Autocatalytic Model with a Diffusion Control Factor.²³ The rate equation can be expressed by the general law:

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \quad (3)$$

where $d\alpha/dt$ is the rate of conversion, t is the reaction time, $k(T)$ is the rate constant, and $f(\alpha)$ is a function of the dependence of conversion. The dependence of the rate constant, $k(T)$, on temperature can be described by the Arrhenius type equation:

$$k(T) = A \exp\left(\frac{-E_a}{RT}\right) \quad (4)$$

where A is the frequency factor, E_a is the activation energy, and R is the gas constant.

A function of cure conversion dependence, $f(\alpha)$, in the thermoset system has been proposed in several forms with different assumptions. For a reaction of n -th order which involves one reacting substance the conventional kinetic equation can be expressed in terms of fractional conversion as follows:

$$\frac{d\alpha}{dt} = k(1-\alpha)^n \quad (5)$$

A general equation based on a phenomenological model to describe the autocatalytic reaction in the thermoset/thermoplastic blends is expressed in Eq. (6) and mostly used to analyze the cure kinetics of amine-cured epoxy system:

$$\frac{d\alpha}{dt} = (k_1 + k_2\alpha^m)(1-\alpha)^n \quad (6)$$

where α is the conversion, k_1 and k_2 are the rate constants referring to the rate constant of n -th order reaction and of autocatalytic reaction, respectively, m and n are the kinetic exponents of the reactions, and $m+n$ is the overall reaction order. In the present study, the autocatalytic model has been used to determine the cure kinetics of anhydride-cured epoxy system. Isothermal DSC data at several temperatures were obtained, and the data were fitted to the kinetic equation. The reaction orders, the rate constants, and the activation energy was calculated simultaneously by using a nonlinear regression method.

A rate equation with a diffusion control factor²³ is a semi-empirical equation based on free-volume considerations, and it has been proposed to explain the retardation of cure reaction in the later stage of the reaction. Due to the vitrification of epoxy resin, the later stage of the reaction is virtually subjected to diffusion control. The diffusion controlled rate constant k_d is as follows :

$$k_d = k_c \exp[-C(\alpha - \alpha_c)] \quad (7)$$

where k_c is the rate constant for chemical kinetics, C is a parameter of diffusion control, and α_c is a critical value of cure conversion. In Eq. (7), as α reaches α_c , the cure reaction becomes controlled by diffusion. The diffusion control factor, $f(\alpha)$ can be expressed as follows :

$$f(\alpha) = \frac{k_e}{k_c} = \frac{1}{1 + \exp[C(\alpha - \alpha_c)]} \quad (8)$$

where k_e is an overall effective rate constant which is given by the following equation :

$$\frac{1}{k_e} = \frac{1}{k_d} + \frac{1}{k_c} \quad (9)$$

The final rate equation can be written as

$$\frac{d\alpha}{dt} = \frac{(k_1 + k_2\alpha^m)(1-\alpha)^n}{1 + \exp[C(\alpha - \alpha_c)]} \quad (10)$$

In the present study, the conversion versus reaction time at 110, 120, and 130 °C of the epoxy/(polyamide copolymer) blends with various compositions of polyamide in the blends are shown in Figure 5. The calculated solid and dashed lines were obtained from Eqs.(6) and (10), i.e., with or without the diffusion control factor, respectively. The calculated lines were compared with the experimental data.

Autocatalytic nature of epoxy resin curing reaction is clearly shown in the initial early stage of the reaction, even in the presence of polyamide in the blends. As cure conversion approaches the final conversion, differences between the model predictions without the diffusion control factor and the experimental data became pronounced, regardless of the cure temperature indicating that at the later stage of reaction, the diffusion control factor in the rate expression should be considered as shown in Eq. (10).

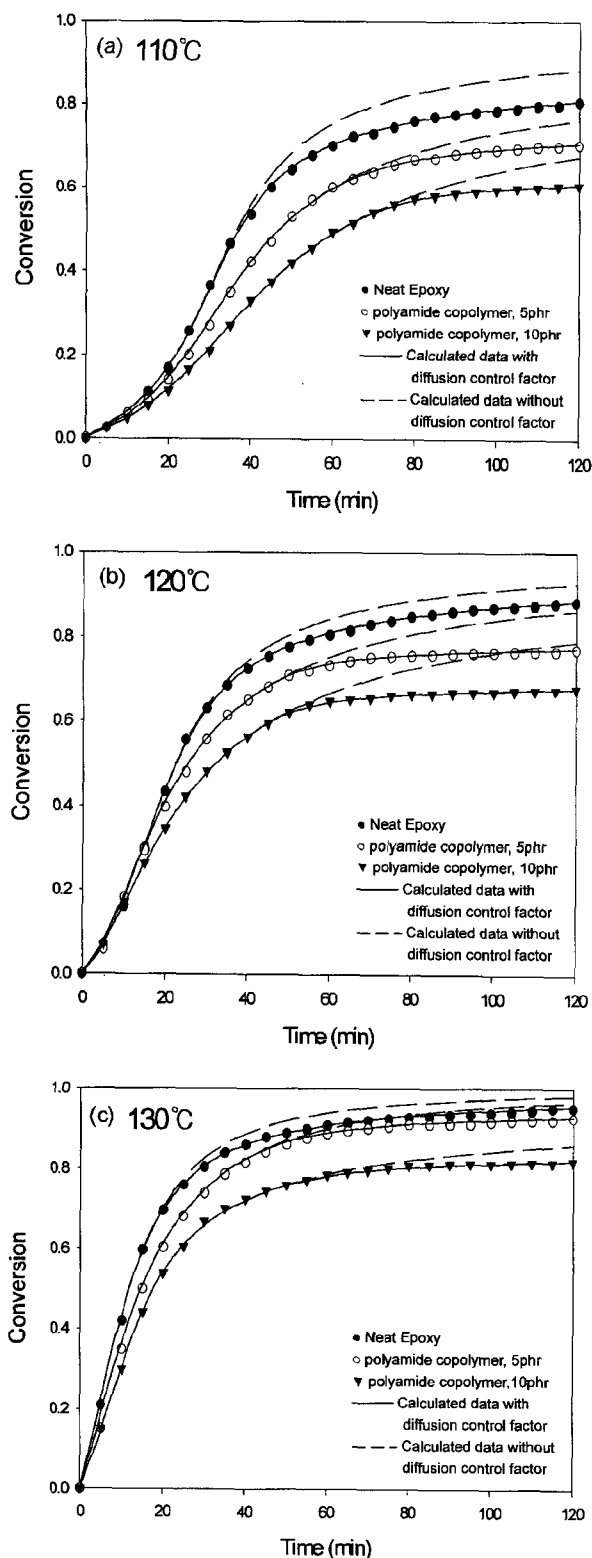


Figure 5. Conversion vs. reaction time for the epoxy/anhydride/(polyamide copolymer) systems; experimental data (symbols) and calculated data (lines) with/without diffusion control factor at various isothermal conditions; at 110°C (a), at 120°C (b), and at 130°C (c).

Table II. Kinetic Constants of Autocatalytic Model for the Epoxy/Anhydride/(Polyamide Copolymer) Blend System

$T(^{\circ}\text{C})$	m	n	$m+n$	$1000 \times k_1$ (min^{-1})	$1000 \times k_2$ (min^{-1})
Neat Epoxy					
110	1.8520	2.8500	4.702	6.31	475.5
120	1.3892	2.2886	3.6778	14.40	244.7
130	0.9848	1.6487	2.6335	41.00	126.2
Polyamide Copolymer, 5 phr					
110	1.6866	3.6478	5.3344	5.43	374.7
120	0.8520	2.4488	3.3008	10.10	123.6
130	0.6643	1.6159	2.2802	9.87	73.4
Polyamide Copolymer, 10 phr					
110	1.5878	4.0956	5.6834	4.62	281.0
120	0.8430	2.8635	3.7065	30.10	106.6
130	1.6423	3.3335	4.9758	29.80	52.44

All parameters in Eq. (10) can be obtained simultaneously by applying a nonlinear regression method and the calculated results are listed in Table II.

The overall reaction order, $m+n$, is in the range of 2.5~5.5 for the anhydride-cured epoxy/(polyamide copolymer) blends with m fluctuating around 1.3 and n ranging from 1.6 to 4.0. In other studies, the value of $m+n$ ranged from 2.5 to 3, with the value of $n \approx 2$ for the anhydride-cured epoxy blends.²⁰ In the present study, values of m depend strongly on the content of polyamide and the value of n increases as the reaction rate decreases, indicating that the reaction may be hindered by the phase separation and vitrification. The term $k_2 \alpha^m$ in Eq. (6) represents the initial autocatalytic reaction. As a result, the values of m are almost constant as approximately 1.3 even though the polyamide content is increased, meaning that neither the curing reaction nor the vitrification affects initial autocatalytic reaction. The values of k_1 were increased consistently according to the temperature and the values of k_2 were decreased consistently according to the temperature. This indicates that the reaction tends to be less dominated by the autocatalytic reaction as temperature increases.

Because of vitrification, the autocatalytic model can fit only up to certain values of conversion, α_c , suggesting that diffusion effects should be considered in the region of vitrification. However in the later stages of the reaction, the vitrification effect on the kinetics can be explained very well by the model equation, which the diffusion control factor is incorporated.

The values of the diffusion factors as a function of conversion are shown in Figure 6, and the values of the critical conversion are listed in Table III.

Using the combined model as shown in Eq. (10), new

Table III. Parameters of Diffusion Control Expression

Samples	Isothermal Temperature (°C)	Critical Conversion, α_c	Constant for Diffusion Control, C
Neat Epoxy	110	0.7100	10.2940
	120	0.8404	10.8078
	130	0.9104	10.6100
Polyamide Copolymer, 5 phr	110	0.6703	36.7556
	120	0.7336	64.9494
	130	0.8968	51.9546
Polyamide Copolymer, 10 phr	110	0.5754	56.9346
	120	0.6366	66.2460
	130	0.7949	67.1982

parameters (such as critical conversion, α_c , and diffusion control parameter C) are obtained by nonlinear regression. The parameters are listed in Table II. In the combined model, the diffusion effects are negligible when the values of the diffusion factors stay near 1.0. The critical conversion value decreases with increasing the content of polyamide in the blends, indicating that in order to properly express the cure kinetics of the present blends, both the hindrance and diffusion effects caused by the polyamide copolymer should be incorporated into the predicted kinetic expression, as shown in Eq. (10). The difference in the values of ($\alpha_f - \alpha_c$) was only 0.04~0.05, regardless of whether polyamide was added to the epoxy resin or not.

Conclusions

The cure reaction of anhydride-cured epoxy/(polyamide copolymer), poly(dimmer acid-co-alkyl polyamine), blends was investigated over a range of composition, and autocatalytic mechanism was observed. A change in the reaction mechanism may affect the total heat of a reaction and the final cure conversions. By increasing the contents of polyamide copolymer in the epoxy system, a decrease in the total heat of the reaction and final cure conversion were observed.

An autocatalytic model with diffusion factor fits well the experimental data in both the early and the later stages of the reaction, since the autocatalytic model includes the change in the reaction mechanism range of conversion near vitrification. This model can explain both chemically controlled and diffusion-controlled reactions in the cure process of the blends containing the polyamide copolymer. As the content of polyamide copolymer increases, the diffusion-controlled reaction takes place in the much earlier stages of the reaction at the same cure temperature. For characterizing kinetic behavior, the rate equation which includes diffusion control factor is applicable to anhydride-cured epoxy/(polyamide copolymer) blends. The value of the reaction order,

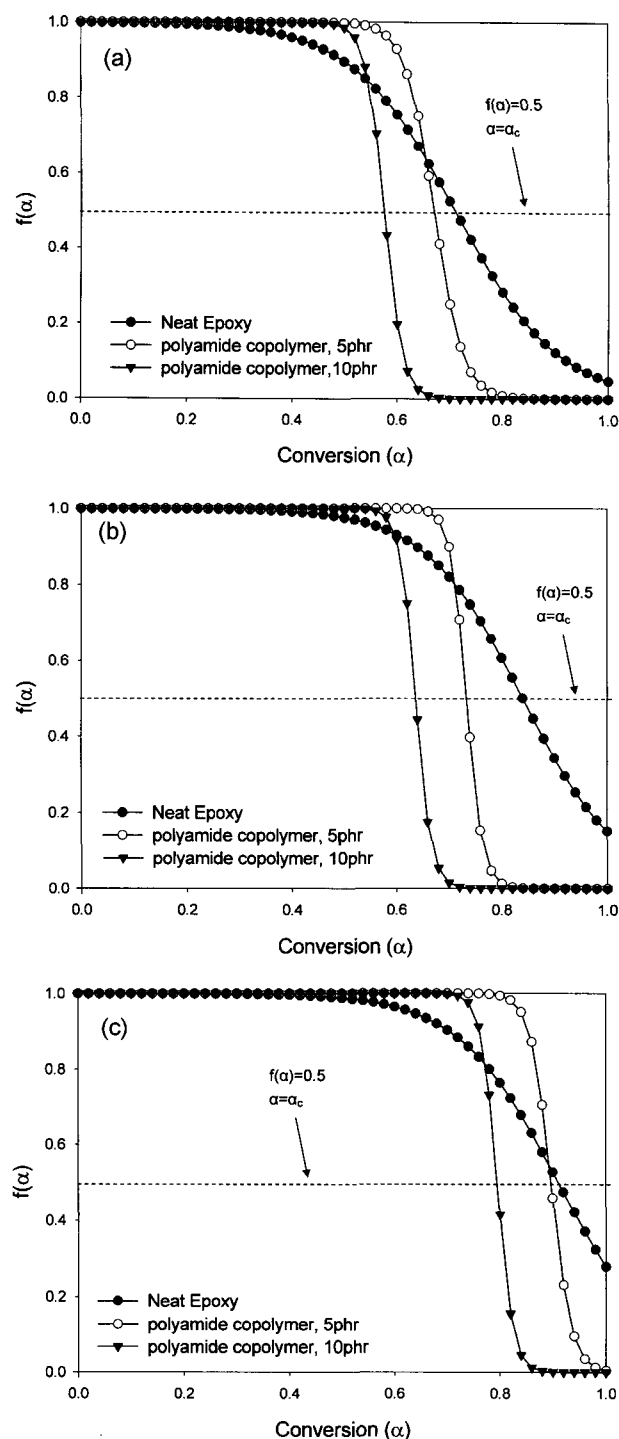


Figure 6. Diffusion control factor vs conversion for the epoxy/anhydride/(polyamide copolymer) system; at 110°C (a), at 120°C (b), and at 130°C (c).

m , for the initial autocatalytic reaction was not affected by blending the polyamide copolymer with epoxy resin, and the value was approximately 1.3. The value of n for the n -th order reaction rate increased when the amount of polyamide

copolymer was increased in the blends, and the value was increased from 1.6 to 4.0, meaning that the reaction of the epoxy resin with the curing agent was hindered by the addition of the polyamide copolymer. The value of the final conversion was very close to that of the critical conversion, i.e., the difference between them was only 0.04~0.05, regardless of whether polyamide copolymer was added to the epoxy resin or not.

A rheological detection of the onset of phase separation in the epoxy/(polyamide copolymer) blend was accomplished. After the onset of phase separation, the viscosity increases rapidly because of increase in the cure reaction rate in the polyamide-free phase in the blends just after the onset of phase separation, which is also an evidence for the advancement of the epoxy-amine reaction in the epoxy/(polyamide copolymer) blends.

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