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A STUDY ON CURING KINETIC OF BISPHENOL-F USING BENZYL DIMETHYL AMINE BY ISOTHERMAL DSC

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The effect of the concentration of benzyl dimethyl amine as a catalyst on the cure reaction of bisphenol-F based epoxy resin(BPF)/nadic methyl ahydride(NMA) system was studied by differential scanning calorimetery using an isothermal approach over the temperature range 115–145°C. Kinetic parameters of the curing reaction including the reaction order, activation energy and kinetic rate constants were investigated. The results were dependent on the cure temperature and catalyst concentration and proceeded through an autocatalytic kinetic mechanism. The curing kinetic constants and the cure activation energies were obtained by the Arrhenius kinetic model. The suggested kinetic model with a diffusion term was successfully used to describe and predict the cure kinetic of BPF resin compositions as a function of the catalyst content and temperature.

Keywords: *benzyl dimethyl amine, bisphenol-F, cure, isothermal DSC, kinetic, nadic methyl anhydride*

Introduction

Most high performance composite materials are produced using thermosetting resins. The process conditions are dictated by the chemorheological properties of the thermosetting matrix and by the heat transfer characteristic of a given manufacturing system. A highly exothermic process occurs during the cure reaction of thermosetting materials, and thus the reaction heat liberated tends to raise the mold temperature and accelerate the curing reaction. Therefore, to control the rate of heat generation and temperature reactions during the processing of these materials, it is essential to understand the kinetic of this cure reaction [1]. The kinetic method for determinung kinetic parameters by calorimetry should be of considerable generality and for favorable cases can permit research of the kinetic of the reaction where the other methods would be very difficult to employ [2, 3]. The kinetic of cure reactions of thermosetting resins are critical for laminate processing [4]. Kinetic analysis of curing epoxies is usually based on a single step kinetic equation [5]. For thermoset matrices such as epoxy resins, probably the most important aspect of the model is an accurate description of the cure reaction kinetics [6–10]. The term 'cure' is used to name the overall transformation from liquid to glassy solid due to chemical reaction [11].

In this study an anhydride was used as curing agent. Anhydride cured epoxy resins generally exhibit improved high-temperature stability over the amines and better physical and electrical properties above their deflection temperature [12]. In the absence of catalyst, the anhydride will not react directly with the epoxy group. Therefore, a tertiary amine was used as catalyst. Tertiary amines are more conventionally used as catalyst. Amount of catalyst could modify the cure reaction as well as the type of catalyst. Hence, the effect of the catalyst concentration on the cure reaction was investigated.

Experimental

Materials and methods

Bisphenol-F based epoxy resin (DER354), nadic methyl anhydride (NMA, curing agent) and benzyl dimethyl amine (BDMA, catalyst), supplied by Dow Chemical Company. All epoxy/anhydride compositions in this study were 100/90. The concentration of catalyst added were 1, 1.5 and 2 phr. BPF resin and NMA were mixed at 60°C until a homogeneous solution was obtained. The mixture was then cooled down to ambient temperature and the catalyst was added and compounds were well mixed.

DSC measurement

Calorimetric measurements carried out under nitrogen atmosphere using a PerkinElmer Differential Scanning Calorimeter (DSC), PE-pyris1, USA. The instrument was calibrated in the 25-400°C region. All measure-

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ments were performed in sealed aluminum pan with sample masses ranging from 15 to 20 mg. The profiles of isothermal reaction exotherms were prepared at 115, 125, 135 and 145°C. Isothermal DSC runs were stopped when no further exotherm is observed.

Results and discussion

If the curing reaction is only a thermal event, then the reaction rate at any time or conversion is equal the rate of heat flow measured through DSC experiments dQ/dt, divided by the overall heat of reaction (dH_r):

$$\frac{d\alpha}{dt}=\frac{dQ/dt}{Q_{tot}} \tag{1}$$

The total heat of curing reaction, Q_{tot}, could be estimated by the area of an exothermic peak in temperature scanning mode at a heating rate of 10°C min^{-1}. The extent of cure of the mixtures under isothermal curing condition was estimated by the area under the exothermic peak as follows:

$$\alpha(t)=\frac{1}{Q_{tot}}\int_0^t \frac{dQ}{dt}dt \tag{2}$$

where $\alpha(t)$ is the extent of cure at a given time and dQ is the heat release at an infinitesimal time increase dt.

A series of isothermal conversion rate curves for BPF/NMA with different amount of BDMA as a function of time are shown in Fig. 1 (a, b, c). As shown in the Fig., with increasing the isothermal temperature and the catalyst concentration the conversion rate peak becomes higher and shifts to shorter times. Figure 2 shows the series of extent of conversion rate as a function of conversion of epoxy resin. As can be seen in Fig. 2 the curing reaction for all compositions proceeds through an autocatalytic mechanism with a maximum conversion rate in the 15–25% conversion region.

Various rate expressions have been proposed for the cure reaction of thermosets. For some thermosetting systems the n-th order rate expression [7, 13], could be shown as:

$$\frac{d\alpha}{dt}=k(1-\alpha)^n \tag{3}$$

where n is the reaction order, and k, the rate constant given by Arrhenius temperature dependence. For autocatalytic curing reactions, an isothermal reaction rate is proposed by Kamal and expressed as shown below [14, 15]:

$$\frac{d\alpha}{dt}=(k_1+k_2\alpha^m)(1-\alpha)^n \tag{4}$$

where k_1 and k_2 are the kinetic rate constants and m and n represent reaction orders. Temperature dependence of the rate constant of the reaction can be determined from the Arrhenius equation as:

$$k_i = A\exp(-E/RT) \qquad i=1,2 \tag{5}$$

where A is the pre-exponential constant, E the activation energy, R the gas constant and T the absolute temperature.

In order to determine the parameters of Eq. (4) several methods have been proposed [16]. Further

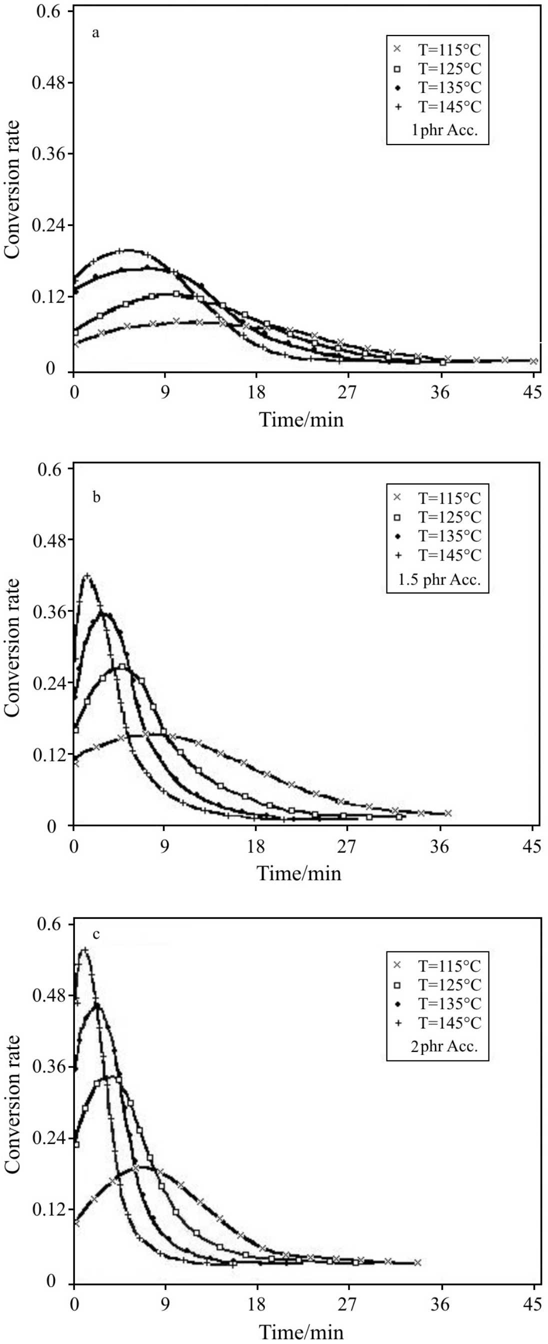

Fig. 1 Conversion rates *vs*. time for DER354/NMA with different amount of BDMA: a – 1 phr, b – 1.5 phr and c – 2 phr

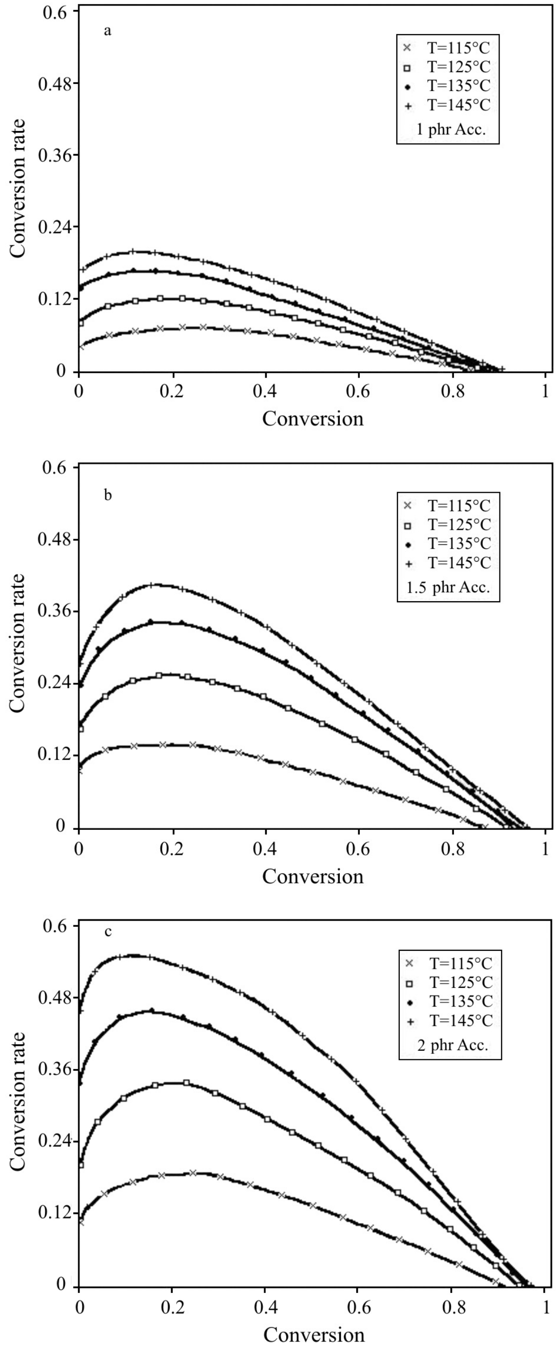

Fig. 2 Conversion rates *vs*. conversion for DER354/NMA with different amount of BDMA: a – 1 phr, b – 1.5 phr and c – 2 phr

more, Eq. (4) also predicts the kinetic behavior of some thermosets characterized by a zero initial reaction rate (k_1=0). The constant k_1 was graphically calculated as the initial reaction rate at α=0, given by the intercept of the thermogram curves in Fig. 1. Equation (4) can be modified in the following forms:

$$\ln(d\alpha / dt) = \ln(k_1 + k_2\alpha^{m}) + n\ln(1-\alpha) \qquad (6)$$

$$\ln\{[(d\alpha / dt) / (1-\alpha)^{n}] - k_1\} = \ln k_2 + m\ln\alpha \qquad (7)$$

$$\ln(d\alpha / dt) - \ln(k_2\alpha^{m} + k_1) = n\ln(1-\alpha) \qquad (8)$$

A first guess of the reaction order *n* can be determined from the slope of a plot of ln(dα/d*t*) *vs*. ln(1–α), as predicted in Eq. (6). Figure 3a shows a plot of ln(dα/d*t*) *vs*. ln(1–α) for the isothermal experiment at 145°C. The value of *n* was determined from the slope of a linear part of the curve in Fig. 3a. Then, using previously computed k_1 and *n* values, the reaction order of *m* and the constant k_2 can be determined

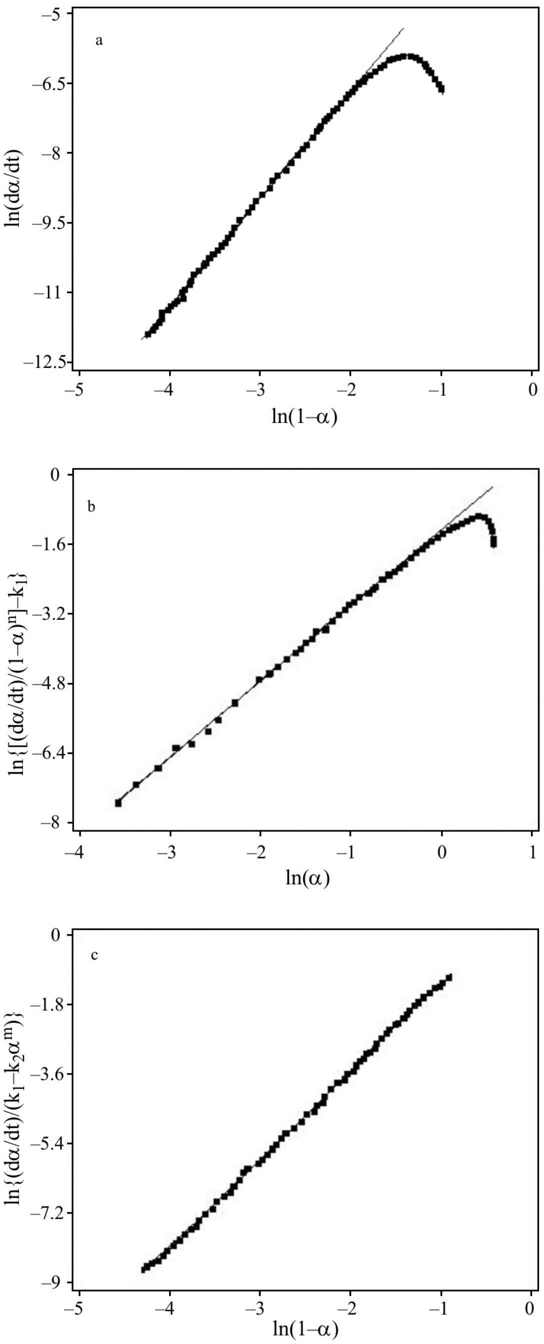

Fig. 3 Graphic representation of a – Eq. (6), b – Eq. (7) and c – Eq. (8) for the isothermal DSC experiment at 145°C

Table 1 Temperature dependence of kinetic parameters for autocatalytic mechanism

Catalyst concentration/phr	Kinetic parameter	Temperature dependence	ave. m	ave. n
1	k_1	0.02	0.215	1.144
	k_2	$1.509\cdot10^5\exp(-5.446\cdot10^3/T)$		
1.5	k_1	0.05	0.233	1.261
	k_2	$4.925\cdot10^5\exp(-8.594\cdot10^3/T)$		
2	k_1	0.07	0.242	1.598
	k_2	$1.966\cdot10^5\exp(-7.154\cdot10^3/T)$		

The unit of activation energy (kJ mole^{-1})

from the slope and the intercept of a plot of $\{[(\mathrm{d}\alpha/\mathrm{d}t)/(1-\alpha)^n]-k_1\}$ *vs*. lnα, as predicted in Eq. (7). Figure 3b shows a plot of $\ln\{[(\mathrm{d}\alpha/\mathrm{d}t)/(1-\alpha)^n]-k_1\}$ *vs*. lnα. To obtain more precise values, an iterative procedure was applied. If k_1, k_2 and m values are given, the new value of n can be determined from Eq. (8). Figure 3c shows a graphic representation of Eq. (8) with previously determined k_1, k_2 and m values. The new value of n was applied to Eq. (7), and thus new values of k_2 and m were obtained from the equation. Using Eqs (7) and (8), the iterative procedure was repeated until values with less than 1% difference between subsequent calculations were obtained.

The resulting data obtained from this method are summarized in Table 1 for all the isothermal experiments. As could be seen in Table 1, the kinetic rate constant and k_2 increased with catalyst concentration at the same curing temperature.

Temperature dependence of the kinetic rate constants were determined from Arrhenius equation and also listed in that table. The reaction orders were determined by averaging the values of all isothermal experiments.

The average values of each reaction order, m and n, also increased, but their increments were relatively small. Typical comparisons between the experimental and theoretical cure parameters based on the autocatalytic model with previously determined model parameters are shown in Fig. 4. Experimental results obtained, show good agreements up to 75%, but beyond that region deviations are observed.

The deviations observed are attributed to the vitrification where the mobility of the reacting groups is hindered and the rate of conversion is controlled by diffusion rather than by kinetic factor [17]. In order to consider the diffusion effect, semiempirical relationships, based on the free volume considerations proposed by Chern and Poehlein [18] have been widely used. They proposed a Williams-Landel-Ferry type function that models the change in polymer properties based on the variation in the free volume [19]:

Table 2 Values of the constants C and α_c at different temperature

Catalyst concentration/phr	Temperature/ °C	C	α_C
1	115	62.54	0.83
1	125	66.69	0.86
1	135	64.35	0.90
1	145	60.74	0.92
1.5	115	57.33	0.85
1.5	125	61.27	0.87
1.5	135	58.52	0.89
1.5	145	56.42	0.92
2	115	59.05	0.89
2	125	53.66	0.91
2	135	55.91	0.94
2	145	49.10	0.97

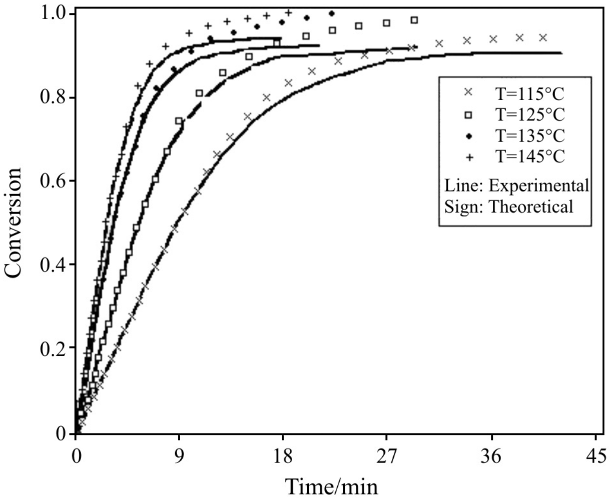

Fig. 4 Comparison of autocatalytic cure model with experimental data for BPF epoxy resin resin with different amounts of catalyst

$$f(\alpha)=\frac{1}{1+\exp[C(\alpha-\alpha_C)]} \qquad (9)$$

where C is the material constant for given epoxy resin composition and α_c represents the critical value of conversion at which the effect of diffusion becomes important. For $\alpha \leq \alpha_c$, $f(\alpha)$ approximately equals unity, the reaction is kinetically controlled and the effect of diffusion is negligible. As α approaches α_c, $f(\alpha)$ begins to decreases, reaching a value of 0.5 at $\alpha=\alpha_c$ and beyond this point decrease and approaches zero, which means that the reaction becomes very slow and effectively stops. We determined $f(\alpha)$ as the ratio of the experimental reaction rate to the reaction rate predicted on the basis of the autocatalytic cure kinetic model in Eq. (4). The values of C and α_c were obtained by fitting $f(\alpha)$ *vs.* α at each temperature and composition. They are summarized in Table 2.

C has no discernible trend but α_c increases with temperature at a given composition, at a given curing temperature, independent of the catalyst concentration.

The model represented by Eq. (4) has been successfully applied to the autocatalytic polymerization reactions where one of the products of the cure process acts as a catalyst as in the cure of epoxy with amines or phenols. The equation does not contain any terms related to catalyst concentration and it is impossible to predict isothermal reaction rate with its concentration. Since the reaction mechanism does not change with the catalyst concentration, namely, the reaction orders are constant, and also the reaction rate constants increase with the catalyst concentration at the same temperature, the autocatalytic cure model can be simply modified by the introduction of the term the catalyst concentration. So, Eq. (4) was expressed as follows [12, 18]:

$$\frac{d\alpha}{dt}=(k_1'+k_2'\alpha^{m})(1-\alpha)^{n}[B] \qquad (10)$$

where $[B]$ is the catalyst concentration and k_1' and k_2' are the normalized kinetic rate constants which can be applied at any catalyst concentration.

As previously described, the reaction orders, m and n, could be determined by averaging the values of all isothermal experiments, which are shown in Table 1. Comparing Eqs (4) and (10), the normalized kinetic constants could be evaluated from the equation below:

$$\frac{k_i}{[B]}=k_i' \qquad i=1,2 \qquad (11)$$

Figure 5 shows the values of $\ln k_2'$ as a function of reciprocal temperature. The pre-exponential factor and the activation energy of k_2' could be calculated from the intercept and the slope of the plot in the Fig. 4. k_1', the Arrhenius form of k_2', m and n are given from Table 3.

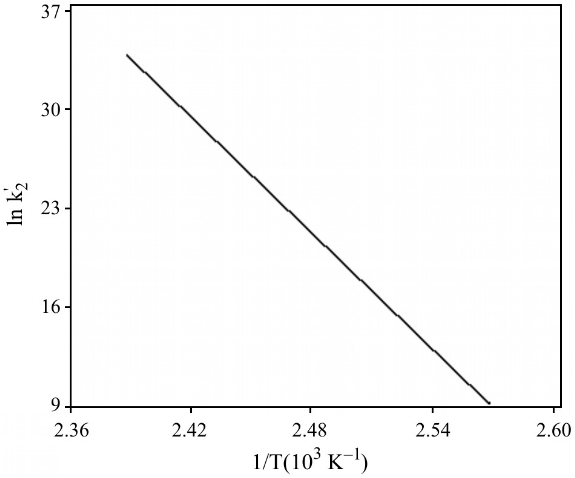

Fig. 5 Temperature dependence of k_2'

With introduction of the diffusion factor, the effective reaction rate at any conversion is equal to the chemical reaction rate multiplied by $f(\alpha)$ [18]:

$$\frac{d\alpha}{dt}=(k_1'+k_2'\alpha^{m})(1-\alpha)^{n}[B]\frac{1}{1+\exp[C(\alpha-\alpha_C)]} \qquad (12)$$

Figure 6 shows the comparison between the experimental values of α with those obtained from the Eq. (12).

Table 3 The normalized kinetic constant, k_1' and k_2'

Kinetic const.	Value/s^{-1}	m	n
k_1'	0.03	0.32	1.55
k_2'	1.426·10^{9}exp(–7.318/RT)		

*kJ mole^{-1}

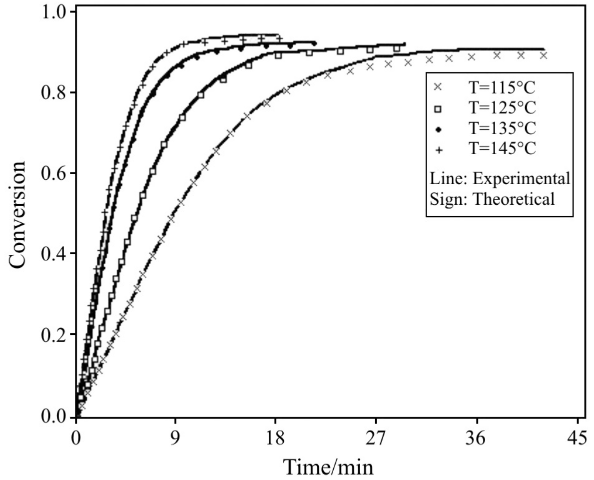

Fig. 6 Comparison of the values obtained from Eq. (9) with experimental data for BPF resin with different amounts of catalyst

The experimental values show good agreement with calculated data. Thus we can employ the proposed generalized kinetic model to predict and describe the progress of cure of our BPF resin system as a function of the catalyst concentration and curing temperature.

Conclusions

In this experiment a mathematical expression representing an autocatalytic kinetic is used. The kinetic constants increased with increasing the amount of catalyst and the reaction orders also slightly increased. In order to determine the progress of the cure reaction of such systems, the autocatalytic cure model in addition to the terms related to the catalyst concentration was simply modified. The autocatalytic cure model was simply modified for determining the progress of curing reaction the systems by the introduction of the terms related to the catalyst concentration. By combination of this proposed kinetic model with a diffusion term, it is possible to describe and predict the cure reaction of BPF resin compositions as a function of the catalyst concentration.

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