Nonisothermal Cure Kinetics of DGEBA with 2,7-Diaminofluorene

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ABSTRACT: Cure kinetics of diglycidyl ether of a bisphenol A-based epoxy resin (DGEBA) with 2,7-diaminofluorene (DAF) as curing agent have been studied by using nonisothermal differential scanning calorimeter (DSC). The values of apparent activation energy (E_a) of nonisothermal cure reaction were calculated by using isoconversional and nonisoconversional methods. The E_a values of the samples containing stoichiometric amount of 26 phr DAF revealed a dependence on the conversion (α) by the isoconversional method of Flynn–Wall–Ozawa (FWO). The E_a values by nonisoconversional methods of Ozawa and Kissinger–Akahira–Sunose (KAS) were 58.27 and 55.68 kJ/mol, respectively. The cure process showed that the autocatalytic behavior dominates the mechanism in the initial stages where the rate-controlling steps are located, but becomes diffusion-controlled in the final stage. Techniques of predicting isothermal cure time from nonisothermal kinetic parameters by ASTM and Vyazovkin methods were used for the cure reaction of DGEBA/DAF system. Thermal stability of the cured resin was also determined by using thermogravimetry analysis (TGA). © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 112: 1311–1318, 2009

Key words: curing of polymers; kinetics; DSC; resin; 2,7-diaminofluorene

INTRODUCTION

The full characterization of the cure process of an epoxy system involves many factors which are all dependent on the type of epoxy resin, curing agent, and the curing conditions were applied. By selecting distinct kinds of curing agents, a large variety of epoxy-based thermosetting materials may be produced with specific mechanical, physical, and chemical properties. The aromatic curing agents improve thermal stability, chemical resistance, and mechanical properties of the cured resin.[1,2] Kinetic characterization of cure reaction of epoxy-aromatic diamine systems is fundamental in the processing of composite materials. Differential scanning calorimeter (DSC) is a method which can measure the heat flow from the strongly exothermic reaction of epoxy-amine. Kinetic data such as: curing rate, variation of rate at various temperatures, and E_a provide information for the curing cycles of epoxies to ensure that the adequately cured epoxy is able to meet the requirements of its end use.[3–13]

Kinetic methods

The phenomenological kinetics of cure can be generally described in the differential form as:

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$$\frac{d\alpha}{dt} = k(T)f(\alpha) = A\exp(-E_a/RT)f(a) \qquad (1)$$

where $d\alpha/dt$ is the rate of cure, α is the fractional conversion at any time t, k is the Arrhenius rate constant, $T(K)$ the absolute temperature, $A(S^{-1})$ the preexponential factor, $\mathbf{R}$ the universal gas constant, and $f(\alpha)$ is the reaction model.

DSC method assumes that for a cure process the measured heat flow (dH/dt) is proportional to the conversion rate, $d\alpha/dt$. This assumption is valid for materials with a single reaction and no other enthalpic events, such as the evaporation of the solvent or volatilization of components, enthalpy relaxation, or significant changes in heat capacity with conversion.
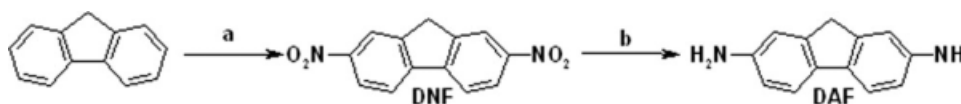
Nonisothermal methods can be used as single-heating rate and multi-heating rate methods. Two multiple-heating rate methods that have been shown to be effective are Kissinger–Akahira–Sunose (KAS)[14,15] and FWO given by Flynn, Wall[16] and Ozawa.[17]

According to the KAS method based on Coats-Redfern approximation,[18] E_a is obtained from the maximum reaction rate where $d(d\alpha/dt)/dt$ is zero under a constant heating rate condition. The basic equation of the method in the integral form is:

$$\mathrm{Ln}(\beta_i/T_{p,i}^2) = \mathrm{Ln}(AR/E_a) - E_a/RT_{p,i} \qquad (2)$$

where β_i is the heating rate and $T_{p,i}$ is the peak temperature at different heating rates. E_a and A can be

Scheme 1 Synthetic route to DAF: (a) glacial acetic acid, fuming nitric acid, 65°C (b) 5% Pd/C, hydrazine hydrate 85%, ethanol, reflux.

calculated from the slope and y intersect of the linear plot of $-\text{Ln}(\beta/T_{pi}^2)$ against $(1/Tp)$, respectively. The value of E_a obtained in eq. (2) is an overall value representing all complex reactions that occur during curing.

The FWO method based on Doyle's approximation [19] is an alternative method for the calculation of E_a and is expressed in the integral form as follows:

$$\text{Ln}(\beta_i) = \text{Const.} - 1.052 E_a/RT_p \qquad (3)$$

A plot of $\text{Ln}\beta$ versus $1/T_p$ should give a straight line with a slope of $1.052E_a/R$. This can provide E_a for different degree of conversion.

The above methods have a limitation because they produce a single value of E_a for the whole process which is a sign of a single-step process. A more complete determination of Ea at any selected conversion can be calculated by the most popular isoconversional eq. (4)[20–23] of FWO that is similar **to** eq. (3) except in $T_{\alpha,i}$ that is the temperature at different conversions at different heating rates:

$$\text{Ln}(\beta_i) = \text{Const.} - 1.052 E_a/RT_{\alpha,i} \qquad (4)$$

The isoconversional method allows complex processes to be detected by a variation of E_α with α.

Prediction of isothermal cure from dynamic scans is of scientific and practical interest. According to ASTM[24] method, eq. (5) that is the integral form of eq. (1) can be used to predict the time of isothermal cure at a selected temperature (T_o):

$$t = g(\alpha)/A \exp(-E_a/RT_0) \qquad (5)$$

where $g(\alpha) = -ln\,(1-\alpha)$, and E_a and A are obtained from KAS eq. (2).

An alternative method which has been developed by Vyazovkin[20,21,25,26] yielded an integrated eq. (6) from eq. (1) at a selected isothermal temperature T_o as:

$$t_a = [\beta \exp(-E_a/RT_0)]^{-1} \int_0^{T_a} \exp(-E_a/RT)dT \qquad (6)$$

where t_α is the time to reach the extent of conversion α at a given temperature (T_o) under isothermal conditions.

In our literature survey, there was only one report[27] about the use of 2,7-diaminofluorene (DAF) to study the liquid crystal properties of DGEBP monomer. The main object of the present work was to study the kinetics of curing of diglycidyl ether of a bisphenol A-based epoxy resin (DGEBA) with an aromatic diamine such as DAF and comparing the results obtained by using nonisothermal DSC data and different kinetic methods of nonisoconversional and isoconversional. An interpretation is given on the dependence of E_a on α in the terms of the reaction mechanism. We have also applied theoretical methods to predict isothermal behavior of the cure reaction from nonisothermal data of the epoxy-amine cure.

EXPRIMENTAL

Apparatus

DSC thermograms were recorded using a Perkin–Elmer DSC-6 instrument. FTIR spectra were obtained using a Bruker, Vector 22 system. Elemental analysis was performed with CHN-600 Leco. Thermogravimetry analysis (TGA) was performed with a Du Pont TGA 951 analyzer. The ^{1}H-NMR spectra were recorded on a Bruker DRX 500 MHz Advance instrument using DMSO-d_6 as solvent.

Materials

DGEBA, average M_n = 377, epoxide equivalent 188.5, clear liquid, viscosity (at 25°C) 100–150 poise, provided from Sigma-Aldrich Co. Other compounds such as: flourene, fuming nitric acid, glacial acetic acid, Pd/C 5%, hydrazinehydrate 85%, HCl, and ethanol were obtained from Merck Co. and used without further purification.

Synthesis

2,7-dinitrofluorene (DNF) and DAF were prepared from flourene as starting material according to the procedure given in the literature,[28] and presented in Scheme 1. The characteristic properties of DNF and DAF by FTIR, ^{1}H-NMR, and elemental analysis were listed in Table I.

Sample mixing

DGEBA and certain amounts of DAF (26 and 36 phr) were carefully mixed by continuous stirring at room temperature to form a homogeneous viscous mixture. The stoichiometric amount of curing agent for DGEBA with epoxy equivalent of 188.5 is 26 phr

TABLE I
Characteristic Properties of DNF and DAF

Comp.	FTIR(KBr) $\nu(cm^{-1})$	^{1}H-NMR(DMSO-d$_6$) (ppm)	Elemental analyses					
			Calculated			Found		
			%C	%H	%N	%C	%H	%N
DNF	3096(Ar—H), 1583(C=C Ar), 1518,1332(—NO$_2$)	3.3 (S, 2H), 7.9 (s, 1H), 8.0 (s, 1H), 8.3 (m, 4H).	60.94	3.12	–	60.72	3.02	–
DAF	3382,3366,3221, 3209,(—NH$_2$), 3001(Ar—H), 1615 (C=C Ar)	3.3 (s, 2H), 7.9 (s, 1H), 8.0 (S, 1H), 8.3 (m, 4H).	79.59	6.12	–	79.12	6.02	–

DNF: m.p. = 296–300°C, Yield = 79%; DAF: m.p. = 160–163°C, Yield = 94%.

and the excess amount of 36 phr was also used. The mixtures were stored in a refrigerator to be used for DSC tests.

DSC analysis

Five milligram of the uniform viscous mixture in a sealed sample pan was scanned in DSC from room temperature to 300°C using different heating rates (5, 10, 15, and 20°C/min) under nitrogen atmosphere (20 cm^3/min).

FTIR analysis

A thin layer of the uniform viscous mixture was cured on KBr plates at a constant temperature (100°C) for various times. The partially cured samples were analyzed by FTIR spectroscopy to record the characteristic band of the epoxide group at 916 cm^{-1}.

TGA analysis

Thermal stability of the cured epoxy was measured using TGA in the temperature range of 50–700°C at the heating rate of 10°C/min under nitrogen atmosphere (20 cm^3/min). The cured sample was pre-pared by pouring the uniform viscous mixture into aluminum cell and heating in an oven at 80°C for 2 h, 120°C for 1 h, and 150°C post cure for 0.5 h. About 3 mg of the cured sample in an aluminum cell was placed in the furnace of TGA and heated to 700°C.

RESULTS AND DISCUSSION

DAF was prepared in two steps, as shown in Scheme 1, according to the procedure given in the literature[27] and data of their characteristic properties by FTIR, ^{1}H-NMR, and elemental analysis were presented in Table I. Figure 1 shows ^{1}H-NMR spectrum of the prepared DAF.

Figure 2 shows the FTIR spectra of DGEBA cured with 26 phr DAF in an oven at 120°C from 0 to 30 min. It is well-known that the characteristic band of the epoxy ring vibration of DGEBA appeared in 916 cm^{-1}, and as the cure reaction preceded this characteristic band of the epoxy ring decreased significantly.

Figure 3 shows the DSC traces of DGEBA cured with DAF as curing agent at two different concentrations and at a similar heating rate. Figure 4 shows
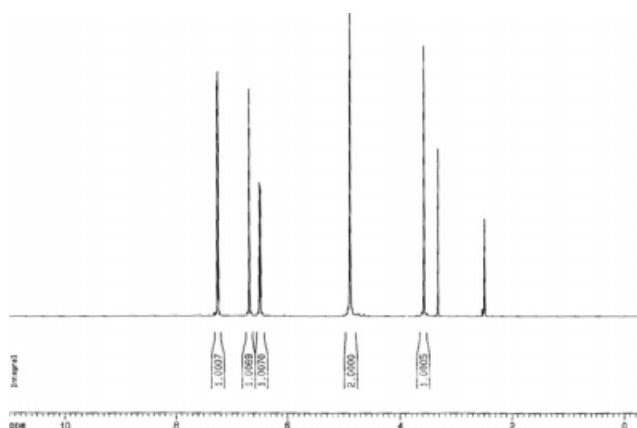

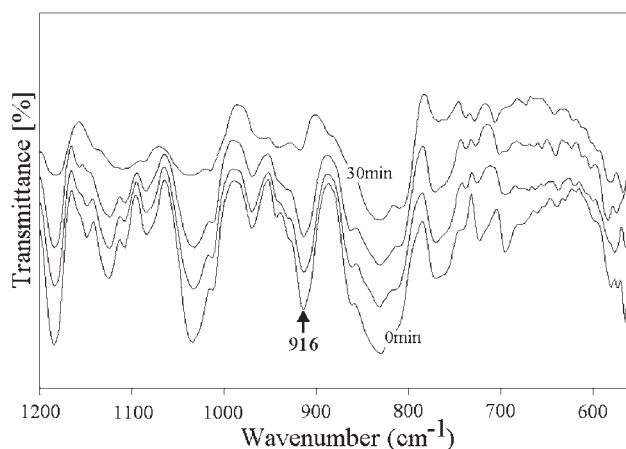
Figure 1 ^{1}H-NMR spectrum of DAF

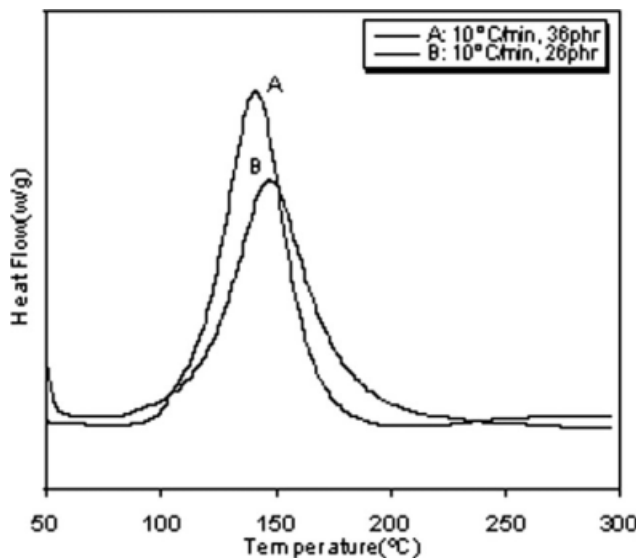Figure 2   FTIR spectrum of DGEBA/DAF system curing at 120°C.

Figure 3 Dynamic DSC thermograms of DGEBA/DAF system at different concentrations.

DSC scans for the resin sample recorded at different heating rates for the sample containing 26 phr DAF. In each case, a broad exothermic peak associated with the curing was observed. As expected, the exothermic peak shifted to the lower temperature with the increasing weight percentage of DAF at a constant heating rate, and shifted to the higher temperatures with the increasing heating rate. The exothermic transition was characterized by noting the following parameters: T_{onset} (the temperature of onset of exotherm, obtained by the extrapolation of steepest portion of the initial side of the exotherm), T_p (the temperature of the peak position of the exo-
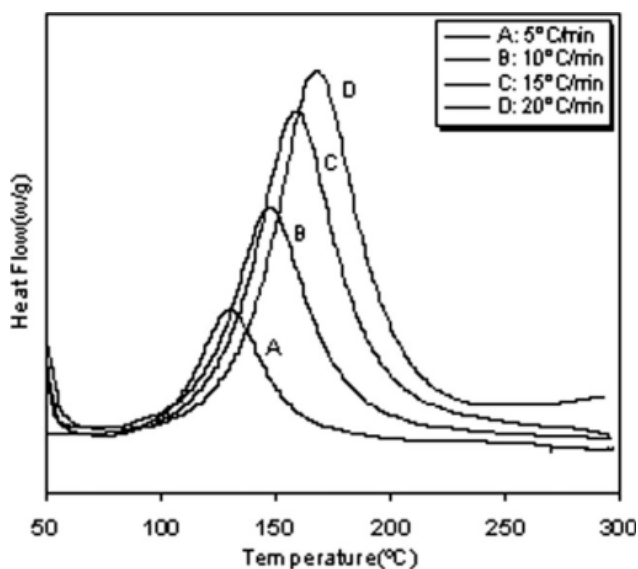
TABLE II
DSC Data for Nonisothermal Curing of DGEBA/DAF System

DAF Conc. (phr)	β (°C/min)	T_i (K)	T_P(K)	Exo.Heat (J/g)
26	5	377.65	404.03	−564.22
	10	388.57	420.08	−552.74
	15	395.25	430.41	−570.87
	20	399.56	435.87	−536.70
36	5	377.34	397.64	−557.66
	10	384.58	411.71	−549.05
	15	392.50	423.77	−546.69
	20	396.07	428.15	−546.19

β = Heating rate; T_i = Onset temperature of the exotherm peak; T_p= Maximum temperature of the exotherm peak.

therm), and ΔH (the heat of curing calculated by the measurement of area under the exothermic transition). The data of DSC scans were summarized in Table II. The functional groups are almost freely movable as DAF is completely soluble in the resin at temperatures above 80°C and it results in a rapid reaction. The exothermic peak showed a very steep slope, meaning that the cure reaction took place rapidly in a short temperature range.

The kinetic parameters of curing were obtained by the data in Table II (T_p and β) and the methods discussed in previous section. According to the method of KAS, eq. (2), the linear plots of $-\text{Ln}(\beta/T_p^2)$ versus $1/T_p$ as shown in Figure 5 were expressed by the following equations for two concentrations of DAF:

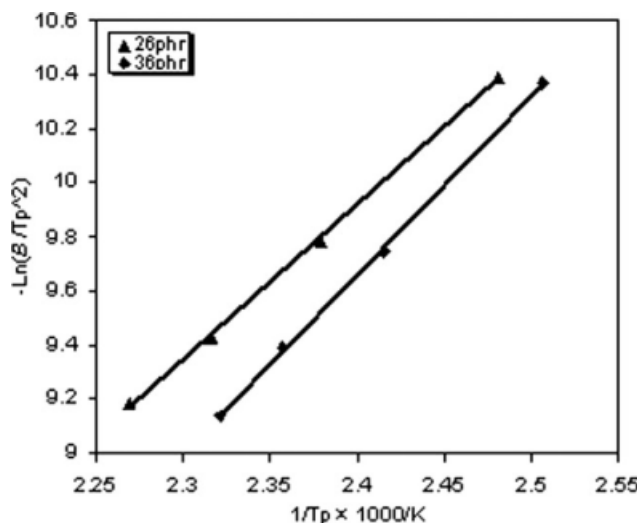$$-\text{Ln}(\beta/T_p^2) = 6.70 \times 10^3(1/T_p) - 6.17$$
$$\text{For } 26 \text{ phr DAF}$$

and

Figure 4 Dynamic DSC thermograms for DGEBA cured with 26 phr DAF at different heating rates.

Figure 5 Kissinger plots for DGEBA/DAF system.

TABLE III
Kinetic Parameters of Nonisothermal Curing of DGEBA/DAF System

DAF Conc. (phr)	$^{a}E_a$ (kJ/mol)	$^{b}E_a$ (kJ/mol)	A (s^{-1})	^{c}k (s^{-1})	$^{d}E_\alpha$ (kJ/mol)
26	55.68	58.27	5.09×10^6	1.93	64.61
36	55.06	57.59	4.79×10^6	2.14	60.69

[a] KAS method.
[b] Ozawa method.
[c] Arrhenius rate constant at 453 K.
[d] Isoconversional E_α.

$$-\mathrm{Ln}(\beta/T_p^2) = 6.62 \times 10^3 (1/T_p) - 6.31$$
$$\text{For 36 phr DAF}$$

The E_a and A values were calculated from the slope and from the y intersect of the linear plots, respectively, and were listed in Table III. The curing reaction rate constant k was compared at 453 K for two concentrations of DAF by using the Arrhenius equation and the obtained values of E_a and A. The values of k in Table III showed increase as the weight percent of DAF increased.

By using Ozawa method, eq. (3), plots of $\mathrm{Ln}(\beta)$ versus $(1/T_p)$ gave straight lines, as shown in Figure 6, with slope of $1.052E_a/R$. The calculated E_a values were listed in Table III, showed increase with increasing the amount of DAF.

The increase in the A value with increasing concentration of DAF is due to the increasing probability of collision between reactant groups. The higher value of E_a for the curing of sample containing an excess of curing agent (36 phr) can probably be attributed to the increasing content of high crosslink density, which restricts the diffusion of functional groups. To support this conclusion, we have mea-
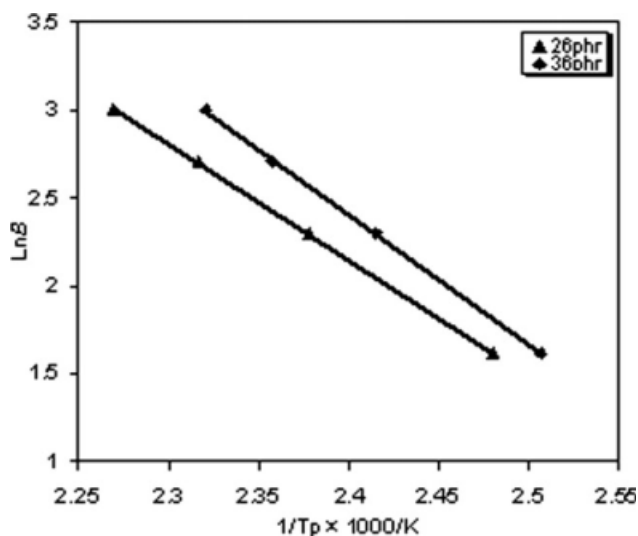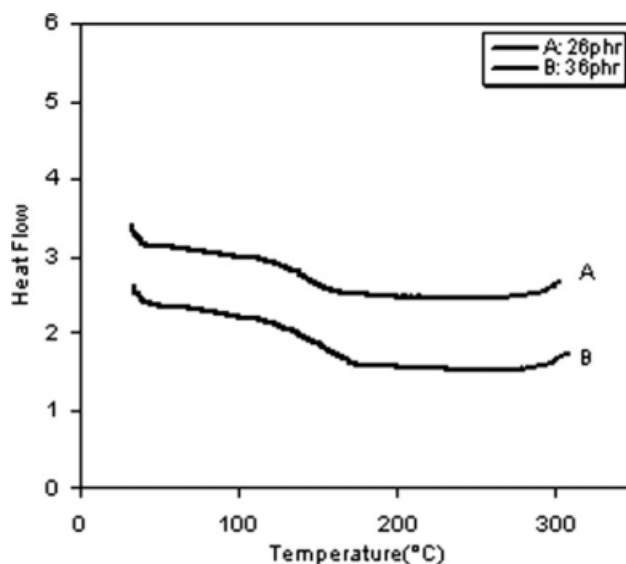

Figure 7 Determination of T_g of the cured samples containing 26 and 36 phr DAF.

sured T_g of the cured samples in the second DSC scan and the results are shown in Figure 7. T_g for the samples containing 26 and 36 phr DAF were found to be 144 and 153°C, respectively.

The E_a values obtained in this study by KAS and Ozawa methods (55.68 and 58.27 kJ/mol, respectively) are almost in the same range of the E_a values reported by other workers[6–9,29,30] for epoxy-diamine systems (45–65 kJ/mol). DSC analysis has shown[29] that etherification occurs at elevated temperatures once all the primary amines are exhausted. High activation energies (>150 kJ/mol by DSC) are characteristic of this process. Therefore, the primary amine addition is considered as a single step taking place during the cure reaction and controls the
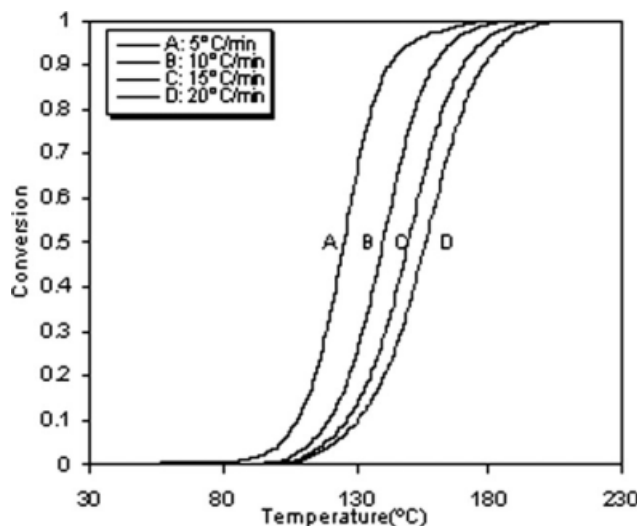

Figure 6 Ozawa plots for DGEBA/DAF system.

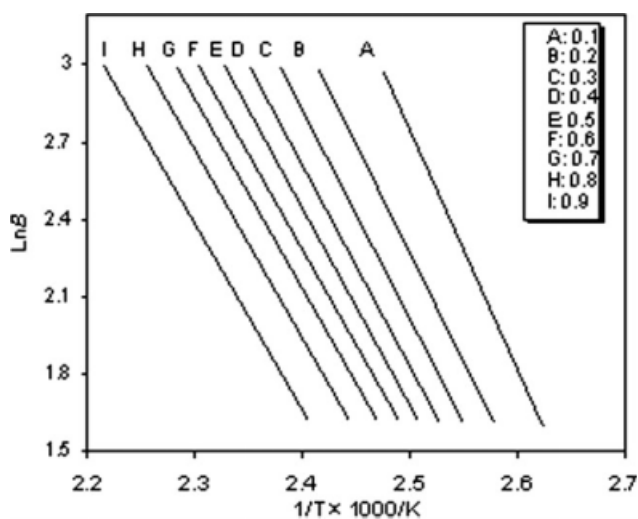**Figure 8** Conversion versus temperature at different heating rates for sample containing 26 phr DAF.

Figure 9 Isoconversional plots of Lnβ versus 1/T at various conversions for sample containing 26 phr DAF.

overall heat release at lower conversions. In the above case, the obtained E_a value is supposed to be constant throughout the entire period of the amine conversion. This idea does not correspond to the autocatalytic mechanism of the process. The E_a value does not remain constant with the progress of cure reaction when compared with the very beginning of the process where the nonautocatalyzed reaction occurs. Therefore, the low values of E_a reported in Table III, most likely represent some average values between the E_a values of nonautocatalyzed and autocatalyzed reactions.

Isocoversional kinetic analysis offers a viable alternative in this situation. The basic idea of this type of analysis is that the reaction rate at a constant conversion depends only on the temperature. To perform isoconversional analysis, the original DSC data (Fig. 4) were transformed into the form α_i versus T_i for each ith heating rate. Conversions were determined as fractional areas of a DSC peak. The resulting dependence of α_i versus T_i for each heating rate was shown in Figure 8 for sample containing 26 phr DAF. Plotting Ln(β) versus 1/T, using eq. (4), produced straight lines as shown in Figure 9 for the same sample as in Figure 8. The E_a value for each conversion was obtained from the slope of the straight line and the resulting dependence of E_a on conversion is presented in Figure 10. As can be seen in this figure, the E_a values in the whole region of conversion from 0.1 to 0.9 for the sample containing stoichiometric amount of DAF (26 phr) are higher than that which contains the excess amount of DAF (36 phr). The E_a values remain almost constant up to $\alpha = 0.6$ and then start to increase marginally. The diffusion of the functional groups and the catalytic effect of the hydroxyl groups become restricted because of the crosslinking reactions occurring dur-

ing gelation process, and this can probably describe that increase in the reported E_a with increasing conversion is not large. This restriction depends on the thermal history of the cure and can be experimentally encountered as early as by $\alpha = 0.4$ and this has also been reported by other worker.[31] The average value of E_a for the whole ranges of conversion was 64.61 kJ/mol for the stoichiometric amount of DAF.

According to ASTM method,[24] for prediction of isothermal cure behavior, the dependencies of α on t at a selected temperature, the Arrhenius parameters (E_a and A) have to be substituted into eq. (5). These parameters (E_a and A) were evaluated by using KAS method, eq. (2), at the maximum peak temperatures for different heating rates ($T_{p,i}$). Figure 11(a) shows the dependencies of α on t at isothermal temperature of $T_0 = 180°C$ by ASTM method for two concentrations of DAF. As can be seen, the time to reach total conversion decreased with the sample containing the excess amount of curing agent (36 phr). Figure 11(b,c) show the dependence curves obtained by using Vyazovkin method,[18] eq. (6), for samples containing 26 and 36 phr DAF, respectively, at isothermal temperature of $T_0 = 180°C$ and for different heating rates. The computations of dependence of α on t at an isothermal temperature by this method require only a dependence of E_a on α (isoconversional method) and experimental values of T_α. As can be seen in these Figures, the dependence curve of α on t at isothermal temperature of 180°C by Vyazovkin method shows strong and direct effect of the heating rate according to the eq. (6). These results according to eq. (6) indicate that at a certain concentration the time required to reach a particular conversion increased with increasing heating rate.
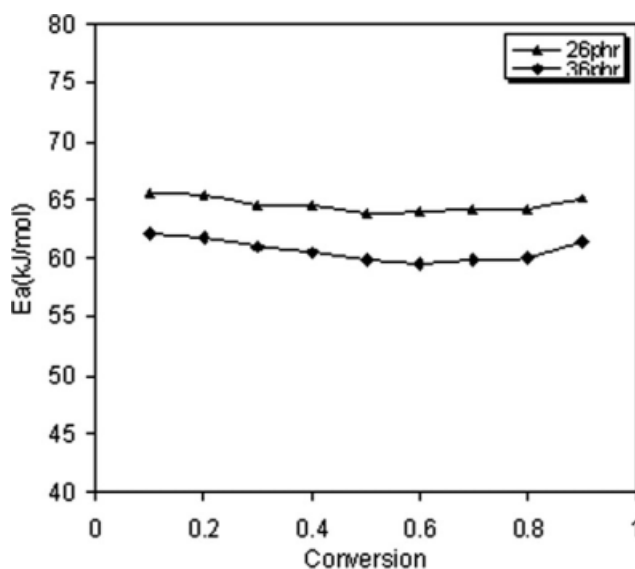

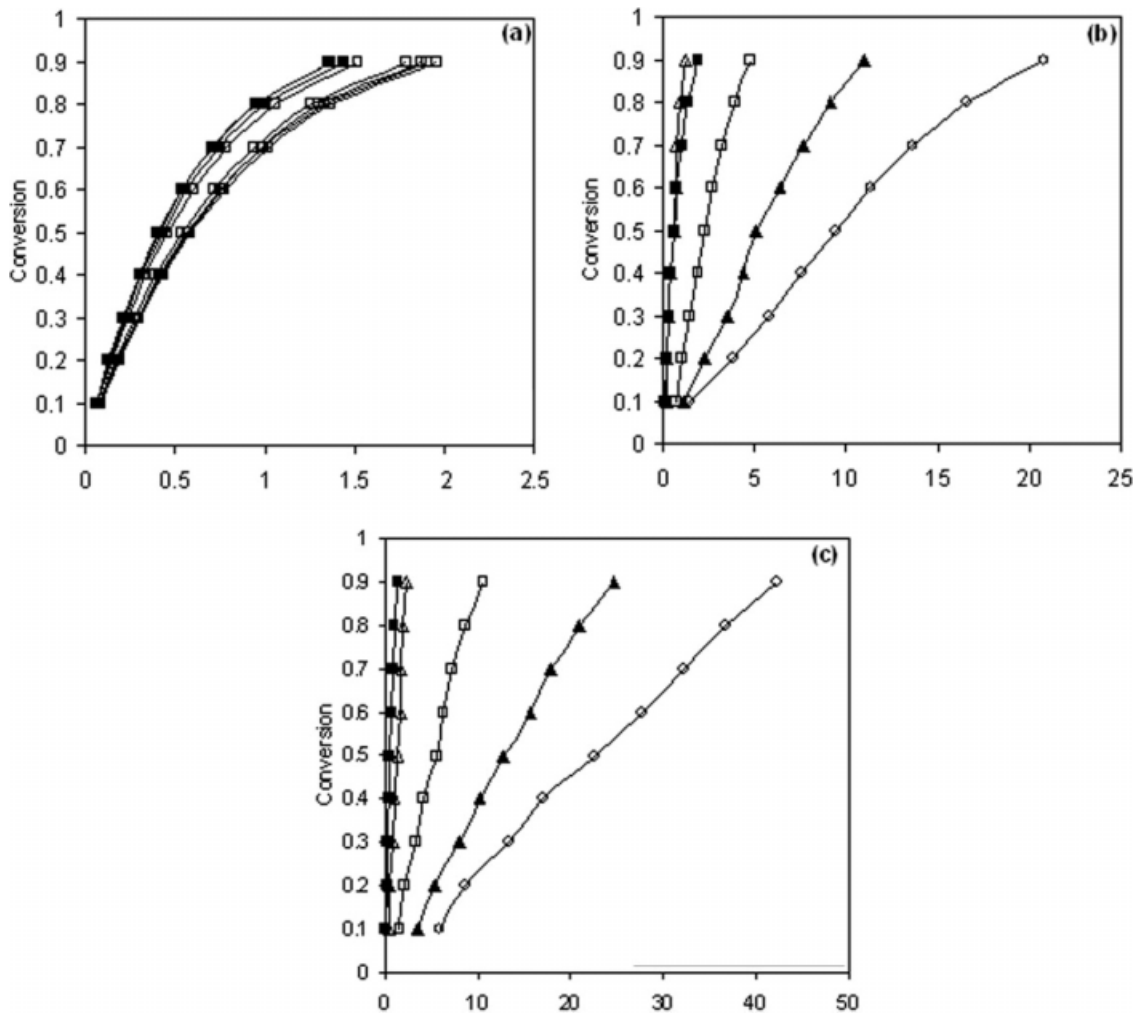**Figure 10** Variation of Ea versus conversion for DGEBA/DAF systems.

Figure 11 Dependence of α on t curves at isothermal temperature of 180°C: (a) By ASTM method: ■ 36 phr DAF and □ 26 phr DAF at heating rates 5, 10, 15, and 20°C/min. (b) By Vyazovkin method for 26 phr DAF at: △ 5, □ 10, ▲15, ○ 20°C/min; and ■ ASTM. (c) By Vyazovkin method for 36 phr DAF at: △ 5, □ 10, ▲15, ○ 20°C/min; and ■ ASTM.
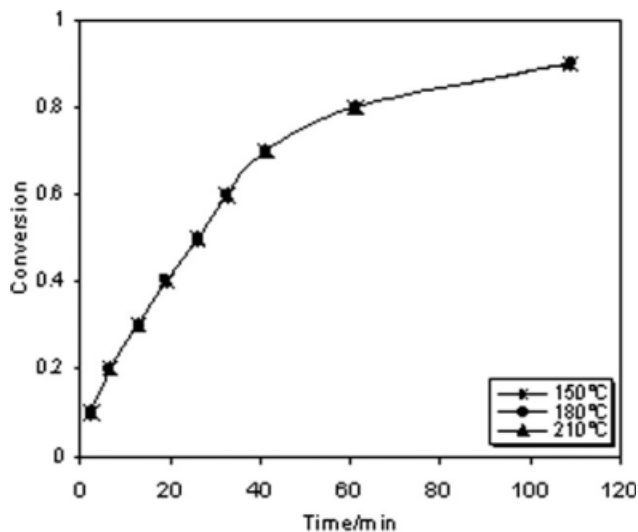

Figure 12 Dependence of α on t curves using ASTM equation at different isothermal temperatures for heating rate 10°C/min and 26 phr DAF.
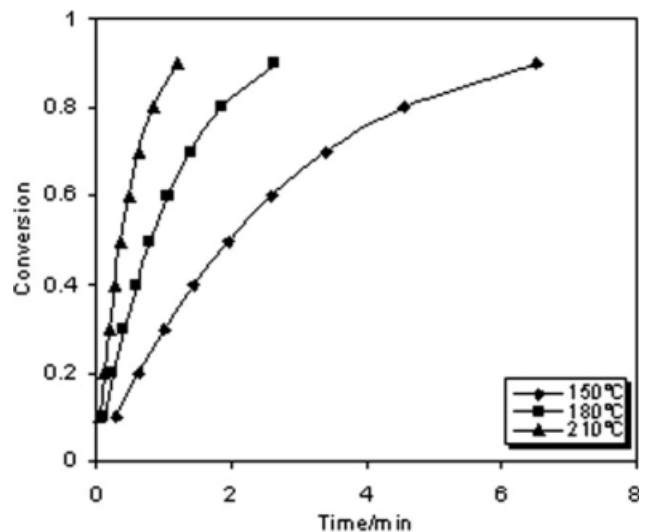

Figure 13 Dependence of α on t curves using Vyazovkin equation at different isothermal temperatures for heating rate 10°C/min and 26 phr DAF.
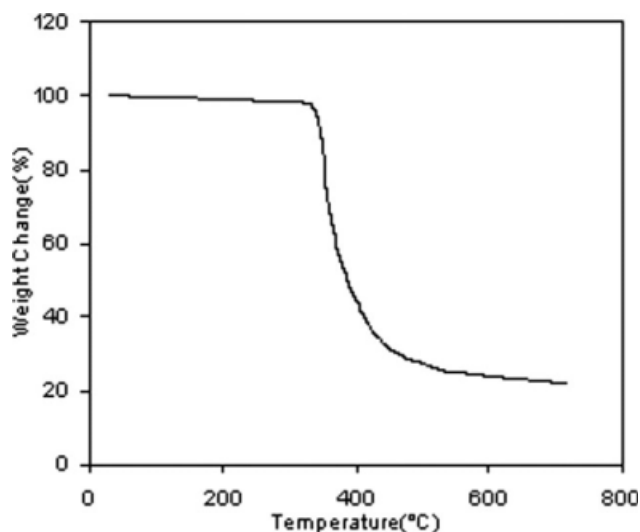
Figure 14 TGA curve for the cured sample of DGEBA/26 phr DAF system.

The prediction of cure behavior by ASTM and Vyazovkin methods were also carried out at three different isothermal temperatures for the sample containing 26 phr DAF. The results in Figures 12 and 13 are what expected to obtain from the eqs. (5) and (6). As can be expected from the eq. (5) and can be seen in Figure 12, changes in isothermal temperature influence on the time required to reach the total conversion, as changes in the heating rate affect the time according to the eq. (6) and the results showing in Figure 11(b,c).

Figure 14 shows TGA curve of the cured sample of DGEBA/DAF system. Single step decomposition was observed in this sample and the cured resin was stable up to 350°C and started loosing weight above this. The relative thermal stability of the cured resin can be evaluated by comparing the temperature of 345°C for 5% decomposition with the temperature of 390°C for 50% decomposition and the percent of char yield at 718°C was 22%.

CONCLUSIONS

An aromatic diamine (DAF), as curing agent for DGEBA, was prepared and its characteristic properties were measured and checked with those reported in the literature. The curing reaction was followed by FTIR measuring the absorption peak of epoxide group at 916 cm^{-1}. The exothermic heat of curing by nonisothermal DSC test appeared as a single peak with T_p in the range of 130–170°C depending on the heating rate. The E_a values by nonisoconversional methods of KAS and Ozawa were found to be 55.68 and 58.27 kJ/mol, respectively, for samples containing stoichiometric amount (26 phr) of DAF. The E_a values by isoconversional method (an average of

64.61 kJ/mol) showed dependence on degree of conversion with the progress of curing up to $\alpha = 0.6$. The catalytic effect of hydroxyl groups formed during the curing may be responsible for the decrease in the E_a value. The low values of E_a most likely represent both nonautocatalyzed and autocatalyzed reactions.

ASTM and Vyazovkin methods were applied to predict the practically complete isothermal cure times at a selected temperature by using nonisothermal data obtained from DSC measurements. The results from these two methods according to the related equations of (5) and (6) showed dependencies, respectively, only on the concentration of curing agent or both on the concentration and heating rate.

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