

Cure Kinetics of Ternary Blends of Epoxy Resins Studied by Nonisothermal DSC Data

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ABSTRACT: The curing kinetics of blends of diglycidyl ether of bisphenol A (DGEBA), cycloaliphatic epoxy resins, and carboxyl-terminated butadiene-acrylonitrile random copolymer (CTBN) in presence of 4,4'-diamino diphenyl sulfone (DDS) as the curing agent was studied by nonisothermal differential scanning calorimetry (DSC) technique at different heating rates. The kinetic parameters of the curing process were determined by isoconversional method given by Malek for the kinetic analysis of the data obtained by the thermal treatment. A two-parameter (m, n) autocatalytic model (Sestak-Berggren equation) was found

to be the most adequate selected to describe the cure kinetics of the studied epoxy resins. The values of E_a were found to be 88.6 kJ mol^{-1} and 61.6 kJ mol^{-1} , respectively, for the studied two sample series. Nonisothermal DSC curves obtained using the experimental data show a good agreement with that theoretically calculated. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 112: 3119–3126, 2009

Key words: DGEBA epoxy resin; cycloaliphatic epoxy resin; CTBN; blends; differential scanning calorimetric analysis (DSC)

INTRODUCTION

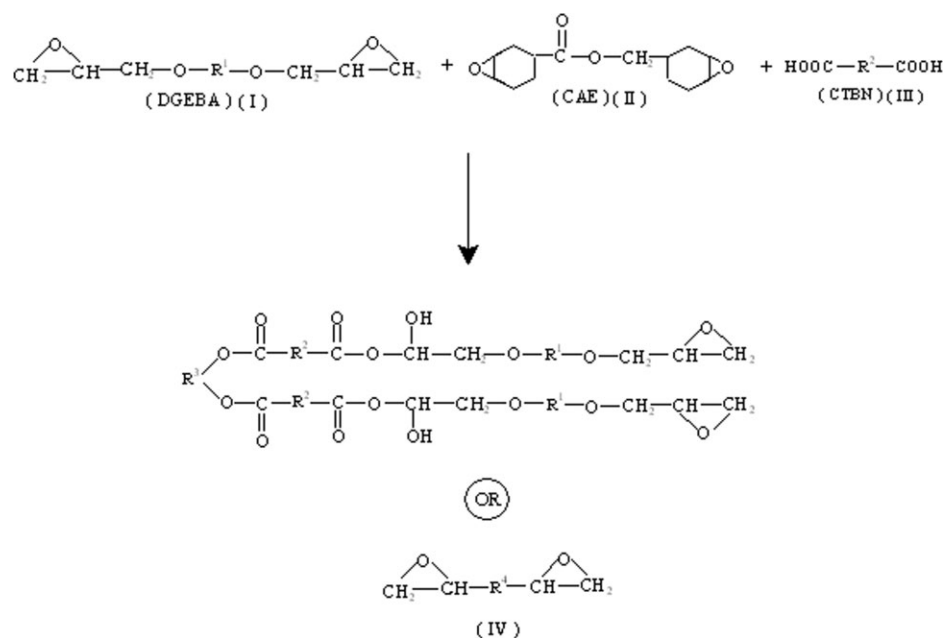
The applications of the cured epoxy resins have been expanded in various fields such as coatings, adhesives, electrical insulators, matrices for fibrous components, etc. However, the cured epoxy resins having high cross-link density are so brittle that they are easily broken by an instant impact. Therefore, many researchers have studied to enhance the toughness of the cured epoxy resins and one of the most well-known methods is to incorporate various amounts of reactive liquid rubbers.^{1,2} The most popular rubbery modifying agent is carboxyl-terminated butadiene-acrylonitrile random copolymer (CTBN) because of its miscibility with the epoxy hardener mixture during the initial polymerization period and also because the carboxyl functional groups in CTBN can react with the epoxide groups, thus, achieving a high level of interfacial adhesion.² The enhancement in toughness is achieved because the elastomeric phase precipitates at some stage of the curing process into particles of very small size.^{3,4}

Cycloaliphatic epoxy resins, in general, are most widely used for cationic UV-curable coating applications⁵ because of their fast cure response. In addition to the fast cure response, cycloaliphatic epoxides

provide excellent adhesion to a wide variety of substrates, flexibility, good color stability, excellent gloss, low potential for skin irritation, low shrinkage, good weather ability, and good electrical properties.^{5,6} The homopolymers of cycloaliphatic epoxide is also brittle and the toughness and impact resistance of such epoxies are, typically, improved by the incorporation of flexible cross-linkers, such as difunctional and trifunctional polyols.^{7,8} Improvement of toughness of cycloaliphatic epoxides by the addition of CTBN is rarely studied.⁹ However, there are no reports on the modification of blends of diglycidyl ether of bisphenol A (DGEBA) epoxy and cycloaliphatic epoxy resins by CTBN. Therefore, this article reports the study of cure kinetics, by dynamic differential scanning calorimetry (DSC) scans at different heating rates, of blends of DGEBA/cycloaliphatic epoxy resins modified by CTBN and is cured with 4, 4'-diamino diphenyl sulfone (DDS) curing agent. Because of mild temperature curing system and high temperature performance cycloaliphatic epoxy resin might play an important role in the studied blend system.

Differential scanning calorimetry (DSC), which measures the heat flow of the sample as function of temperature, has extensively used to study the cure kinetics of various thermosetting polymers.^{10–13} An optimal curing process depends on understanding the curing kinetics, the curing mechanism (as shown in Schemes 1 and 2), and accurate modeling of the curing process. This modeling includes

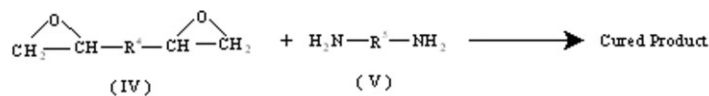
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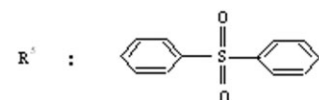
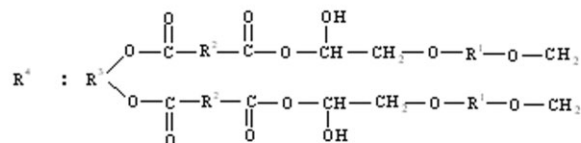
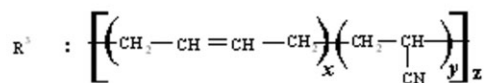
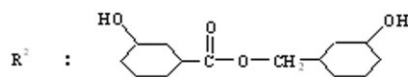
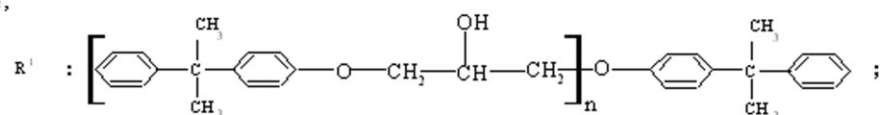
Scheme 1 Formation of prepolymer.

determination of the mechanism, or appropriate kinetic equation for an analyzed system, measurement of reaction order, and activation energy of the reaction.

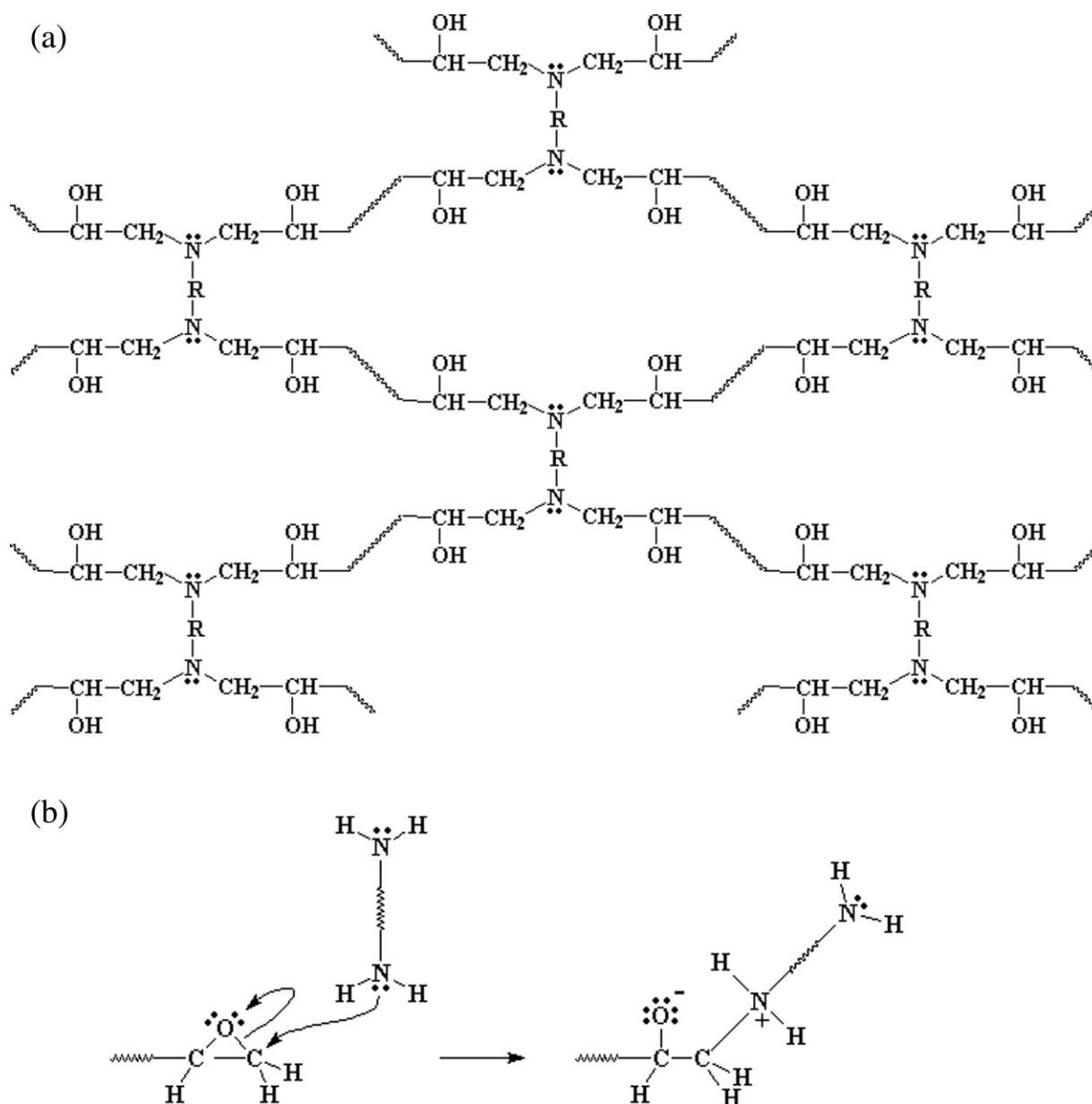
This article reports the cure kinetics of the ternary blend system and determination of the kinetic parameters of the cure reaction [Schemes 2 and 3(a,b)] from nonisothermal DSC measurements, applying the



where,



Scheme 2 Curing reaction of prepolymer.



Scheme 3 (a) Final cured product (by the reaction of IV and V) and (b) The diamine's electron attack the carbon atom next to the epoxide oxygen, giving us a negative charge on the oxygen, and a positive charge on the nitrogen.

simple and consistent method^{14,15} on kinetic analysis of the data obtained by the thermal treatment. The used method allowed us to select the most convenient model for the curing reaction (Sestak-Berggren equation)¹⁶ of the studied ternary blend system.

EXPERIMENTAL

Materials

DGEBA epoxy resin (LY 556) and cycloaliphatic epoxy resin (CY 230) were the commercial products (M/s Ciba Specialty Chemicals, Mumbai) having epoxide equivalent weight of 192 and 145 g eq⁻¹, respectively.¹⁷ Cure agent 4,4'-diamino diphenyl sul-

fone (DDS) was also arranged by the same firm at Mumbai, India. The elastomer employed was carboxyl-terminated butadiene-acrylonitrile copolymer (CTBN) (viscosity: 625,000 mPas at 27°C) (Trade name: Hycar 1300 × 13) and was procured from M/s Emerald Performance Materials, LLC, Hong Kong with molecular weight, \overline{M}_n of 3500 containing acrylonitrile content 27% and carboxyl content 32%.

DSC measurements

DSC, a thermo analytical technique, was used to study the cure kinetics of the blend of DGEBA-epoxy (DGE) and cycloaliphatic epoxy (CAE) resins in presence of CTBN. To investigate the cure kinetics,

the DGEBA epoxy resin/cycloaliphatic epoxy resin/CTBN/DDS were well-mixed at 110°C¹⁷ to prevent the cure reaction during the mixing and stored at -13°C. The curing of thermal data were obtained using a TA Instruments DSC 2920 type calorimeter, which was heated from 25 up to 325°C with different heating rates (5, 10, and 15°C min⁻¹), in a nitrogen atmosphere. Pure indium was used as a standard for calorimetric calibration. The study of the curing reaction was carried out using an equal weight ratio of DGE and CAE.

A small quantity of the sample (2.5–4.0 mg) was used for the DSC studies in an aluminum cell. An identical empty cell was taken as reference. The heat flow data, as a function of temperature and time, were obtained using the area under the peak of the exotherm. They were processed further to obtain a fractional conversion (α) and the rate of the reaction $d\alpha/dt$.

The rate of the kinetic process can be described by eq. (1)^{10,14}

$$\frac{d\alpha}{dt} = K(T)f(\alpha) \quad (1)$$

where, $K(T)$ is a temperature-dependent reaction rate constant, and $f(\alpha)$ a dependent kinetic model function.

There is an Arrhenius type dependence between $K(T)$ and temperature according to eq. (2).

$$K(T) = A \exp\left(-\frac{E_a}{RT}\right) \quad (2)$$

where, A is the pre-exponential factor, and E_a is the apparent activation energy.

For nonisothermal conditions, when the temperature varies with time with a constant heating rate β dT/dt , eq. (2) is modified as follows:

$$\frac{d\alpha}{dT} = \frac{A}{\beta} \exp\left(-\frac{E}{RT}\right) f(\alpha) \quad (3)$$

Usually, E_a values are determined using the integral forms of eq. (3), the most popular derivative modes being those proposed by Ozawa,¹⁸ Flynn and Wall,¹⁹ and Doyle,²⁰ which give E_a from the plot $\ln\beta_i$ against $T_{\alpha,i}^{-1}$ (i is the ordinal number of DSC runs performed at different heating rates, β_i). Generally, the E_a values found by these equations require further corrections,²¹ which can be avoided using the methods suggested by ASTM E 698-79,^{22,23} according to which the E_a is evaluated from the plot $\ln(\beta_i/T_{m,i}^2)$ against $T_{m,i}^2$ where, $T_{m,i}$ are the temperatures corresponding to peak maxima at different heating rates. The latter has been used in present computations of E_a at different values of α . The experimentally evaluated values of E_a were used to find the appropriate kinetic model which best describes the conversion function of the process studied.

The kinetic parameters of the curing process were determined by the isoconversional method given by Málek.^{14,15} Once E_a has been determined, the special functions $y(\alpha)$ (4) and $z(\alpha)$ (5) must be evaluated as follows:

$$y(\alpha) = \left(\frac{d\alpha}{dt}\right) e^x \quad (4)$$

$$z(\alpha) = \pi(x) \left(\frac{d\alpha}{dt}\right) \frac{T}{\beta} \quad (5)$$

where, x is reduced activation energy (E_a/RT), β the heating rate (K min⁻¹), T absolute temperature (K), and $\pi(x)$ is the expression of the temperature integral. As was pointed out,¹⁰ $\pi(x)$ function can be well approximated using 4th rational expression of Senum and Yang,²⁴ as in eq. (6)

$$\pi(x) = \frac{(x^3 + 18x^2 + 88x + 96)}{(x^4 + 20x^3 + 120x^2 + 240x + 120)} \quad (6)$$

For practical reasons, the $y(\alpha)$ and $z(\alpha)$ functions are normalized within (0,1) range. The maximum α_M of the $y(\alpha)$ function and α_p^∞ of the $z(\alpha)$ function suggest the choice of the most suitable kinetic model characterizing the curing process studied. Once the kinetic model has been determined, and using the value of E_a , other kinetic parameters can be determined, such as pre-exponential factor and kinetic exponents. The pre-exponential factor A was calculated according to eq. (7):

$$A = -\left\{\frac{\beta x_p}{T f'(x_p)}\right\} \exp(x_p) \quad (7)$$

where, $f'(x_p)$ is the differential form of the kinetic model $[df(\alpha)/d\alpha]$, α_p is the conversion corresponding

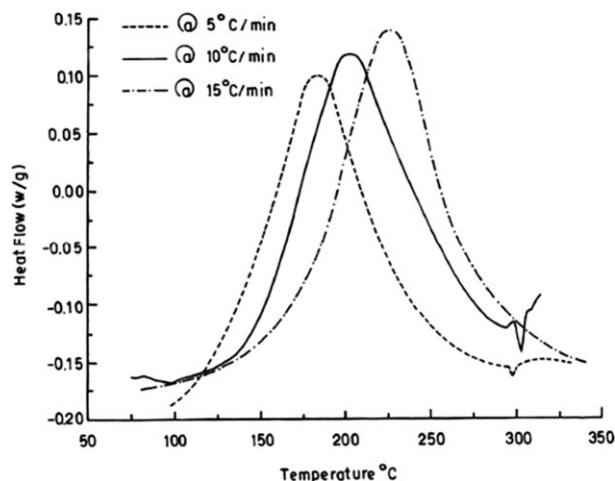


Figure 1 Dynamic DSC scans of DGE/CAE/CTBN blend system containing 10 wt % CTBN at three different heating rates.

TABLE I
Blend Samples Analyzed for DSC and Curing Characteristics Evaluated from DSC Thermograms at Heating Rate 10°C/min

Sample no.	Weight ratio of different components		Sample code	Heating rate (°C min ⁻¹)	Date from DSC scans				
	DGE : CAE/CTBN	DDS			T_i (°C)	T_p (°C)	T_f (°C)	Cure time (min)	ΔH (J g ⁻¹)
1.	1 : 1/5%	34.2	A	5	106	207	289	36.6	231.8
				10	113	209	288	17.5	194.8
				15	94	186	284	12.7	184.2
2.	1 : 1/10%	32.4	B	5	99	207	292	38.6	278.3
				10	109	210	291	18.2	231.0
				15	89	190	281	12.8	184.2

to the maximum on DSC curve and p is the maximum of DSC curve.

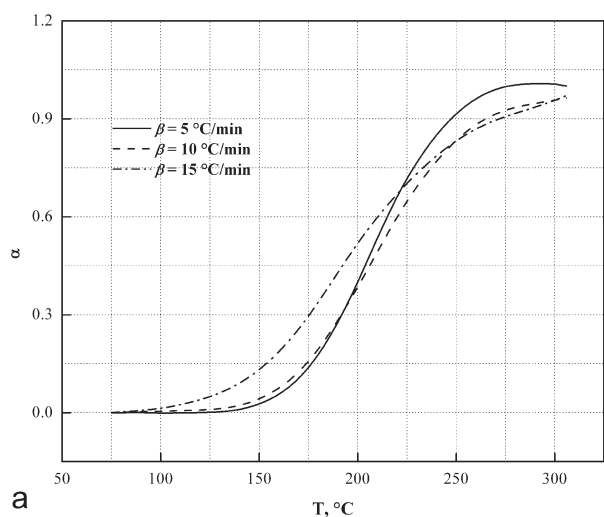
RESULTS AND DISCUSSION

Figure 1 shows DSC curves for DGE/CAE/CTBN blend systems containing 10 wt % CTBN (Samples B

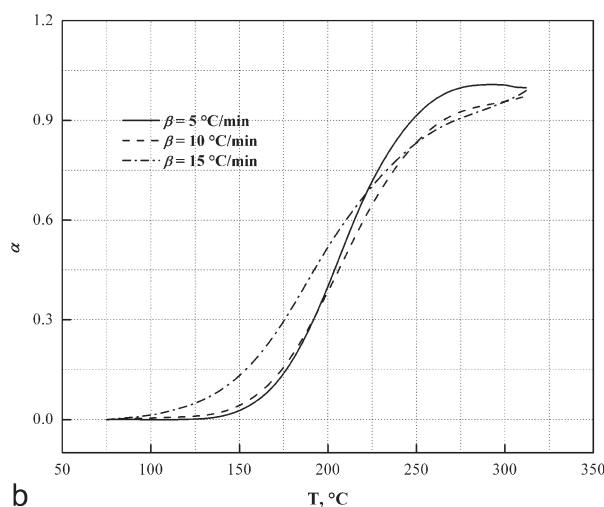
in Table I) at three different heating rates 5, 10, and 15°C min⁻¹, respectively. As can be noted from the curves that cure reaction took place in one stage regardless of heating rate and the total heats were 194 and 210 J g⁻¹ of epoxide group for samples A and B, respectively.

Figure 2(a,b) shows the conversion curves for blend sample B, respectively, at the three heating rates, which could be obtained from integrating the DSC curves of Figure 1. On the curve of 5°C min⁻¹, the conversion increased very slowly in the initial stage and rose abruptly in the 135–271°C and 127–274°C for blend samples A and B, respectively, and it was almost constant in the final stage. The abrupt increment of cure rate in the low temperature range could be explained by the autocatalytic cure mechanism.^{1,25} All curves for other heating rates, for both the blend samples A and B, showed the s-shape and they shifted to right hand side with the increasing heating rate.

The isoconversional temperatures at three different heating rates could be obtained from the cross



a



b

Figure 2 Plots between conversion and temperature at different heating rates for blend sample A.

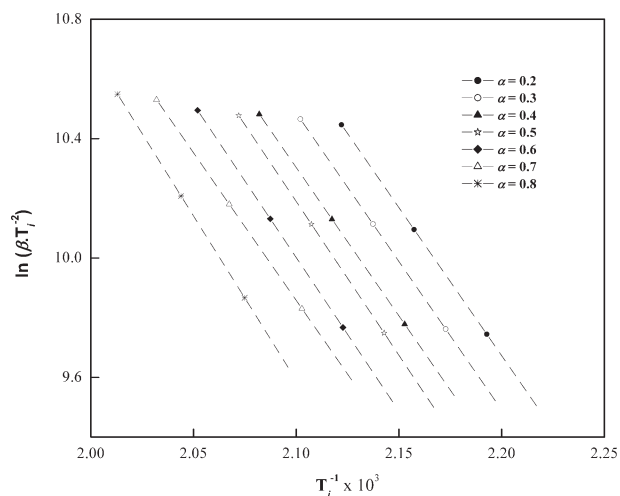


Figure 3 Arrhenius plots for blend sample A in the interval $0.2 < \alpha < 0.8$.

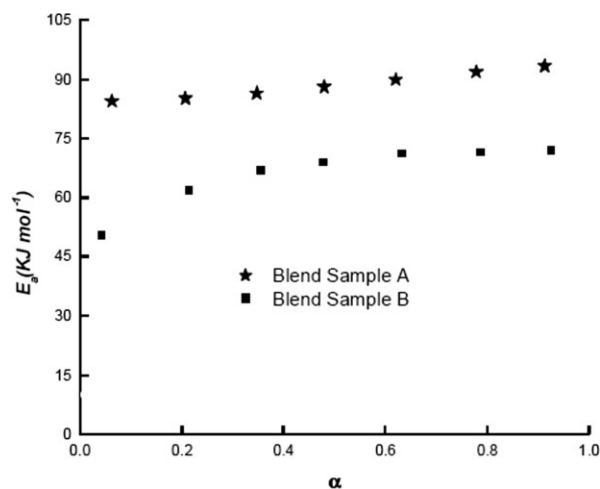


Figure 4 Variation of E_a versus conversion.

points of the conversion curves and the dotted lines at various selected conversion curves. For each blend sample, E_a was evaluated from the plot of $\ln(\beta/T_i^2)$ against T_i^{-1} ,²³ where, T_i are the temperatures corresponding to different values of α ranging between 0.1 and 0.8 (Fig. 3). Further, the variation of E_a with conversion α for the two blend samples is shown in Figure 4.

The values of E_a changed slightly in the range 85.1–91.9 kJ mol⁻¹ for blend sample A, whereas the values changed largely in the range 61.6–71.5 kJ mol⁻¹ for blend sample B at different degree of conversions ranging in between 0.2 and 0.8. For blend sample A, the value decreased with the increasing conversion in the initial stage and showed minimum value at $\alpha = 0.4$ (refer Fig. 4). Such trend was not observed for blend sample B. The decrement of activation energy may be due to the autocatalytic role of hydroxyl group in the cure reaction.^{1,25} One hydroxyl group was generated by

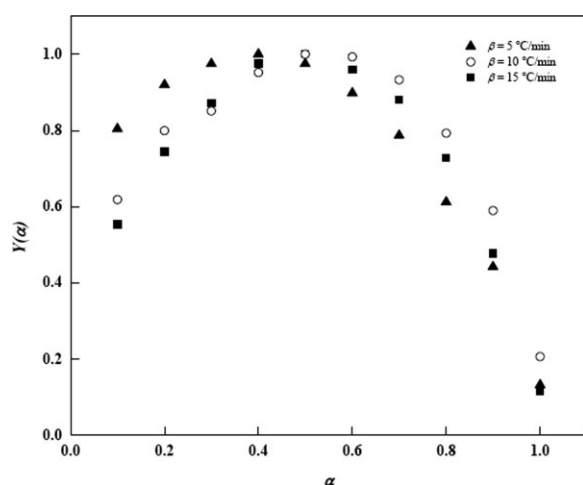


Figure 5 Variation of $y(\alpha)$ function versus conversion for blend sample A.

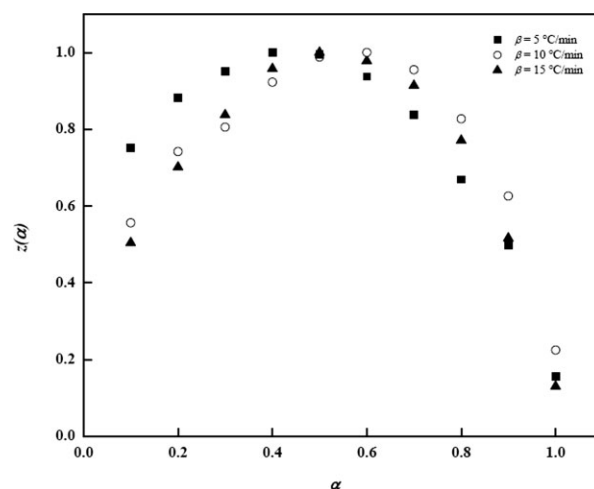


Figure 6 Variation of $z(\alpha)$ function versus conversion for blend sample A.

the reaction between an epoxide group and an amine group and the generated hydroxyl group acted as a catalyst for the reaction between another epoxide group and amine group. As the cure reaction proceeded, the concentration of hydroxyl group increased, so the cure rate steeply increased at final conversion due to the increased viscosity and cross-link, which reduced the mobility of the unreacted functional groups.²⁶ Regarding blend sample A, it can be noted that for conversions between 0.2 and 0.8, there was very low variation of E_a with conversion (mean values for blend samples A and B are 88.6 and 61.6 kJ mol⁻¹, respectively). The presence of more carboxyl groups might accelerate the cure reaction, and, so the value of E_a increased with conversion, in the case of blend sample B.

The mean values of E_a determined from DSC data were used to calculate both $y(\alpha)$ and $z(\alpha)$ functions using eqs. (11) and (12), respectively. Figures 5 and 6 show the variation of $y(\alpha)$ (Fig. 5) and $z(\alpha)$ (Fig. 6) values with conversion for blend sample A. The values of both $y(\alpha)$ and $z(\alpha)$ were normalized between (0, 1) interval of blend systems for various heating rates. These functions exhibit maxima at α_M and α_p^∞ , respectively. Both α_M and α_p^∞ help to decide the choice of the kinetic model.¹⁵ Table II lists the values

TABLE II
The Values of α_p , α_M and α_p^∞ Obtained from DSC Thermograms Analysis

Sample	Heating rate (°C/min)	α_p	α_M	α_p^∞
A	5	0.48	0.49	0.50
	10	0.55	0.56	0.60
	15	0.49	0.40	0.40
B	5	0.46	0.48	0.51
	10	0.51	0.52	0.53
	15	0.38	0.40	0.42

TABLE III
The Kinetic Parameters Evaluated for the Curing of the Total Epoxy Resins

Sample	Heating rate (°C min ⁻¹)	E_a (kJ mol ⁻¹)	lnA	m	Mean	n	Mean
A	5	88.6	18.32	0.633	0.530	0.659	0.574
	10			0.522		0.411	
	15			0.435		0.653	
B	5	61.6	14.78	0.604	0.482	0.654	0.556
	10			0.432		0.399	
	15			0.410		0.615	

of maxima α_M and α_p^∞ corresponding to the functions $y(\alpha)$ and $z(\alpha)$ for all the studied samples, together with the α_p taken as the maximum of the DSC peaks.

As was noted, data in Figures 5 and 6, respective in Table II, show that α_M and α_p^∞ and α_p values are independent of the heating rate. Simultaneously, the values of α_M are lower against the values of α_p , whereas α_p^∞ exhibits the lower values than 0.632. These remarks indicated that the studied curing process can be described using the two parameter autocatalytic kinetic model Sestak-Berggren [eq. (8)].¹⁶

$$f(\alpha) = \alpha^m (1 - \alpha)^n \quad (8)$$

where, m and n are the kinetic exponents.^{15,27} The kinetic parameter n is obtained by the slope of the linear dependence $\ln[(d\alpha/dt)e^x]$ versus $\ln[\alpha^p(1 - \alpha)]$ from eq. (3) and $m = pn$, where, $p = \alpha_M/(1 - \alpha_M)$.

Table III lists some kinetic parameter evaluated for the proposed Sestak-Berggren kinetic model. As it is shown in Table II, the variation of the kinetic parameters values with the heating rate is placed in the experimental errors limit (within 10% of the average value).

The correctness of the kinetic model proposed using the Sestak-Berggren equation was verified by plotting $d\alpha/dt$ versus temperature (experimental

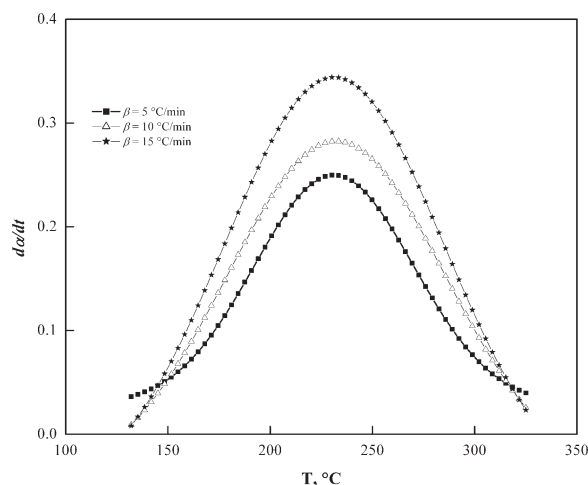


Figure 7 Comparison of experimental (symbols) and calculated (full lines) DSC curves for blend sample 1.

curves), using the data listed in Table II, with the curves obtained by computational processing of the thermograms (calculated curves). An example is given in Figure 7 for the DGEBA epoxy/cycloaliphatic epoxy/CTBN/DDS system (e.g., Sample A). It is observed that the two parameters Sestak-Berggren model well describes the studied curing process.

CONCLUSIONS

The cure kinetics of two compositions of DGEBA-epoxy/cycloaliphatic epoxy/CTBN/DDS system using nonisothermal DSC data is presented. Several measurements at various heating rates provide a determination of activation energy and a simple, reliable method of kinetic analysis enables us to select the most convenient model for the curing reaction. The mean values of E_a were found to be 88.6 kJ mol⁻¹ and 61.6 kJ mol⁻¹, respectively, for the studied two sample series. The values of E_a in the conversion interval between 0.2 and 0.8 were increasing and independent of the experimental conditions.

It was established that the curing reaction of the cured system can be described by two parameter autocatalytic model (Sestak-Berggren equation) is the most suitable for description of the studied curing process. The kinetic parameters, which were experimentally determined, were used to calculate the theoretical DSC curves. This shows a good agreement with that experimentally determined.

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