

Influence of manganese acetyl acetonate on the cure-kinetic parameters of cyanate ester–epoxy blend systems in fusion relevant magnets winding packs

Subrata Pradhan · Priyanka Brahmhatt ·
Janardhanan Devaki Sudha · Jisha Unnikrishnan

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Abstract Blending cyanate ester (CE) with epoxy resins offers the possibility to manufacture radiation resistant insulations at a low price compared to pure CE materials. Therefore, it is of special interest to study the influence of the CE content and also the effect of catalyst on the curing behavior of these insulation systems. Here, we present the curing behavior of the CE–epoxy blend system studied by non-isothermal differential scanning calorimetry in combination with Fourier infra red (FTIR) spectroscopy. Effect of amount of catalyst, compositional change, heating rate on the conversion, and enthalpy change were studied. The activation energy (E_a) and pre-exponential factor (A), rate constant of different blend systems with and without catalyst, were computed from the modified Ozawa and Kissinger model equations using isoconversional methods. Studies suggested that cure-kinetic parameters calculated from both the models are found to be matching. It was observed that the activation energy is less in the case of catalyzed system than the uncatalyzed system. Predicting the cure profile of this resin system is important under a given set of conditions for achieving the desired, controlled polymerization. This is the first report on the studies of the cure-kinetic parameters of the CE–epoxy blend system, and these observations will definitely pave the way for tuning

the process parameters and temperature profile for achieving the desired properties of these insulation systems in fusion relevant magnetic winding packs.

Keywords Differential scanning calorimetry · Cure kinetics · Nonisothermal · Cyanate ester · Epoxy · Activation energy · Thermosetting resin

Introduction

Extensive research work has been carried out to find suitable insulation impregnation materials for fusion grade magnets winding packs that would be operating in moderate irradiated environments in fusion devices like Tokamaks [1]. CE resins have been receiving increasingly importance because of their enhanced temperature and radiation resistance compared to conventional epoxy resins. They are envisaged to experience fast neutron fluence up to $1 \times 10^{22} \text{ m}^{-2}$ ($E > 0.1 \text{ MeV}$) in International Thermonuclear experimental reactor systems. Thus, the interpenetrating network system of co-cured CE with epoxy resin possesses excellent dimensional stability, resistance to irradiation, low dielectric constant, low out-gassing property endowed with a wide range of physico-chemical, electrical and thermal properties [2–4]. It is also reported its excellent adhesion property with glass/kapton fibers for the fabrication of composites [5]. These characteristic properties make them amenable to produce advanced composites for applications in microelectronics, fusion relevant prototype magnetic winding packs as well as in space craft structures. However, the cost of the CE resins are higher by a factor of about 10 compared to the epoxies and delicate in its application due to the possible high exothermic reactions associated with it. The chemistry of curing of the CE–epoxy

S. Pradhan (✉) · P. Brahmhatt
Institute for Plasthermogrma Research, Bhat, Gandhinagar,
Gujarat 382428, India
e-mail: Pradhan@ipr.res.in

J. D. Sudha (✉) · J. Unnikrishnan
National Institute for Interdisciplinary Science and Technology,
CSIR, Thiruvananthapuram, India
e-mail: sudhajd2001@yahoo.co.in

systems has been examined and documented [6]. Upon heating, CE functional groups will undergo acyclotrimerization reaction to form a triazine linkage [7]. The epoxide functionality also reacts with other epoxy groups to form polyether. Also, the epoxide reacts with the triazine to form a five-membered oxazoline ring [8, 9] and each of these reactions occurs in varying amounts depending on the ratio of the blend and the presence of catalysts [10, 11]. It is known that properties of the cured system depend on the composition of the blend system, conversion, rate of reaction and so forth.

The processing of the blend systems had been subjected to extensive studies, and a large variety of catalysts have been identified for the cure-reaction of these blend systems. Researchers have found that transition metal acetyl acetonates are preferable to carboxylates and the resulting network showed better thermal stability and lesser moisture absorption. However, a systematic study on the metal acetyl acetonate and quantitative information on the catalytic efficiency in terms of the cure-kinetic parameters are not available in the literature. With a view to generate quantitative information, a detailed study of the thermal cure of CE–epoxy blend system was undertaken. Different techniques based on thermal analysis, spectroscopic analysis, and so forth have been employed for studying the cure reaction of various thermosetting systems [12].

Among thermal techniques, thermogravimetric analysis, differential thermal analysis and differential scanning calorimetry are widely reported for the evaluation of kinetic parameters. DSC which measures the heat flow of the sample as a function of temperature has been extensively used for studying the cure kinetics of various thermosetting polymers. [13–15]. This technique is very versatile and gives reliable data for thermal cure of resin systems like the present one associated with considerable enthalpy change during cure. The information on cure parameters could possibly help to identify the best blend system and its concentration and to predict the cure profile of this very important blend system under a given set of conditions for achieving the desired, controlled polymerization.

There are two approaches to study the cure kinetics using DSC, namely isothermal (nondynamic) and nonisothermal (dynamic). The basic assumption for the application of DSC technique to the cure of the thermoset polymers is that the rate of the kinetic process (dx/dt) is proportional to measured heat flow. The cure kinetics of uncatalyzed thermosetting systems like CE has been established to follow second-order autocatalytic model as shown in Eq. 1 and in some cases, for catalyzed and uncatalysed systems an n th order as has been found to satisfactorily explain the cure profile as shown in Eq. 2 [16, 17].

$$d\alpha/dT = k_1(1 - \alpha)^2 + k_2(1 - \alpha)^2\alpha \quad (1)$$

$$d\alpha/dT = k(1 - \alpha)^n \quad (2)$$

Dynamic kinetic model can be used to measure activation energy, rate constant, and frequency factor of cure reaction on applying the thermal data obtained from multi heating rate dynamic scans. In the reaction rate equation (1), the extent of cure (α) is proportional to the heat generated during the reaction rate and the reaction is expressed by a function of conversion.

$$(d\alpha/dt) = k(T)f(\alpha), \quad (3)$$

where t is the time, $k(T)$ the rate constant, and $f(\alpha)$ is the model function that depends on the reaction mechanism.

The explicit temperature dependence of the rate constant is introduced by replacing $k(T)$ by the Arrhenius equation, which gives

$$(d\alpha/dt) = A \exp(-E_a/RT)f(\alpha), \quad (4)$$

where A is the pre-exponential factor, E_a the activation energy of the process, which is independent of conversion and R the gas constant in Eq. 4. From these equations activation energy, rate constant, and pre-exponential factor can be calculated.

There are many model equations such as Ozawa [18] and Kissinger [19] which are often appropriated to portray the cure-kinetic parameters of complex reactions of thermosetting resins. These models relate the heating rates ' β ' to the peak exothermic temperatures T_p of dynamic curve to obtain the activation energy of overall cure process. This model does not assume any definite form of the reaction and allows for variation in activation energy as the reaction progresses. Thus, these equations can be used in isocoversional techniques which are also based on dynamic kinetic analysis by DSC [20]. An isoconversion method which assumes the activation energy and pre-exponential factor are both functions of the degree of cure can be used to analyse the multi heating rate scan data [21, 22]. This makes it equally effective for analysing both n th order and autocatalytic reactions.

This article discusses effect of catalyst, amount of catalyst, and compositional ratio of epoxy–CE on the cure-kinetic parameters of the blend system. Cure reaction of CE–epoxy system is catalyzed by manganese acetyl acetonate as catalyst and nonylphenol as cocatalyst, and data measurements were made using dynamic DSC in combination with FTIR spectroscopy. Various cure-kinetic parameters of the CE–epoxy blend system have been computed using two modified model equations of Kissinger and Ozawa by applying isoconversional technique. Possible correlation of activation energy, cure temperature maximum, reaction rate constant, and frequency factor of various blend compositions have been computed and possible correlation of the curing system is established.

Experimental

Materials

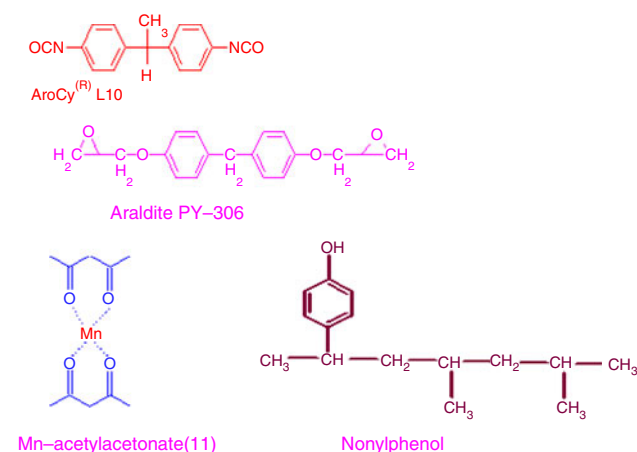
The epoxy resin used in this study is araldite PY 306 which is bisphenol F diglycidyl ether an epoxy monomer—a mixture of para/para, ortho/para, and ortho/ortho stereoisomers with exceptionally low viscosity. Arocy L-10 is a bifunctional cyanate ester which is a low viscous liquid dicyanate monomer which derives its liquid physical state from an asymmetric linkage in the bisphenol unit. Manganese acetyl acetonate (MAA) in nonyl phenol (NP) is used as the catalyst and cocatalyst, respectively. MAA in NP is used to minimize the moisture plasticization and thermo-oxidative degradation in the cured polycyanurate. All these chemicals were supplied by Huntsman. Chemical structures of all the reagents are shown in Scheme 1.

Preparation of catalyst

MAA was dissolved in NP with a molar ratio of 25:1(NP:MAA) at 80 °C for 1 h. In each case, the molar ratios of CE/epoxy blend:MAA was kept 1,000:1.

Blend preparation

Catalyst and blend was then mixed at 60 °C for 30 min. CE and epoxy resins were mixed in different proportions and 0.1% MAA in NP (10 PPM) was added dropwise and was heated at 60 °C for 30 min for making it homogeneous before taking for conducting studies on nonisothermal DSC measurements. Curing experiments were performed with 5–50 ppm of catalyst concentration.



Scheme 1 Chemical structure of Arocy L-10, Araldite PY-306, Mn-acetylacetonate and Nonylphenol

Differential scanning calorimetry measurements

DSC data during curing studies of epoxy resin and cyanate ester were obtained by means of TA instruments 2020 type differential scanning calorimeter [21, 22]. Dynamic DSC was performed at 10 °C min⁻¹ in static air using a TA 2920 Thermal Analyzer system in conjunction with a TA processor and a standard DSC-20 apparatus. Analysis was carried out using the software Universal Analysis 2000. The temperature and heat flow calibrations were done using pure indium metal of melting point 156.4 °C and heat of fusion, $\Delta H_f = 6.80 \text{ cal g}^{-1}$. The peak area integration and subsequent fractional conversion (α) temperature calculations were done with universal analysis software. The integration was done after determining the baseline of the exotherm by joining the temperature of interception of reaction (T_i) and that of completion (T_f). The latter were taken as points where the base line of the curve extrapolated to the exotherm starts to deviate. Experiments were performed on samples weighing in the range of 5–10 mg in a hermetically sealed and pressed aluminium pan. The sealed pan was placed inside DSC, and the sample was heated under varying rate of 0.5, 1, 2, 3, 5, 10, 20, and 30 °C min⁻¹ from 30 to 500 °C.

Dynamic kinetic model is used to measure activation energy of the reaction. Decrease in the activation energy causes an accelerating effect on the cure reaction. The basic assumption for the application of DSC technique to the cure of the thermoset polymers is that the rate of the kinetic process ($d\alpha/dt$) is proportional to measured heat flow.

According to modified Kissinger's approach, Eq. 5, the maximum reaction rate $d\alpha/dt$ occurs at T_p , where $d^2\alpha/dt^2 = 0$ and the kinetic equation can be expressed as

$$\ln(\beta/T_p^2) = \ln(AR/E_a) - E_a/RT_p \quad (5)$$

According to modified Ozawa's approach Eq. 6

$$\text{Log}\beta = -0.4567E_a/RT_p + A \quad (6)$$

where β is the heating rate, E_a the activation energy, and R is the gas constant.

Experiments were performed under different heating rate and peak at the maximum in the curing process is noted for the analysis. Then the activation energy computed from the slope of the plot of $\ln(\beta/T_p^2) - 1/T_p$.

Conversion at any temperature, α_T was found from the relation, Eq. 7

$$\alpha_T = \Delta H_f/\Delta H_T, \quad (7)$$

where ΔH_f is the fractional enthalpy at that temperature and ΔH_T , the total heat of reaction. Indirectly, these are obtained by the fractional and total areas, respectively, under the exothermic curve.

Fourier transform infra red spectroscopy (FTIR) studies

The FTIR spectroscopy was used to monitor the extent of reaction and to investigate the cure chemistry. FTIR measurements were performed using fully computerized Nicolet impact 400D FTIR spectrophotometer. Thin films of the neat and blended resins were cast on salt plates prior to spectral analysis. The gelled/cured samples were made into pellets with potassium bromide. Spectra were taken periodically during the cure process to monitor the extent of reaction and determine which bands were appearing/disappearing/diminishing.

Results and discussion

Effect of catalyst (MAA in NP) on the cure reaction mechanism

The curing reaction of CE–epoxy is shown as per the Scheme 1 and effect of catalyst on the curing reaction is illustrated in Scheme 3. MAA is acting as catalyst and NP as cocatalyst and was evaluated for its catalytic efficiency indirectly by estimation of their cure parameters using dynamic DSC in static air. Effect of catalyst on the curing mechanism of CE and epoxy resins was studied by performing the curing studies in the presence and absence of the catalyst. Typical DSC curves of 60:40 blend systems studied under nonisothermal condition with heating rate of $0.5\text{ }^{\circ}\text{C min}^{-1}$ in the absence and presence of catalyst is given in Fig. 1. DSC curves showed clear evidence for the effect of catalyst on the cure profile of CE–epoxy blend system. DSC experiments were performed in the presence

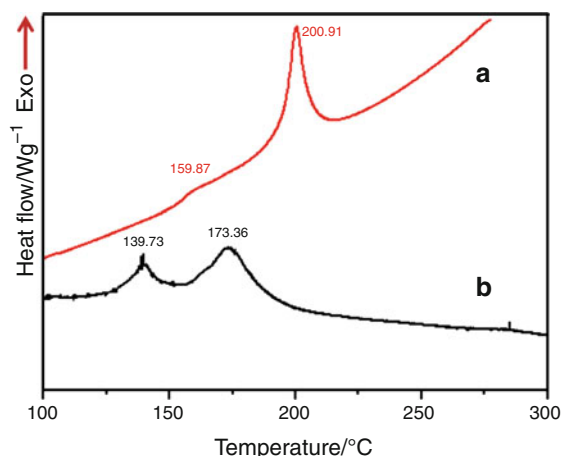


Fig. 1 DSC Graph of 60:40 epoxy:cyanoate blend system at heating rate $0.5\text{ }^{\circ}\text{C min}^{-1}$ (a) with catalyst, (b) without catalyst

of catalyst exhibited two exotherms at 139.7 and 173.36 $^{\circ}\text{C}$ suggesting that the cure reaction is taking place in two stages. However, the same system in the absence of catalyst exhibited a weak shoulder at 159.6 $^{\circ}\text{C}$ and a well-defined exotherm at 200.9 $^{\circ}\text{C}$. It is evident from the DSC scan that catalyst could reduce the curing temperature and also altered the curing path. When the catalyst was added, the curing temperature shifted to lower value as observed from a systematic drift in the cure characteristics. Enthalpy value also exhibited a lower value (200 J g^{-1}) for systems performed in the presence of catalyst compared to those performed without catalyst (320 J g^{-1}).

Effect of heating rate on cure temperature maximum (T_p), percentage conversion were investigated by performing non-isothermal curing studies under different heating rates starting from 0.5, 1, 2, 3, 5, 10, 20, and $30\text{ }^{\circ}\text{C min}^{-1}$ and typical DSC scans for the 60:40 performed in the presence of catalyst is shown in Fig. 2. It was observed that on increasing heating rates starting from 0.5 to $30\text{ }^{\circ}\text{C min}^{-1}$, the peak maximum in the exotherm referring to the 2nd stage of curing shifted from 173.03, 199.4, 211, 231, 235, 271, 282 $^{\circ}\text{C}$, respectively, and that referring to the 1st stage disappeared at higher heating rates. As the heating rate increased from 0.5 to $30\text{ }^{\circ}\text{C min}^{-1}$, peak exotherm exhibited enhancement in the T_p value by 109 $^{\circ}\text{C}$. Figure 3 shows the DSC scan cure profile of 60:40 blend system conducted without catalyst. Similar observations in the T_p values were made and when

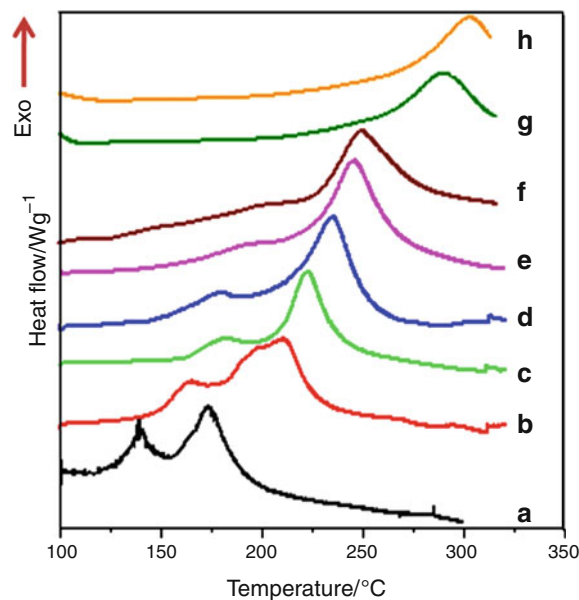


Fig. 2 DSC Graph of 60:40 epoxy:cyanoate blend system (with catalyst) at heating rates (a) $0\text{ }^{\circ}\text{C min}^{-1}$, (b) $1\text{ }^{\circ}\text{C min}^{-1}$, (c) $2\text{ }^{\circ}\text{C min}^{-1}$, (d) $3\text{ }^{\circ}\text{C min}^{-1}$, (e) $5\text{ }^{\circ}\text{C min}^{-1}$, (f) $10\text{ }^{\circ}\text{C min}^{-1}$, (g) $20\text{ }^{\circ}\text{C min}^{-1}$, (h) $30\text{ }^{\circ}\text{C min}^{-1}$

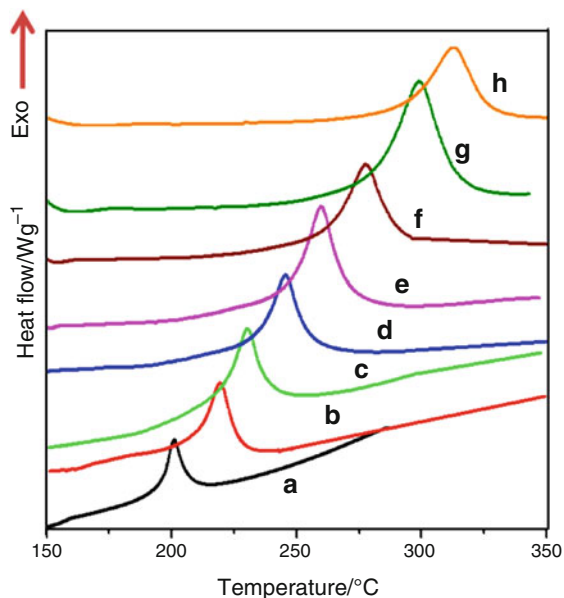


Fig. 3 DSC scans 60:40 epoxy:cyanoate blend system (without catalyst) at heating rates (a) 0.5 °C min⁻¹, (b) 1 °C min⁻¹, (c) 2 °C min⁻¹, (d) 3 °C min⁻¹, (e) 5 °C min⁻¹, (f) 10 °C min⁻¹, (g) 20 °C min⁻¹, (h) 30 °C min⁻¹

the heating rate increased from 0.5 to 30 °C min⁻¹ the peak maximum shifted from 200 to 312 °C, respectively. Details of the heating rate against temperature (T_p) and enthalpy change at the cure maximum for 60:40 blend system are given in Table 2. As the heating rate increases from 0.5 to 30 °C min⁻¹, the unanalyzed system exhibited enhancement in the T_p value of 111.5 °C. Moreover, change in enthalpy values also showed a decreased value when performed in the presence of catalyst and the details are shown in Table 1. Thus, presence of catalyst could reduce the cure temperature at the maximum in the exotherm and could reduce the enthalpy change during curing. When experiments performed in the presence of catalyst under slow heating rates, exhibited two exotherms implying reaction is taking place in two stages. These observations were strengthened by the studies made by FTIR spectral analysis and are discussed elsewhere.

Cure-kinetic parameters of CE–epoxy blend systems

Although a large number of qualitative studies have been reported on cure catalysis, a reliable quantitative or comparative data on the cure-kinetic parameters and catalytic efficiency of CE–epoxy blend system are not available. Effects of catalyst, amount of catalyst, compositional variation of epoxy–CE on the cure-kinetic parameters were studied by conducting nonisothermal DSC experiments. Cure-kinetic parameters like rate constant, energy of activation, and pre-exponential factors were computed using two modified model equations like Kissinger and Ozawa by applying dynamic kinetic isoconversional analysis. Details of the model equations and calculation method were as shown in the “Experimental” section.

Typical kissinger plot showing $\ln(\theta/T_p^2)$ vs. $1/T_p$ (60:40 epoxy/CE blend system) is shown in Fig. 4.

Ozawa’s approach gives a simple relationship between the activation energy, the heating rate and isoconversion temperature as shown in Eq. 8

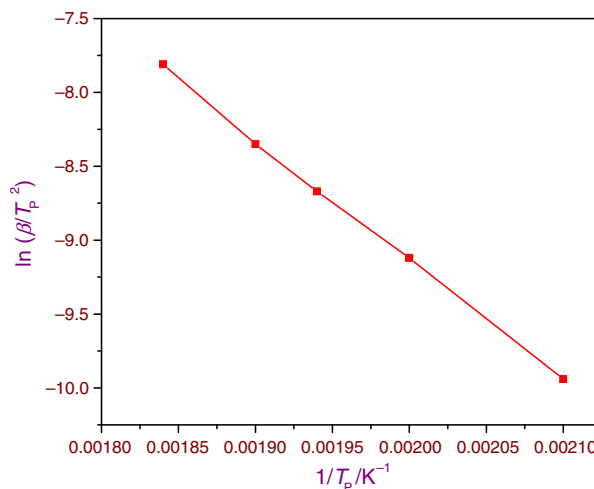


Fig. 4 Typical kissinger plot showing $\ln(\theta/T_p^2)$ vs. $1/T_p$ for 60:40 epoxy/cyanoate ester blend system

Table 1 Effect of heating rate on curing temperature and enthalpy change

Heating rate/°C min ⁻¹	T_p /°C (W)	$\Delta H/J g^{-1}$ (W)	T_p /°C (WO)	$\Delta H/J g^{-1}$ (WO)
0.5	139.73,173.36	211.35	200.91	364.4
1	158.69,199.41	222.13	218.64	533.3
2	174.39,211.35	231.06	230.10	576.7
5	185.05,231.06	235.18	259.41	597
10	235.52	270.84	277.94	564.4
20	271.04	211.35	298.83	533.3
30	282.14	222.13	312.41	576.7

W with catalyst, WO without catalyst

$$\text{Log}\beta = -0.4567E_a/RT_i + A' \quad (8)$$

where for each degree of conversion, A' is a constant that can be expressed as Eq. 9

$$\left[A' = \log \frac{AE_a}{g(\alpha)R} \right], \quad (9)$$

and $g(\alpha)$ is function of dependence of conversion (19). Similarly a plot of $\log \beta$ vs. $1/T_i$, at each degree of conversion gives a slope proportional to the corresponding activation energy E_a and an intercept the pre-exponential factor A' . Figure 5 shows the isoconversional analysis Ozawa's plot showing the effect of catalyst concentration on the apparent conversion-temperature profiles and activation energy variation and pre-exponential factor upon extent of cure. Therefore, the relationship of activation energy and the conversion can be measured through the whole reaction. Figure 5e-f shows that activation energy initially decreases with increase of conversion, reaching a minimum value and then increases until about 70% conversion before decreasing again at high conversions. The decrease of activation energy at the beginning may be due to the autocatalytic effect of the curing process and the subsequent increase of activation energy may be caused by the formation of the cross-linked network which restricts diffusion of the unreacted monomer. At high conversions, the reactions no longer follow the autocatalytic kinetics and more complex mechanism such as diffusion control are involved in the cure process. The pre-exponential factor A' also showed similar trend as E_a with conversion is as shown in Fig. 5. Computed values using both Kissinger's and Ozawa's plots are shown in Table 2 and it exhibited a very good linear relationship between parameters based on the experimental data and the results. Ozawa approach gives lower value than obtained from Kissinger method. Substituting values of enthalpy change, temperature at the

maximum of the exotherm (T_p) and conversion values (α), cure-kinetic parameters were computed using these two model equations.

Catalytic efficiency of the catalyst system (MAA in NP) on the cure-kinetic parameters was studied by performing curing studies with CE-epoxy (60:40) blend system. Experiments were performed with catalyst having varying concentrations, and cure-kinetic parameters were evaluated using modified Ozawa and Kissinger plot and using isoconversional methods of analysis. Typical curves showing the temperature conversion profile for different amount of catalyst is shown in Fig. 6a-c, respectively. DSC showed a systematic shift in the curing temperature maxima with increasing concentration of catalyst. ΔH has been found to be lower for catalysed systems. In this study, the catalyst concentration varied from 0 to 30%, and ΔH was found to fall by 25% which is attributed to a possible change in the reaction mechanism in the presence of catalyst [24].

The decrease in ΔH may also arise from the diffusion-controlled kinetics during later stages of cure. Once the reaction is diffusion limited, it requires higher thermal activation for cure completion which could be attained only at a higher temperature (250 °C). Dependence of fractional conversion (α) on temperature at different concentrations of catalyst reached at lower temperatures due to increasing catalytic efficiency. The relationship between catalyst concentration and E_a has been established for increasing concentration of the catalyst which brings down the activation energy considerably and thereby facilitates cure and gelling of the polymer. At gelation, the molecular mobility is restricted to a greater extent and the reaction enters the diffusion controlled zone from the chemically controlled zone. This diffusion limitation imposes reactants mobility restriction, and the polymer segments need more thermal activation for reaction. Consequently, the activation energy

Fig. 5 Isoconversional analysis ozawa's plot showing the effect of catalyst concentration on the apparent conversion-temperature profiles and activation energy variation upon extent of cure obtained by ozawa's method

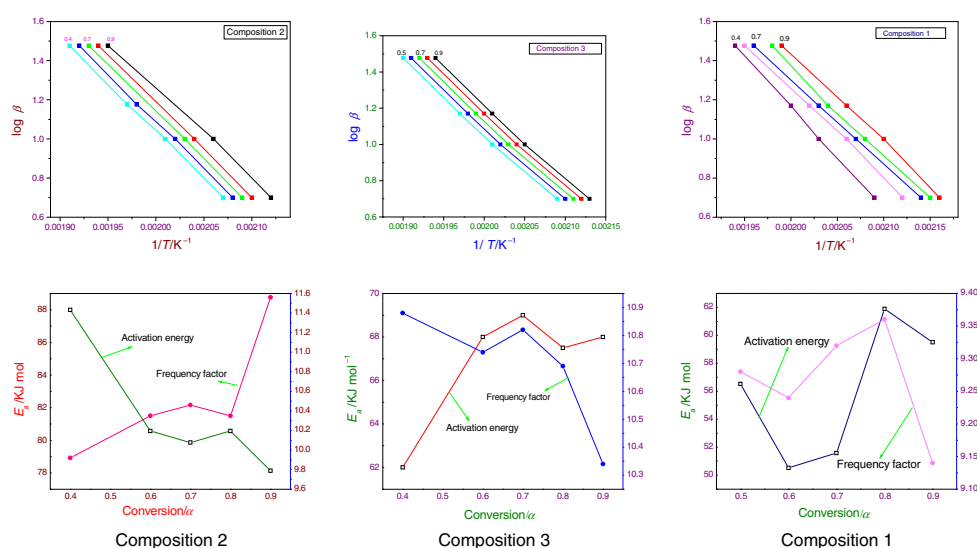
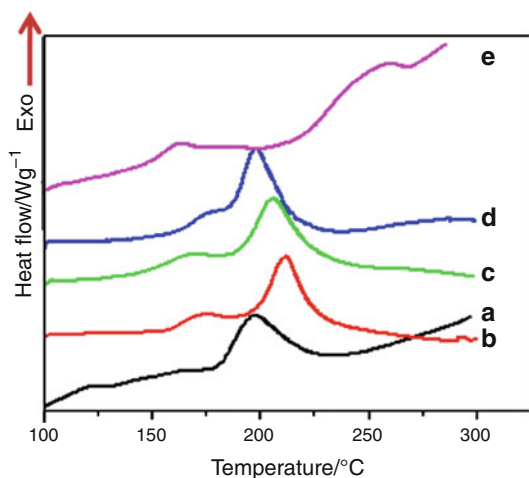


Table 2 Effect of catalyst on the cure-kinetic parameters computed by isoconversional technique (Composition 40:60)

Amount of catalyst PPM (MAA + NP)	Kissinger method			Ozawa method (modified)		
	$E_a/\text{kJ mol}^{-1}$	Pre exp factor A	Rate constant $K/\text{s}^{-1}(\times 10^{-2})$	$E_a/\text{kJ mol}^{-1}$	Pre exp factor A	Rate constant $K/\text{s}^{-1}(\times 10^{-2})$
0	73.64	4.78×10^8	30.4	80.71	4.78×10^6	30.8
5	72.64	5.1×10^8	31.0	80.52	4.41×10^6	31.2
10	70.64	6.96×10^7	32.1	79.91	9.208×10^7	32.8
20	67.4	7.078×10^7	33.2	77.05	10.65×10^7	33.5
30	58.52	7.349×10^7	37.3	66.00	11.694×10^7	38.0
40	57.21	7.51×10^7	38.2	63.00	12.194×10^7	39.2
50	55.34	7.85×10^7	39.21	61.50	13.201×10^7	40.4

**Fig. 6** DSC scans of different blend systems of CE-epoxy at heating rate of $2\text{ }^\circ\text{C min}^{-1}$ (with catalyst) (a) 50:50, (b) 60:40, (c) 70:30, (d) 80:20, (e) 90:10

increases for this zone as shown in Fig. 5d–e. The discrepancy observed in the computed values can be explained as during gelation, the molecular mobility is restricted to a greater extent, and the reaction enters the diffusion controlled zone from the chemically controlled zone. [25]. A linear relationship between the activation energy and T_p values implies the significance of the kinetic parameter in predicting and determining the cure profile of the CE-epoxy blend system.

Effect of compositional variation on the cure-kinetic parameters of the CE-epoxy system without and with catalyst on the activation energy, free exponential factor, and rate constant are given in Tables 3 and 4, respectively. Generally, all catalyzed blend systems exhibited a decreased value of activation energy during curing when compared to the uncatalysed systems. Decreased value in the activation energy causes an accelerating effect on the cure reaction, revealing that less amount of energy is

Table 3 Details of cure-kinetic parameters of cyanate ester-epoxy blend system without catalyst at heating rate $10\text{ }^\circ\text{C min}^{-1}$

Composition	Peak temperature, T_p/K	E_a (Kissinger) $E_a/\text{kJ mol}^{-1}$	E_a (Ozawa)/ kJ mol^{-1}	Rate constant/ s^{-1}	Pre exponential factor A
50:50 wo	543.14	77.75	85.42	30.3	9.09×10^6
60:40 wo	550.94	75.96	83.60	30.0	4.78×10^6
70:30 wo	541.97	77.76	85.15	36.0	1.23×10^7
80:20 wo	537.04	80.35	87.97	27.8	1.82×10^7

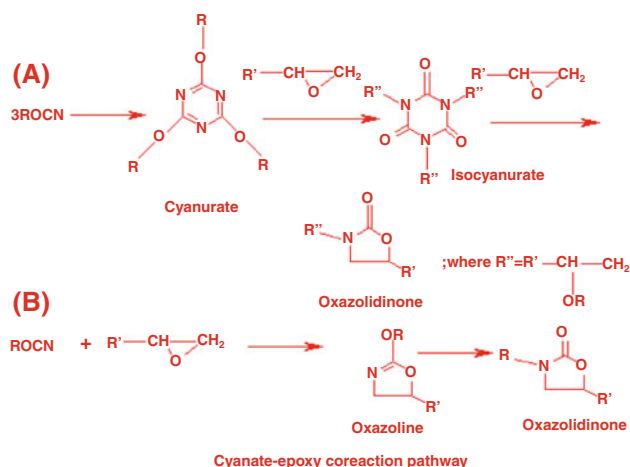
Table 4 Details of cure-kinetic parameters of cyanate ester-epoxy blend system with catalyst at heating rate $10\text{ }^\circ\text{C min}^{-1}$

Composition	Peak temperature, T_p/K	E_a (Kissinger)/ kJ mol^{-1}	E_a (Ozawa)/ kJ mol^{-1}	Rate constant (K)/ $\text{s}^{-1}(\times 10^{-2})$	Pre exponential factor A
50:50 w	509.91	72.26	80.65	33.3	9.69×10^6
60:40 w	508.32	73.64	80.71	30.4	7.54×10^6
70:30 w	507.45	74.92	82.91	33.3	1.72×10^7
80:20 w	511.19	73.59	80.65	34.6	1.25×10^7
90:10 w	613.24	101.31	109.77	31.7	1.35×10^8

required for the curing reactions for the systems conducted in the presence of catalyst. Activation energy evaluated using both Kissinger and Ozawa showed similar discrepancies with increasing concentration of epoxy content in the blend system. Activation energy computed using Kissinger method exhibited values as 77.7, 75.9, 77.9, and 80.9 kJ mol⁻¹ for 50/50, 60/40, 70/30, and 80/20 uncatalysed CE–epoxy cured systems. But systems catalyzed by MAA in NP exhibited values of 72.2, 72.8, 74.9, and 73.5 kJ mol⁻¹ for 50/50, 60/40, 70/30, and 80/20, respectively, for epoxy–CE blend systems. It showed positive variation in the rate constant with increasing amount of epoxy in the system.

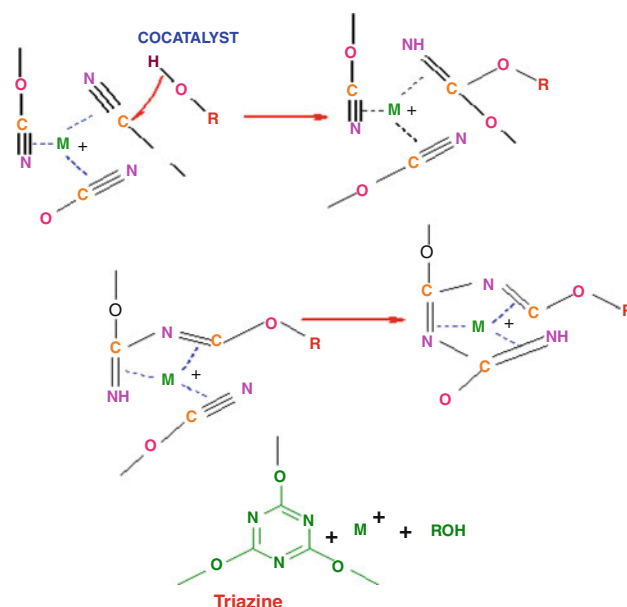
Fourier transform infrared spectroscopy (FTIR) study

Further evidence for the cure profile of the CE–epoxy blend system was studied by performing FTIR experiments at various stages of curing process. The co-cure reaction kinetics between CE and epoxy resin were previously explained by other researchers [26, 27]. Cyanurate (triazine) is formed through the trimerization of CE. Insertion of glycidyl ether epoxide into aryl cyanurate results in the rearrangement of the aryl cyanurate into alkyl isocyanurate. Oxazoline and oxazolidinone are then formed depending on the cure conditions. Thus, the overall reaction can be considered happening in two steps: cyclotrimerization of CE to produce triazine rings as the intermediate product, and coreaction of epoxy and triazine rings to form oxazolidinone rings at higher temperature. The proposed two-step process in the cure reaction path of CE–epoxy accounting the formation of triazine, oxazoline, oxazolidinone are given in Scheme 2.



Scheme 2 Co-curing process of CE–epoxy system in the absence of catalyst

DSC scan of CE–epoxy system revealed that the cure reaction proceeds at a much lower temperature and also exhibited two well-defined exothermic processes when conducted in the presence of catalyst. Thus, the curing reaction of CE–epoxy in the presence of catalyst is expected to form a different path (Scheme 3). FTIR spectra taken under various stages of curing in the presence and absence of catalyst are given in Figs. 7 and 8, respectively. Nature of spectra exhibited clear changes in the position and intensity of the absorption peak in the FTIR spectra revealing the role of catalyst in tuning the nature of the cured product. The peak heights were monitored as a function of events to analyze the chemistry of the reactions for different blend systems. Spectra were taken periodically during the cure to monitor the extent of reaction and also to determine which bands were appearing/disappearing/diminishing. FTIR spectra of CE–epoxy blend system cured in the presence of catalyst depicted in Fig. 7. Initially the FTIR spectrum exhibited bands characteristic for CE functionality located as a doublet in the region of 2,235 and 2,270 cm⁻¹. Bands for the epoxide, located at 915 and 3,000 cm⁻¹, were also clearly visible. The spectrum taken immediately before gelation exhibited a decrease in intensity of the characteristic peak of CE (2,235 and 2,270 cm⁻¹) and at the same time new peaks were appeared at 1,369 and 1,679 cm⁻¹, which are characteristic for the formation of triazine ring (cyanurate). Moreover, it was also observed that the intensity of the characteristic peak corresponding to epoxy peak (912 cm⁻¹) remained intact. Thus, catalyst could accelerate the cure reaction and decrease the cure temperature and the mechanism for the catalytic effect of metal chelates for trimerization of CE to



Scheme 3 Homopolymerization of CE in the presence of catalyst

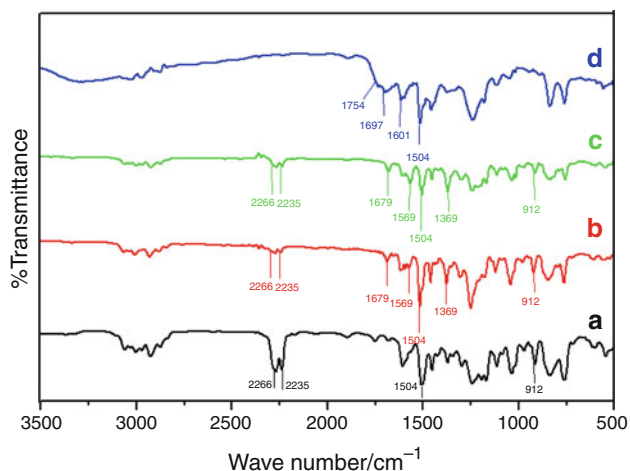


Fig. 7 FTIR of 60:40 (epoxy:cyanate) with catalyst (a) 60:40 mix, (b) 60:40 1, (c) 60:40 2, (d) 60:40 cured

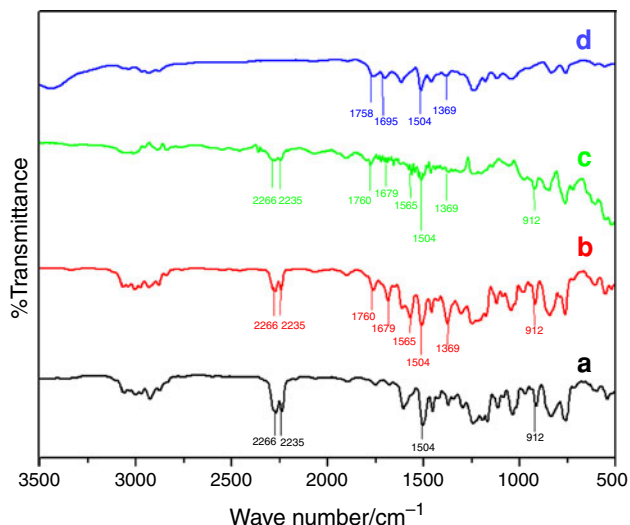


Fig. 8 FTIR of 60:40 (epoxy:cyanate) without catalyst (a) 60:40 mix, (b) 60:40 1, (c) 60:40 2, (d) 60:40 cured

form triazine is schematically illustrated in Scheme 3. The mechanism involves the formation of a metal complex intermediate with reduced electron density at the carbon of the cyanate that reacts with the nucleophilic nitrogen of another cyanate to form triazine, thus regenerating the catalyst. In other words, in the presence of catalyst, the transition metal coordinates with the nitrogen enhancing the electrophilicity of the nitrile group for the addition of another cyanate group as shown in the Scheme 3. Once the triazine is generated, it reacts with the epoxy to form the five-membered oxazoline (1,760 cm^{-1}) and immediately it rearranges to form oxazolidinone (1,695 cm^{-1}). The maximum rate of epoxy consumption was observed after almost the entire CE had been consumed. Moreover, the spectra of the cured product did not exhibit any characteristic peak of the CE (2,235 and 2,270 cm^{-1}), and the intensity of the

triazine peak (1,369 cm^{-1}) also became very weak. Thus, the initial exothermic peak appeared in the DSC scan, exclusively due to the homopolymerisation CE to form triazine and the second exotherm corresponds to the co-reaction of triazine with epoxy to form oxazoline/oxazolidinone.

Structural change taking place during the curing process of the uncatalysed CE–epoxy blend system (60:40) was also studied by FTIR spectroscopy and the spectrum recorded under different stages of curing is depicted in Fig. 8. Here also the before curing the FTIR spectra of the blend exhibited absorption peak characteristic of CE at 2,266 and 2,235 cm^{-1} and the characteristic absorption peak of epoxy group at 912 cm^{-1} and phenyl group appeared at 1,504 cm^{-1} . The spectra recorded just before gelation exhibited absorption peak at 2,266, 2,235, 1,760, 1,679, 1,369, and 912 cm^{-1} corresponding the characteristic group CE, oxazolidinone, oxazoline, and triazine, respectively. FTIR spectra recorded of the gelled sample exhibited weak absorption peak at 2,266 and 2,235 cm^{-1} characteristic of CE and weak absorption peak of epoxy group at 912 cm^{-1} . Spectrum also showed characteristic peak of oxazoline and oxazolidinone at 1,760 and 1,679 cm^{-1} . Here, the characteristic peak of triazine (1,369 cm^{-1}) appeared as very weak. FTIR spectra of final cured product did not exhibit characteristic absorption of CE revealing the complete conversion of CE. Here also the spectra exhibited peak corresponds to the oxazoline (1,758 cm^{-1}), oxazolidinone (1,695 cm^{-1}), and triazine (1,369 cm^{-1}). Thus, the cured product comprises mixture of triazine, oxazoline, and oxazolidinone. That is why the DSC profiles of this system exhibited single exotherm. Thus, the presence of catalyst in the blend system could reduce the exothermic temperature as well as can tune the product profile.

Effect of compositional variation of the epoxy/CE on the cure temperature, conversion at the maximum cure temperature was evaluated by performing nonisothermal DSC studies with and without the presence of catalyst. Experiments were performed under different heating rates. For comparison, we took the cure profile conducted at 2 $^{\circ}\text{C min}^{-1}$ for all the blend systems. Typical DSC curves of the 90/10, 80/20, 70/30, 60/40, and 50/50 epoxy–CE blend systems with the presence of catalyst are depicted in Fig. 8 and the results of DSC measurements with and without catalyst are depicted in Table 2. Generally, DSC profiles of blend systems performed in the presence of catalyst exhibited a decreased value for the cure temperature (T_p) with reference to unanalyzed systems irrespective of the composition. Comparing Fig. 4 with Fig. 5 the presence of catalyst showed a decreased value of enthalpy change at higher heating rate during curing suggesting the reaction could be controlled in the presence of catalyst. Conversion at the maximum in the exothermic peak temperature (T_p) evaluated using software universal analysis and it exhibited

values of 197(80.6), 211.3(61.16), 206.8(42.7), and 198.3(54.01) for 50/50, 60/40, 70/50, and 80/20 blend system, respectively. But when the curing conducted in the absence of catalyst, these systems exhibited higher value of T_p with less value of conversion. Discrepancy observed for T_p and conversion can be explained due to the formation of intermediate structures having different functionality. When dicyanate in CE is converted to triazine, functionality will be changing from 2 to 3. Moreover, the composition of the different species present initial stage can alter the conversion and T_p values.

Extent of reaction (conversion) ' p ' can be defined as the fraction of the functional groups that reacted at time t , [28]. Then

$$C = C_0(1 - p) \quad (10)$$

C is the concentration of the reactant at time t and C_0 is the initial concentration

Degree of polymerization for thermosetting resin,

$$X_n = N_0/N = 1/1 - p. \quad (11)$$

here N is the total number of functional group in the system and N_0 is the number of functional group initially present.

For uncatalysed system long time is require to reach high degree of polymerization. Thus, improvement in conversion can be achieved by performing in the presence of catalyst and in this case concentration of catalyst may be included in the rate constant [29]. Gelation point also depends upon the functionality of the reacting molecules by the equation [30]

$$[\alpha_c] = 1/f - 1, \quad (12)$$

where f is the functionality of the reacting units

It is suggested to write: Thus, the conversion, gel point and temperature at which maximum cure takes place, are purely determined by the functionality of the reactive groups and the catalyst present in the system [31].

The difference in T_p in the presence and absence of catalyst for compositions 80:20, 70:30, 60:40, and 50:50 are ~ 20 , 30, 35, and 40 °C, respectively. Results suggested that on increasing the amount of cyanate ester will contribute to an autocatalytic curing effect.

Conclusions

Studies reveal that in the presence of catalyst, curing reaction takes place at lower temperature with less enthalpy change (200 J g^{-1}) in comparison with noncatalyzed systems (364 J g^{-1}). FTIR studies suggested that in the presence of catalyst, CE undergoes trimerisation in faster rate at low temperature and then undergoes co-curing with epoxy to oxazoline and oxazolidinone. Since functionality

variation of reactants is taking place in the initial stage, discrepancy could be observed in the conversion values. But uncatalysed system, in the initial curing stage itself exhibited characteristic peak of CE, triazine, oxazoline and oxazolidinone suggesting complex reaction in the initial stage. Energy of activation and temperature at the maximum cure observed to less for catalyzed systems suggesting curing process can be made under control for catalyzed systems. Moreover, the linear relationship between activation energy and T_p implies the significance of the cure-kinetic parameters in predicting and determination of the cure profile of CE–epoxy blend based insulation systems.

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