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Nonisothermal curing kinetics of epoxy resin composite utilizing Ga (III) xanthate as a latent catalyst

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ABSTRACT: Cure kinetics and curing mechanism of epoxy resin composite utilizing gallium (III) xanthate as a latent catalyst was investigated and compared with the commercial latent catalyst UCAT3512T formulation. Nonisothermal differential scanning calorimetric technique at different heating rates was employed to investigate the kinetic parameters. Activation energy was determined using Kissinger's and Flynn-Wall-Ozawa methods. Ga (III) xanthate was found to possess superior latent properties compared with UCAT3512T since the activation energy value obtained was higher for epoxy resin composite consisting of Ga (III) xanthate than UCAT3512T. Friedman's isoconversional method was utlizied to for kinetic modeling. An autocatalytic model was found to be successful in describing the curing reaction for both of the formulations. The calculated conversion rate as a function of temperature obtained by solving the autocatalytic equation showed a very good fit with experimental values. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 42149.

KEYWORDS: catalysts; crosslinking; kinetics

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INTRODUCTION

Cured epoxy resins are one of the important industrial materials having wide range of applications such as thermosets,[1] coatings,[2,3] high-performance composites,[4] insulating materials,[5] microelectronics,[6] and encapsulants.[7] Various properties responsible for excellent engineering performance of epoxy resin include high temperature performance,[8] creep resistance,[9] high stiffness,[10] high electrical, and mechanical properties.[11] The precise understanding of the curing process is essential for determining the optimal processing parameters that assures the highest productivity rate along with satisfactory product properties.[12] Curing kinetics allows to compare the cure behavior of different compositions utilizing different matrices, catalysts, fillers, and additives.[13] The curing parameters such as degree of cure and reaction rate impacts the physical properties and processability of cured epoxy resins and these in turn are dependent on curing conditions such as curing time and temperature.[14] Curing of epoxy resins is an activated process and differential scanning calorimeter (DSC) has been popularly used to elucidate the key cure process parameters.[15]

Traditional cross linking agents such as acids and bases which are commonly being used[16,17] for curing of epoxy resins suffer from the drawback of reduced shelf life even under ambient conditions.[18] Latent catalysts, therefore, are one of the possible alternatives since by utilizing these catalysts the curing reaction can be precisely controlled. As they can initiate the curing process only when desired upon triggering by external stimuli and simultaneously enhancing the working life of epoxy resin composite.[19] We have recently reported that gallium sulfide obtained by thermolysis of gallium (III) xanthate precursor works as an *in-situ* latent catalyst for the curing of epoxy resin beyond 170°C. This metal xanthate precursor route not only offers processable fabrication of corresponding metal sulfides but also offers latent behavior towards preparation of metal sulfides at their threshold triggering thermolysis temperature.

In this article, we would like to elucidate the curing kinetics and mechanism of epoxy resin composite utilizing Ga (III) xanthate as latent catalyst and compare the curing kinetics with commercial epoxy curing catalyst UCAT3512T. Both of the catalyst systems were examined by nonisothermal DSC technique. To calculate the activation energy, DSC data under dynamic conditions was applied to Kissinger's and Flynn-Wall-Ozawa methods. Using the activation energy obtained by Flynn-Wall-Ozawa method, the conversion rate and conversion degree with respect to the temperature was determined for the entire range of curing. The kinetic model of the curing process was evaluated by employing Friedman method.

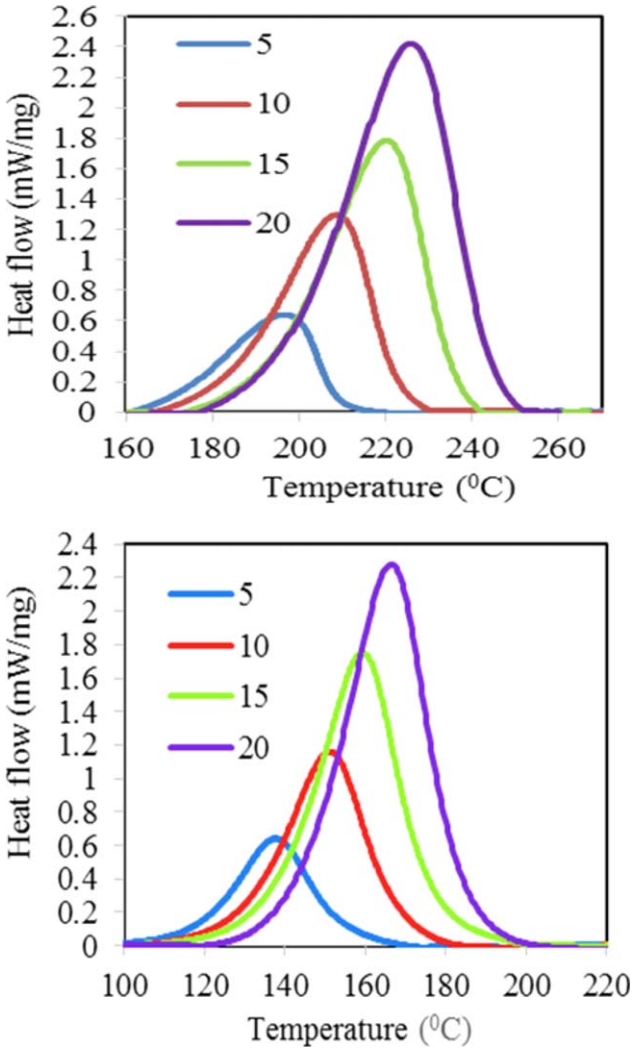

Figure 1. Dynamic DSC thremograms for curing of epoxy composite consisting of Ga (III) xanthate (top) and 5% commercial standard catalyst UCAT3512T (bottom) at different heating rates (°C/min). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

EXPERIMENTAL

Materials

Anhydrous gallium (III) chloride was purchased from Tokyo Chemical Corporation, Japan. Potassium tert. butoxide and carbon disulphide were purchased from Wako Chemicals, Japan and 2, 2-dimethyl-3-pentanol was purchased from Sigma Aldrich, Japan. The synthesis and characterization of the Gallium (III) xanthate used in this work was done as per our earlier publication.[20] Commercially available Ortho-cresol Novolac epoxy resin (CNE200ELB65) melting point 65°C, Novolac phenolic resin (BRG556) melting point 80°C and curing catalyst UCAT3512T were used for this study.

Techniques

A differential scanning calorimeter (DSC-60, Shimadzu) was employed to study the exothermic curing reaction. The reaction mixture was cured in DSC under nonisothermal conditions at heating rates of 5, 10, 15, and 20°C min^{-1} in the temperature range from 30 to 300°C under constant flow of nitrogen with flow rate of 10 mL min^{-1}. A 1 : 1(w/w) ratio of epoxy resin and phenolic resin composite with 5% catalyst was used for the DSC study 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.

RESULTS AND DISCUSSION

DSC curves at different heating rates for 5% Ga (III) xanthate and 5% UCAT3512T compositions are presented in Figure 1. DSC thermograms reveal a single exothermic peak associated with gelation (crosslinking) of the epoxy resin composite for both of the catalyst compositions. It is interesting to note that in the case of both UCAT3512T and Ga (III) xanthate catalysts, it takes 3.5 min to complete the cross-linking when dynamic DSC was run at the scan rate of 20°C/min. It is clear that exotherms shift towards higher temperatures as a function of heating rate. Compared with standard catalyst, the composite including Ga (III) xanthate shows an overall higher onset temperature. The peak temperature values which determine the nature of curing at various heating rates for both of the catalytic compositions are shown in Table I. The values shift to higher temperatures as the heating rate increases. The increase in peak values with increasing heating rate is due to shortened reaction time with higher heating rate.

Dynamic Kinetic Methods: Kissinger and Flynn–Wall–Ozawa Methods

Kinetic characterization of curing of epoxy resins in terms of curing rate, temperature dependence of curing and energy of activation are of fundamental importance in understanding the structure, property, and processing relationships of thermoset resins. The dynamic and isothermal methods have been widely used for detailed understanding of the cure kinetics. The advantage of utilizing the dynamic methods over isothermal methods in determining the cure kinetic parameters lies in the fact that a prior knowledge of the reaction mechanism is not required in order to quantify kinetic parameters.[21] A very widely implemented Flynn-Wall-Ozawa and Kissinger's methods were employed to determine the activation energy (E_a) in the present investigation before discussing the kinetic model in detail.

Flynn-Wall-Ozawa Method. The integral form of the rate equation by Flynn-Wall-Ozawa method[22] is generally expressed as

$$\log \beta = A' - 0.4567 \frac{E_a}{RT} \quad (1)$$

$$A' = \log \frac{AE_a}{g(\alpha)R} - 2.315 \quad (2)$$

where, β is heating rate, T is temperature, R is ideal gas constant, A is pre-exponential factor, and $g(\alpha)$ is an integrated form of the reaction model. Assuming that the degree of conversion is independent of the heating rate at the peak temperature,[23] the plot of log β versus $1/T_p$ (peak temperature) gives a straight line with a slope of $-0.4567E_a/R$ leading to the estimation of E_a from the Ozawa plot.

Kissinger's Method. Kissinger's method has been widely used for the investigation of curing of epoxy resins in order to

Table I. Kinetic Parameters for Curing Reaction of 5% Ga (III) Xanthate and 5% UCAT3512T Epoxy Resin Composites

Curing agent (5% by mass)	Heating rate (°C/min)	Peak temperature (°C)	Activation energy Flynn-Wall-Ozawa method (kJ)	Activation energy Kissinger's method (kJ)
Ga (III) xanthate	5	196.51	109.98	107.72
	10	206.55		
	15	210.51		
	20	220.17		
UCAT3512T	5	137.70	69.27	65.83
	10	151.17		
	15	159.36		
	20	166.49		

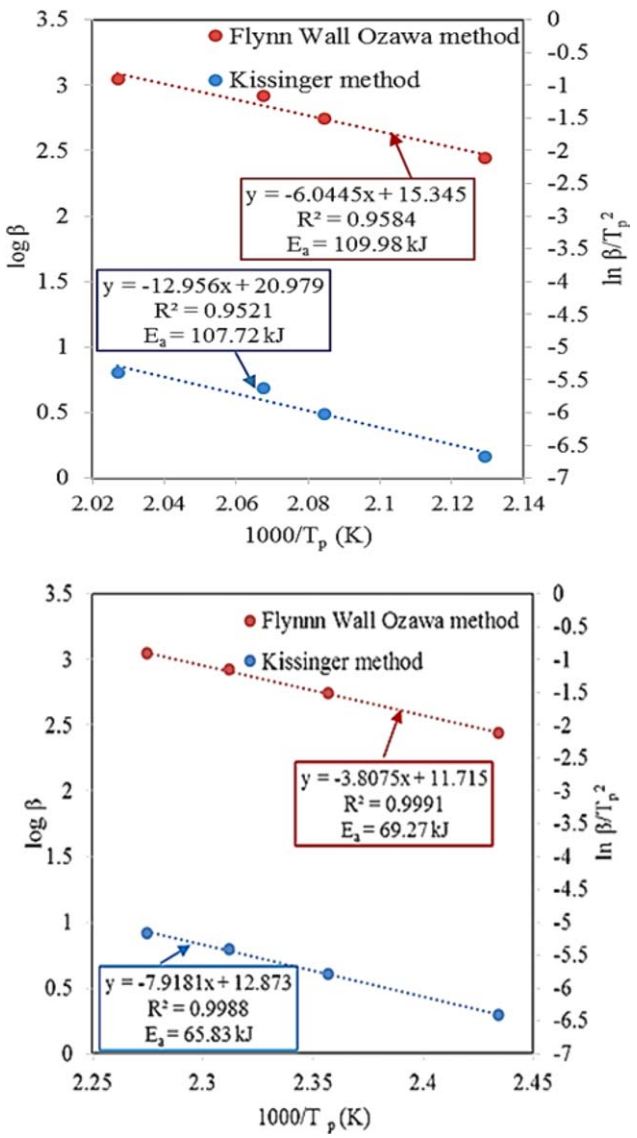

Figure 2. Ozawa and Kissinger's plot for curing of epoxy resin composite utilizing 5% of catalysts Ga (III) xanthate (top) and 5% UCAT3512T (bottom). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

estimate the kinetic parameters such as E_a and A from dynamic DSC data. At the peak temperature where the rate of curing is maximum[24] activation energy can be obtained by utilizing the following equation.

$$\ln(\beta/T_2)^2 = \ln(AR/E_a) - E_a/RT_p \quad (3)$$

Equation (3) indicates that by plotting $\ln(\beta/T_p)^2$ against $1/T_p$, we can estimate E_a and A from slope of the linear fit and intercept at the Y-axis, respectively.[25] Linear plots by Flynn-Wall-Ozawa method and Kissinger's method applying at the maximum rate of conversion for both of the catalyst systems are shown in Figure 2. Activation energy obtained by both the catalyst formulations are shown in Table I. The values obtained by Kissinger's method are similar to Flynn-Wall-Ozawa method even though slightly lower. This behavior is in accordance with the literature reports on curing kinetics.[26] E_a is basically the energy barrier required to overcome for the curing reaction to proceed. Since the activation energy of Ga (III) xanthate is higher than that of the standard catalyst UCAT3512T, it can be concluded that the former possess better latent catalytic activity than the later.

Nonisothermal Kinetic Modeling and Mechanism

Constitutive modeling equations for the cure kinetics of epoxy resins fall under two general categories: n^{th}-order and autocatalytic.[27] In case of n^{th}-order model, conversion rate is proportional to concentration of unreacted material. The reaction rate is dependent only on the amount of unreacted material remaining and the reaction products are not involved in the reaction.[28] On the other hand, autocatalyzed model assumes that at least one of the reaction products is involved in propagating the reaction and characterized by maximum degree of conversion[29] between 20 and 40%. To predict the cure kinetics over the whole range of conversion, the analysis by Friedman isoconversioanl method was employed for nonisothermal dynamic DSC data.

Friedman Method. This method is one of the isoconversional methods based on assumption that kinetic parameters E_a and A vary with extent of the reaction.[30] The Friedman method is based on the following equation.

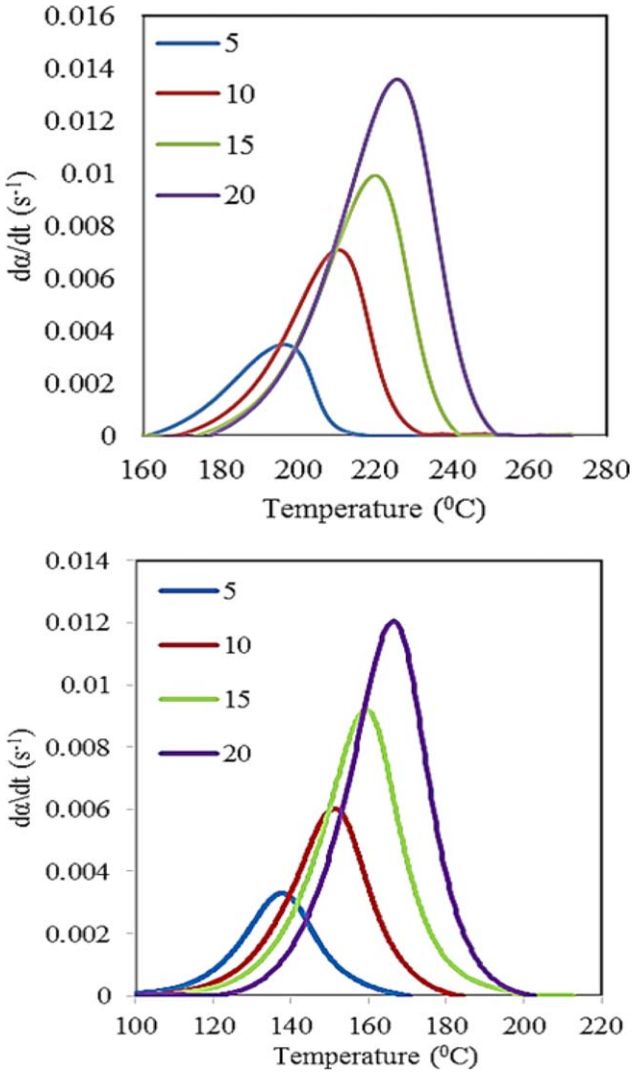

Figure 3. Curing reaction rate as a function of temperature at different heating rates (°C/min) for epoxy resin composite curing utilizing 5% Ga (III) xanthate (top) and 5% UCAT3512T (bottom). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

$$\frac{d\alpha}{dt} = q\frac{d\alpha}{dT} = kf(\alpha) \tag{4}$$

Where, $f(\alpha)$ is function of degree of reaction model, k is rate constant, and is a function of temperature. $d\alpha/dt$ is the reaction rate. Friedman's isoconversioanl method relates the logarithm of reaction rate to the inverse of temperature for a given degree of curing. By introducing the Arrhenius equation,[31] the Friedman equation can be rearranged as follows:

$$\ln\frac{d\alpha}{dt} = \ln q\frac{d\alpha}{dT} = \ln[Af(\alpha)] - \frac{E_a}{RT} \tag{5}$$

Plots of curing conversion rate as a function temperature for both of the catalytic systems are presented in Figure 3. In either of the cases, the peak maxima advanced with increasing heating rate. This behavior was very similar to dynamic DSC thermograms at different rates as shown in the Figure 2. The values of these curing reaction rates at different temperatures were utilized to estimate $\ln[Af(\alpha)]$ values as shown in Eq. (5). Reaction rate can be obtained from nonisothermal DSC data using the following equation.

$$\frac{d\alpha}{dt} = \frac{dH/dt}{H_{tot}} \tag{6}$$

Where, $dH\ dt$ is given by the peak height of the DSC thermogram at time t, H_{tot} is the total heat of reaction for complete curing.[32] Curing degree[33](α) is defined as the ratio between heat released up to time t (ΔH_t) and total heat of reaction ΔH_{tot}.

$$\alpha = \frac{\Delta H_t}{\Delta H_{tot}} \tag{7}$$

Nonisothermal dynamic DSC conducted at different heating rates has been widely accepted to provide relatively more accurate kinetic parameters in a short period of time. Figure 4

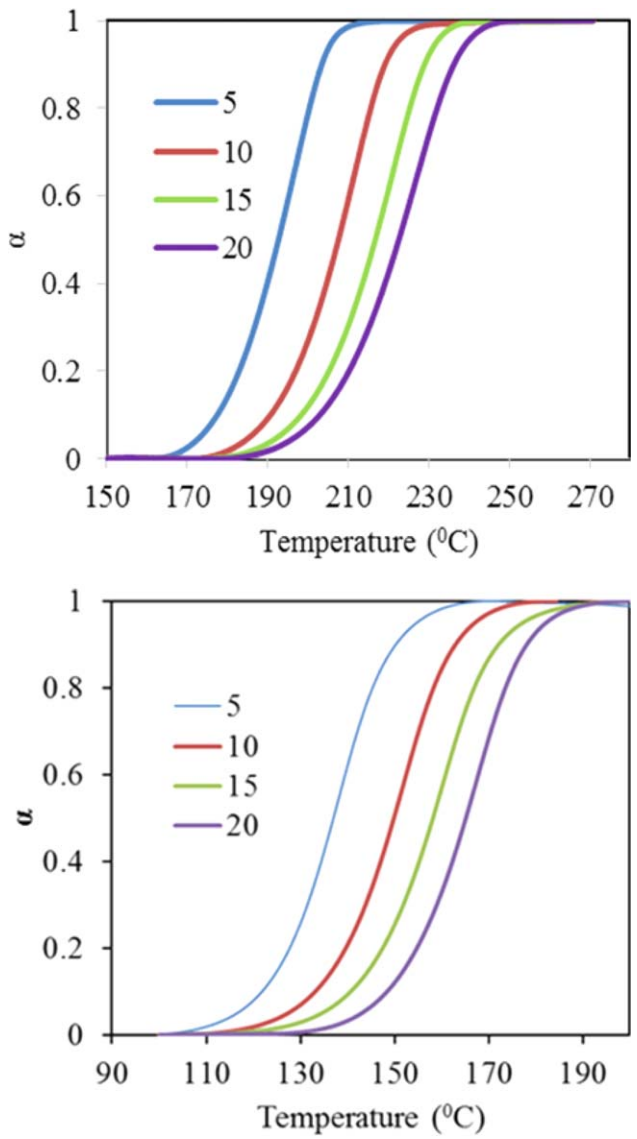

Figure 4. Degree of conversion as function of temperature at different heating rates (°C/min) for epoxy resin composite curing utilizing 5% catalytic composition of Ga (III) xanthate (top) and 5% UCAT3512 (bottom). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

exhibits the plot of extent of conversion (α) as a function of temperature obtained from dynamic DSC data using 5% Ga (III) xanthate and standard catalyst UCAT3512T composites. It is very clear that heating rate implied under dynamic DSC run affects the extent of conversion as a function of temperature. It is well known that heating rate has great influence on curing process, with exothermic peaks having lower temperatures at lower heating rates.

The nature of conversion with respect to temperature gives the latent capability of the catalyst. The curing reaction was initiated at much lower temperature in case of UCAT3512T compared with Ga (III) xanthate. This indicates the superiority of Ga (III) composite over UCAT3512T in extending the working life of a formulated mixture by passivation of the catalyst activity until triggered up to a threshold temperature by the external stimulus. Thus after obtaining the rate of conversion and conversion degree at various heating rates, the Friedman method can be successfully applied to predict the reaction model during the epoxy curing process. In case of autocatalytic conversion, $f(\alpha)$ in the Friedman model can be expressed as

$$f(\alpha)=(1-\alpha)^n\alpha^m \tag{8}$$

While in the case of n^{th} order reaction kinetics, $f(\alpha)$ can be defined as

$$f(\alpha)=(1-\alpha)^n \tag{9}$$

Where, n and m are the order of reaction.

Substituting both the Eqs. (8) and (9), Eq. (5) will yield the following equations[34]

$$\ln\frac{d\alpha}{dt}+E_a/RT=\ln A+n\ln(1-\alpha) \tag{10}$$

$$\ln\frac{d\alpha}{dt}+E_a/RT=\ln A+n\ln(1-\alpha)+m\ln(\alpha) \tag{11}$$

The values of $\ln[Af(\alpha)]$ in Eq. (5) can be obtained from the known values of $\ln[d\alpha/dt]$ and E_a/RT. The plot of $\ln[Af(\alpha)]$ and $\ln(1-\alpha)$ can be used to determine the nature of mechanism. If a straight line is obtained, the slope and intercept gives the reaction order (n) and the natural logarithm of the frequency factor and is predicted to follow nth-order kinetics. For autocatalytic process, the plot of $\ln[Af(\alpha)]$ and $\ln(1-\alpha)$ is nonlinear with a peak maximum approximately around -0.51 to -0.22 which is equivalent to degree of curing[35] of 0.2−0.4. This could be attributed to the fact that autocatalytic mode of epoxy curing exhibits the maximum rate of reaction[36] at 20−40% completion of conversion. $\ln(1-\alpha)$ values were derived from degree of conversion. Thus the obtained $\ln[Af(\alpha)]$ and $\ln(1-\alpha)$ values at various heating rates were used for the investigation of curing kinetics using the Friedman plots. The Friedman plots of $\ln[Af(\alpha)]$ and $\ln(1-\alpha)$ for both catalyst systems are presented in Figure 5.

A perusal of Figure 5 clearly corroborates that in the case of both of the catalytic compositions there is a nonlinear increase before the peak reaches its maximum between -0.51 and -0.22 followed by linear decrease as function of $\ln(1-\alpha)$. This indicates that the curing of epoxy resin composite by catalytic systems under investigation follows autocatalytic mechanism. To

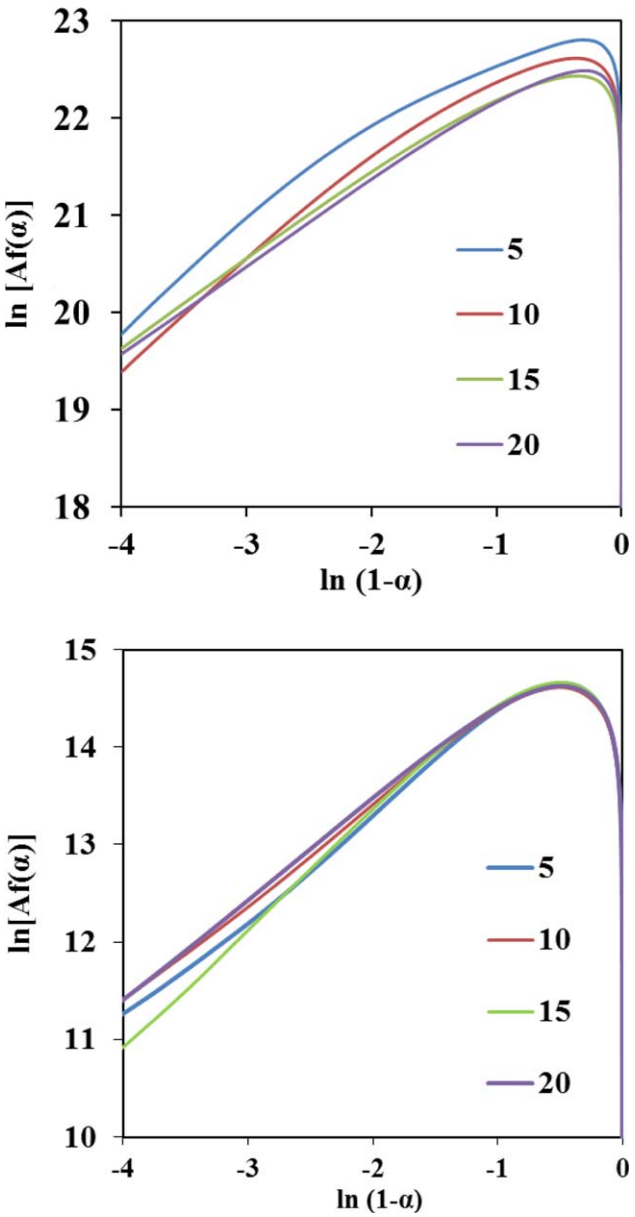

Figure 5. Curing rate at different heating rates (°C) for epoxy resin composite curing utilizing 5% Ga (III) xanthate (top) and 5% UCAT3512T (bottom). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

further verify the validity of autocatalytic mechanism in the present system, Eq. (11) was solved by multiple linear regression. The $\ln(d\alpha/dt)$ was taken as a dependent variable, and $\ln\alpha$, $\ln(1-\alpha)$ and $1/T$ were taken as independent variables. The average activation energy obtained by Flynn-Wall-Ozawa method[28] was utilized for estimating the values of A, m, and n. The degree of curing employed to solve regression are from the beginning and until the maximum peak for degree of curing[37] which is ranging from 0.1 to 0.5. The multiple linear regressions analysis results for all heating rates for both of the catalytic compositions were listed in Tables II and III. Based on results obtained for $ln\ A$, reaction orders (n and m) by multiple linear regression and average E_a values obtained by Flynn-Wall-Ozawa

Table II. Kinetic Parameters for the Epoxy Resin Composite Curing Utilizing 5% Ga (III) Xanthate Using Freidman Model

Heating rate (°C/min)	ln A (S^{-1})	Mean	*n*	Mean	*m*	Mean
5	23.23	23.20	0.8	0.8	0.3	0.3
10	23.26		0.7		0.4	
15	23.12		0.8		0.3	
20	23.20		0.9		0.3	

method, the validity of autocatalytic mechanism by Friedman plot can be cross checked by Eq. (11). The Eqs. (12) and (13) are framed for the autocatalytic equations for the curing of epoxy resin using Ga (III) xanthate and UCAT3512T, respectively, by introducing the calculated values of *lnA*, reaction orders (*n* and *m*) and E_a.

$$d\alpha/dt = \exp\ (23.20).\ \exp\ (-13,228/T).(1-\alpha)^{0.8}.(\alpha)^{0.3} \quad (12)$$

$$d\alpha/dt = \exp\ (15.66).\ \exp\ (-8331/T).\ (1-a)^{0.9}.(\alpha)^{0.5} \quad (13)$$

The calculated results of conversion rate ($d\alpha/dt$) obtained by solving these autocatalytic Eqs. (12) and (13) are plotted as a function of temperature and shown in Figure 6 along with the experimental results as shown in Figure 3.

It can be clearly observed that a very good match between the calculated (dotted line) and experimental (solid line) results exists. Since a very good fit can be observed for the calculated and experimental results an autocatalytic mechanism can be proposed for both the catalyst systems. An autocatalytic mechanism can be explained by the acceleration of the reaction process by the free phenol groups generated while the epoxy group begins to open during the reaction process.

CONCLUSIONS

The cure kinetics for Ga (III) xanthate and UCAT3512T epoxy resin composite were studied using dynamic DSC technique. Almost similar energy of activation was determined for Ga (III) xanthate resin composite using Flynn-Wall-Ozawa (109.98 kJ) and Kissinger (107.72 kJ) methods which was higher than that observed for UCAT3512T composite. The rate of curing and cure degree as a function of temperature was estimated for both of the formulations followed by analysis using Friedman isoconversioanl kinetic modeling. A perusal of the Friedman plot ($\ln[Af(\alpha)]$ vs. $\ln[1-\alpha]$) indicates a nonlinear increase between

Table III. Kinetic Parameters for the Epoxy Resin Composite Curing Utilizing 5% UCAT3512T Using Friedman Model

Heating rate (°C/min)	ln A (S^{-1})	Mean	*n*	Mean	*m*	Mean
5	15.77	15.66	1	0.9	0.6	0.5
10	15.59		0.9		0.4	
15	15.69		0.8		0.5	
20	15.61		0.9		0.5	

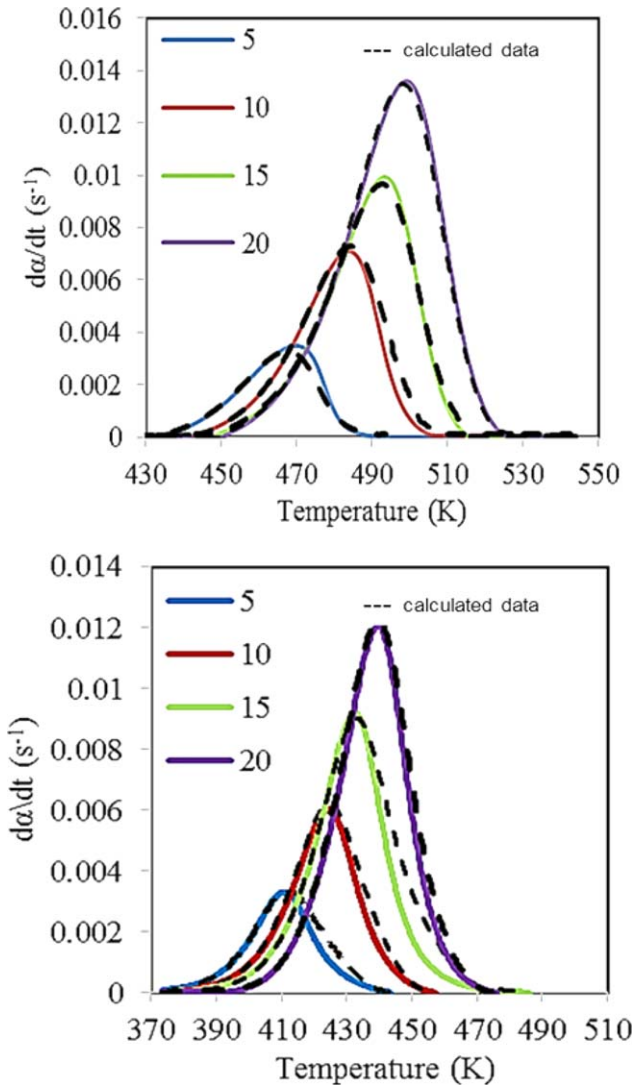

Figure 6. Plot of curing rate as a function of temperature at different heating rates (°C/min) for the curing of epoxy resin composite utilizing 5% Ga (III) xanthate (top) and UCAT3512T (bottom) dotted lines : calculated values; solid lines: experimental values. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

−0.51 and −0.22 followed by a linear decrease as a function of $\ln(1-\alpha)$ indicating the autocatalytic mechanism of curing by both of the catalytic systems. Calculated rate of curing determined using the parameters obtained by solving the autocatalytic equation were in good agreement with the experimentally determined curing rate.

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