

# Study of Cure Kinetics of Diglycidyl Ether of Bisphenol A with Ni(II) and Cu(II) Complexes of Benzil Bisthiosemicarbazone

Mousa Ghaemy, Hossein Behmadi, Mohammad Barghamadi

Department of Chemistry, Mazandaran University, Babolsar, Iran

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**ABSTRACT:** The curing reaction kinetics of the diglycidyl ether of bisphenol A (DGEBA)-based epoxy and inorganic complexes curing agents based on Ni(II) and Cu(II) chelates with benzil bisthiosemicarbazone  $LH_6$  as a ligand was studied using differential scanning calorimetry (DSC). The curing reaction with the ligand and the complexes was characterized by high cure onset and peak maximum temperatures. The kinetics of the curing reaction was evaluated using three kinetic models; Kissinger, Ozawa-Flynn-Wall, and Málek. For the  $NiLH_4$  and  $CuLH_4$  the average values of  $E_a$  were calculated to be 82.3 and 116 kJ/mol, respectively. For both complexes, their activation energies at 40 and 30 phr are equal. The values of activation energy ( $E_a$ ), and

initial and maximum temperatures of the exothermic curing peak ( $T_i$  and  $T_p$ ) of the ligand are smaller than those of the complexes, and the values of these parameters of the DGEBA/ $NiLH_4$  system are lower than those of DGEBA/ $CuLH_4$  system. These results indicate the order of reactivity of  $LH_6 > NiLH_4 > CuLH_4$  toward epoxy resin. The effect of hardener concentration, heating rate, and type of metal ion on the cure kinetic parameters and the shape of DSC thermograms were investigated. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 106: 4060–4066, 2007

**Key words:** kinetics; epoxy resin; curing of polymers; DSC; benzil bisthiosemicarbazone complexes

## INTRODUCTION

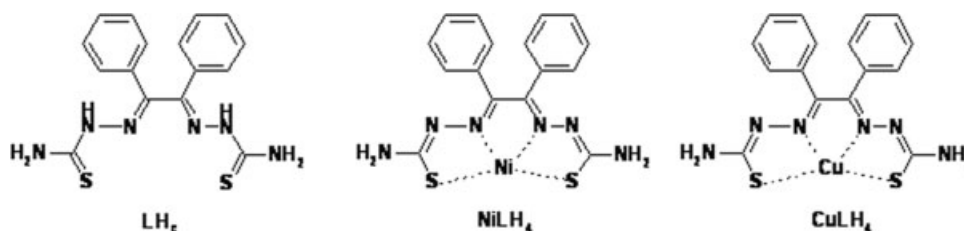
Epoxy resins have been commercially widely used in modern industries because of their advantage of low shrinkage on cure, good adhesion to substrate, superior electrical and mechanical resistance, etc.<sup>1</sup> They are easily cured without evolution of volatiles or byproducts by a broad range of chemical species. A great number of compounds have been screened for their suitability as curing agents for epoxy resins. There are several factors on which the choice of curing agent to be used with an epoxy resin will depend: (1) handling characteristics; (2) cure, post-cure time, and temperature requirements; (3) properties of the cured system; and (4) cost of curing agent. The extent and nature of intermolecular crosslinking will, therefore, be determined in part by the correct choice of curing agent. Aliphatic, cycloaliphatic, and aromatic amines are widely used as curing agents.<sup>2–6</sup> To meet some application requirements, several approaches have been used to enhance the thermal properties of epoxy resins. If the chemical structures of cured epoxy resins are constituted with aromatic rings, heterocyclic rings, or both, their thermal resist-

ance is superior to those of constituents with flexible or aliphatic chains. In recent years, modified amines are extensively used as curing agents. The modification of amine curing agents improves the workability as follows: (1) extends the pot life, (2) increases or decreases the curing speed, (3) improves compatibility with resins, (4) reduces reactivity to carbon dioxide in the air, (5) reduces toxicity and irritation to the skin, and (6) decreases weighing error because loading amount is increased. The incorporation of transition metals and their derivatives in epoxy resin have been examined in recent years. It was shown that the final properties of cured epoxy can be controlled by the change of composition of curing agent. Few workers<sup>7–11</sup> have recently published articles concerning curing properties of epoxy resin with several Ni and Cu complex curing agents.

Synthesis and structural studies of neutral tetracoordinated transition metal compounds derived with strategically placed donor atoms (O, N, and S) have received considerable attention in the past. Bis(thiosemicarbazones) form nickel and copper complexes which show a broad spectrum of biological activity and so are of great pharmacological interest.<sup>12–15</sup>

The main object of the present work was to study kinetics of curing reaction of diglycidyl ether of bisphenol A (DGEBA) with benzilbisthiosemicarbazone ( $LH_6$ ) and with Ni(II) and Cu(II) complexes.

Correspondence to: M. Ghaemy (ghaemy@umz.ac.ir).



**Scheme 1** Structure of ligand and complex curing agents.

Different nonisothermal kinetic methods such as Kissinger,<sup>16,17</sup> Ozawa-Flynn-Wall,<sup>18,19</sup> and Málek<sup>20</sup> were applied to differential scanning calorimetry (DSC) data, to test their applicability in these new epoxy-hardener systems. We have also investigated the effects of hardener concentration, heating rate, and type of metal ion on the cure kinetic parameters.

## EXPERIMENTAL

### Materials

Benzil and thiosemicarbazide were purchased from Fluka (Germany) and used without purification. Nickel chloride and copper acetate were also obtained from Fluka. The epoxy compound used in the study was a diglycidyl ether of bisphenol A-based epoxy (DGEBA), Epidian 5 provided from Iran Petrochemical Industry: Epoxide equivalent 196–208, clear liquid, viscosity (at 25°C) 25,000 mPa s. Scheme 1 displays the structure of the curing agents used in this work.

### Apparatuses

A Mettler Toledo differential scanning calorimeter (DSC822<sup>e</sup>), a Bruker vector 22 FTIR spectrometer, a Bruker AM 100 MHz <sup>1</sup>H NMR spectrometer, and an elemental analyzer of Themofinnigan Flash EA 1112.

### Preparation of Ligand

Benzilbisthiosemicarbazone LH<sub>6</sub><sup>21</sup>

The thiosemicarbazide (3.64 g, 40.30 mmol) was dissolved in 40 mL of methanol, 40 mL of 2N HCl and 1 mL of concentrated HCl, and then added to a suspension of benzil (4.24 g, 20.20 mmol) in 50 mL of methanol and a few drops of concentrated HCl. The

mixture was stirred for 6 h at room temperature, and the yellow solid was filtered off, washed with methanol, and dried in a vacuum oven at 70°C for 2 h. A yellow solid product was obtained in 75% yield, with a melting point of 241°C.

<sup>1</sup>H NMR spectra: δ 8.8 (2H, s), 7.6 (6H, m), 7.4 (4H, m), 6.6 (4H, s).

### Preparation of Complex Curing Agents

(1) Benzil bis(thiosemicarbazonato) copper(II) CuLH<sub>4</sub> was prepared using a standard method.<sup>22</sup> Copper(II) acetate monohydrate (144 mg, 0.722 mmol) was added to a solution of LH<sub>6</sub> (257 mg, 0.722 mmol) in ethanol (15 mL). The mixture was heated under reflux for 5 h, cooled, and the resulting solid collected, washed with ether, and dried in vacuum oven at 70°C to give CuLH<sub>4</sub> as a dark brown powder (144 mg) in 48% yield, with a melting point of 240°C.

<sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>): δ 7.5 (4H NH<sub>2</sub>, s), 7.1–7.3 (10H Ph, m).

(2) Benzil bis(thiosemicarbazonato) nickel(II) NiLH<sub>4</sub> was prepared using a standard method.<sup>23</sup> A solution of nickel(II) chloride (0.20 g, 0.8 mmol) in methanol (10 mL) was added to a suspension of LH<sub>6</sub> (0.30 g, 0.8 mmol) in 20 mL of the same solvent. The mixture was stirred for 3 h at room temperature. The reddish solid formed was filtered off, washed with methanol, and dried in a vacuum oven at 70°C in 73% yield, with a melting point of 250°C.

<sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>): δ 7.6 (4H NH<sub>2</sub>, s), 7.1–7.3 (10H Ph, m).

### Preparation of Epoxy-Complex Curing Agents

The complex curing agents were well dried in vacuum and were completely powdered to obtain fine

**TABLE I**  
Elemental Analysis Results for the Curing Agents

Complex	C (%)	H (%)	N (%)	M (%)	S (%)
LH <sub>6</sub>	54.15 (53.93) <sup>a</sup>	4.49 (4.59)	23.29 (23.08)	–	– (18.4)
NiLH <sub>4</sub>	46.41 (46.52)	3.42 (3.39)	20.20 (20.30)	14.49 (14.26)	– (15.53)
CuLH <sub>4</sub>	45.87 (45.98)	3.38 (3.35)	19.87 (20.12)	15.12 (15.19)	– (15.36)

<sup>a</sup> Values in parentheses indicate percentages.

TABLE II  
Selected IR Data for the Curing Agents

Complex	$\nu$ (NH <sub>2</sub> ) at 3000–3500 cm <sup>-1</sup>	$\nu$ (C=N) at 1500–1700 cm <sup>-1</sup>	$\nu$ (N–M), $\nu$ (S–M) at 420–490 cm <sup>-1</sup>	$\nu$ (C=S)
LH <sub>6</sub>	3420, 3330, 3250, 3150	1610, 1585	–	848
NiLH <sub>4</sub>	3450, 3273, 3119	1625, 1615, 1610	489, 432	–
CuLH <sub>4</sub>	3343, 3327, 3102	1626, 1600, 1569	449, 428	–

particles. The epoxy resin was thoroughly mixed with the complex curing agents and, to facilitate the mixing, a small amount of acetone was added to mixing composition. The stoichiometric of the curing agents were calculated through the number of active amino hydrogens. Based on this calculation, we have used concentrations of 40 phr (stoichiometric) and 30 phr for both complex curing agents to study the effect of concentration. The stoichiometric concentration used for the ligand is 30 phr. The difference in atomic mass of the two elements (Ni and Cu) is very small and negligible in comparison with the molecular weight of the ligand.

#### DSC measurement

DSC thermograms were recorded using a Mettler Toledo instrument (DSC 822<sup>e</sup>) over the temperature range of 50–350°C at different heating rates (5, 10, 15, and 20°C/min.). The instrument was first calibrated with pure indium for thermal response with the heat of fusion and the temperature with the

melting point. A 5 mg well mixed and uniform viscous liquid was put into a DSC sample pan and covered with an aluminum lid and closed tightly under pressure.

The recorded heat flow data were processed to obtain the fractional conversion,  $\alpha$ , and the rate of reaction under the basic assumption that the heat flow ( $dH/dt$ ) is proportional to the reaction rate,  $d\alpha/dt$ . For an exothermic reaction, eq. (1) applies

$$d\alpha/dt = (dH/dt)/\Delta H_{Tot}, \quad (1)$$

where  $d\alpha/dt$  is the rate of the kinetic process,  $dH/dt$  is the measured heat flow, and  $\Delta H_{Tot}$  is the enthalpy of the curing reaction. The rate of the kinetic process in the kinetic analysis can be described as

$$d\alpha/dt = K(T)f(\alpha) \quad (2)$$

where  $K(T)$  is a temperature-dependent reaction rate constant;  $f(\alpha)$  is a function of the fractional conversion,<sup>24</sup>  $\alpha$ , and  $d\alpha/dt$  is the rate of conversion at a given time and temperature.

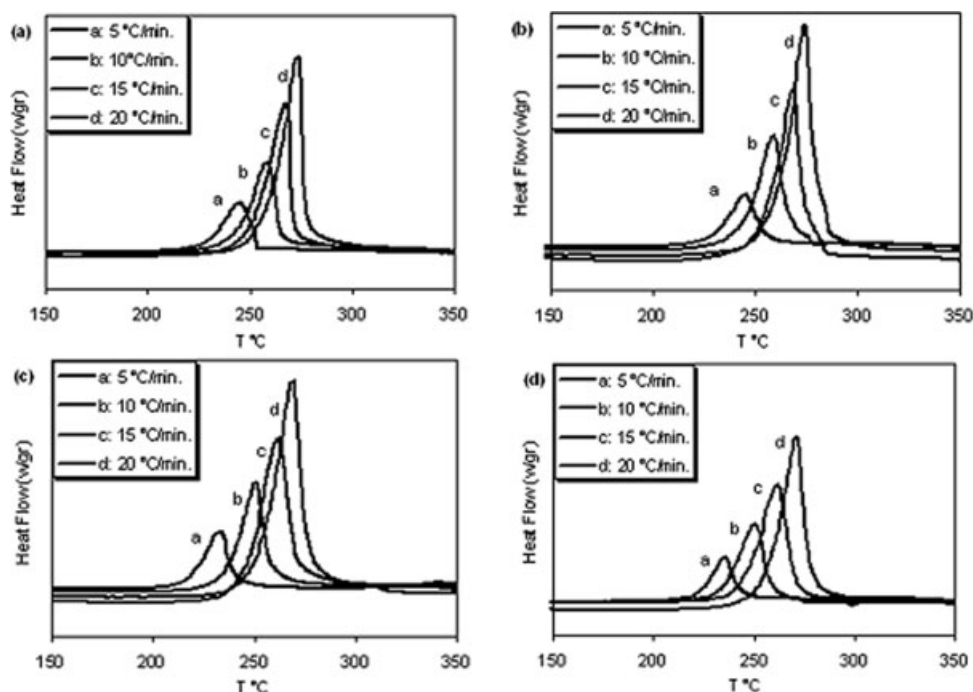
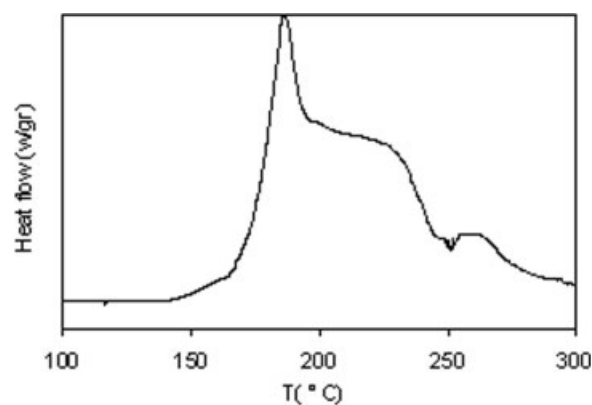


Figure 1 DSC curves of DGEBA cured at different heating rate with (a) CuLH<sub>4</sub> at 40 phr, (b) CuLH<sub>4</sub> at 30 phr, (c) NiLH<sub>4</sub> at 40 phr, and (d) NiLH<sub>4</sub> at 30 phr.



**Figure 2** DSC thermogram of DGEBA cured with the 30 phr ligand LH<sub>6</sub> at 10°C/min.

The fractional conversion was calculated by eq. (3):

$$\alpha_t = \Delta H_t / \Delta H_{\text{Tot}} \quad (3)$$

where the subscript  $t$  indicates the value of conversion at time  $t$ .  $K(T)$  is assumed to have an Arrhenius-temperature dependence. Equation (4)

$$K(T) = A \exp(-E_a/RT) \quad (4)$$

where  $A$  is the pre-exponential factor;  $E_a$  is the activation energy;  $R$  is the gas constant. Therefore, the  $E_a$  value can be determined by an isoconversional method under the assumption of  $f(\alpha)$  being the same at different heating rates ( $\beta$ ) when the value of  $\alpha$  is the same i.e., in eq. (5),  $f(\alpha)$  does not depend on the heating rate at a fixed value of the variable  $\alpha$ . From the logarithmic form of eq. (2), we can have

$$\ln(d\alpha/dt) = \ln[A f(\alpha)] - E_a/RT \quad (5)$$

## RESULTS AND DISCUSSION

### IR and Elemental Analysis of Curing Agents

IR and elemental analysis data for two curing agents of the present work are in good agreement with the results reported in the literature. The results of elemental analysis are given in Table I.

Only two regions of the IR spectra are of particular interest, the 3000–3500  $\text{cm}^{-1}$  ( $\text{NH}_2$  asymmetric and symmetric stretch) and 1500–1700  $\text{cm}^{-1}$  (double bond region). Table II lists the characteristic bands that are indicative of the formation of ligand and complexes. In the complexes, the number of bands corresponding to  $\nu(\text{N}-\text{H})$  vibrations have decreased due to deprotonation and the others appear at higher frequencies probably due to the intramolecular hydrogen bonding that has decreased. The  $\nu(\text{C}=\text{N})$  band is shifted to

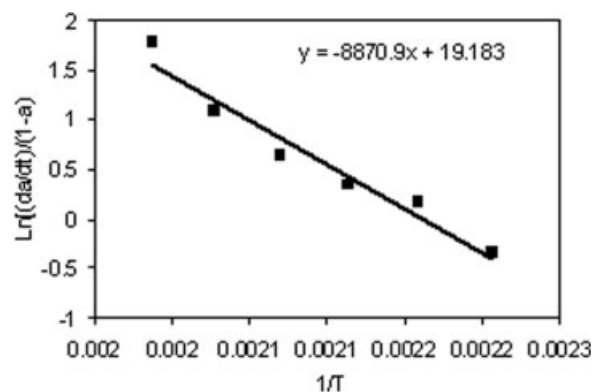
higher frequencies in both complexes, a clear sign of coordination via the azomethine nitrogen atom.

$^1\text{H}$  NMR spectra of both complexes are very similar. In both of them, the signal of hydrogen atoms of the secondary amine has disappeared and the signal corresponding to the terminal amine hydrogen atoms is shifted to high field. These facts agree with that, in both complexes, the ligand is dideprotonated.

### Cure Kinetics

The curing behavior of the DGEBA/ $\text{CuLH}_4$  and DGEBA/ $\text{NiLH}_4$  systems were studied by DSC at different heating rates (5, 10, 15, and 20°C/min) and the results are shown in Figure 1 for two different concentrations. The difference in concentration did not show any significant influence on  $T_i$ ,  $T_p$ , and  $E_a$ . DSC thermogram for the cure reaction of DGEBA with the ligand alone LH<sub>6</sub> is shown in Figure 2 for comparison with DSC thermograms of DGEBA with the complexes.

The cure reaction of DGEBA with the ligand LH<sub>6</sub> occurs at 180°C, with a shoulder exothermic peak at the temperature higher than 200°C. The exothermic peak is due to the polymerization and etherification reactions of the epoxide groups with the amine groups of the curing agents and the hydroxyl groups present, and also subsequently formed along the polymer main chains during polymerization. The small shoulder exothermic peak in the DSC thermogram of DGEBA/LH<sub>6</sub> can be related to the contribution of the secondary amine in the ligand structure (LH<sub>6</sub>) in cure reaction with the epoxide groups. As can be seen in Figure 1 for the complexes, the shoulder peak probably due to the exothermic reaction of the secondary amine with the epoxide group disappears, and this is consistent with the complex structures given in Scheme 1. Although we have not observed the characteristic absorption band of the thiol ( $-\text{SH}$ ) in the FTIR spectrum of the ligand at



**Figure 3** Freeman-Carroll plot for the cure reaction of DGEBA/30 phr LH<sub>6</sub>.

**TABLE III**  
Curing Characteristics for Complex Curing Agents at 40 phr

Heating rate (°C/min)	DGEBA/NiLH <sub>4</sub>			DGEBA/CuLH <sub>4</sub>		
	<i>T<sub>i</sub></i> (°C)	<i>T<sub>p</sub></i> (°C)	$\Delta H_i$ (J/g)	<i>T<sub>i</sub></i> (°C)	<i>T<sub>p</sub></i> (°C)	$\Delta H_i$ (J/g)
5	207	231.7	406.7	210	244	426.2
10	217.8	249.5	398.5	224.2	259	476.2
15	228.7	261.3	435.5	231	267.8	449.4
20	233.3	266.7	410.8	236.7	270	459.5

room temperature, there is the possibility of tautomerization and formation of the thiol group at high temperature which can contribute in the reaction with the epoxide group and responsible for the shoulder exothermic peak.

We have applied the expanded Freeman-Carrole method<sup>25</sup> for the single dynamic DSC experiment to analyze the curing reaction of DGEBA with LH<sub>6</sub>. This method, which is also known as a mechanistic model, is expressed in the following form:

$$\ln[(d\alpha/dt)(1-\alpha)^n] = \ln A - E_a/RT \quad (6)$$

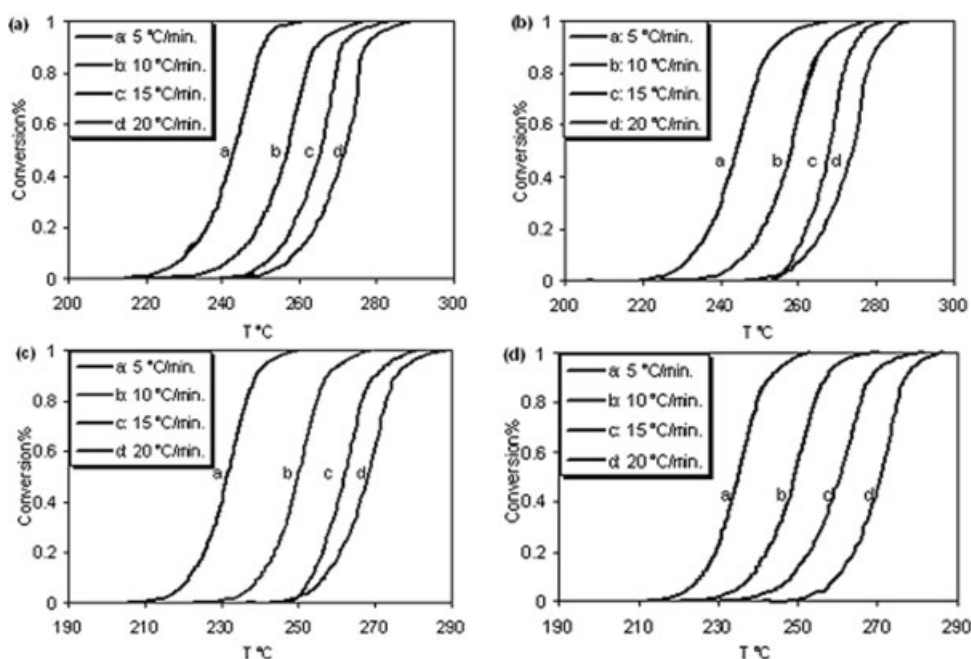
According to eq. (6), a plot of  $\ln[(d\alpha/dt)/(1-\alpha)^n]$  versus  $1/T$  should give a straight line with a slope of  $-E_a/R$  for a suitable reaction order, as shown in Figure 3. Several values of  $n$  (0.5, 1, 1.5, 2) were tried and found that the best linear fitting of experimental results have been obtained by using a reaction order of 1. The calculated activation energy using this method is 75.36 kJ/mol. The high value of  $E_a$  for the

curing reaction of DGEBA with the ligand in comparison with those previously reported for the reaction of free primary amine with the epoxide group can be due to the fact that the amine groups in the ligand are connected to the electronegative elements which reduce the rate of reaction with the epoxide group.

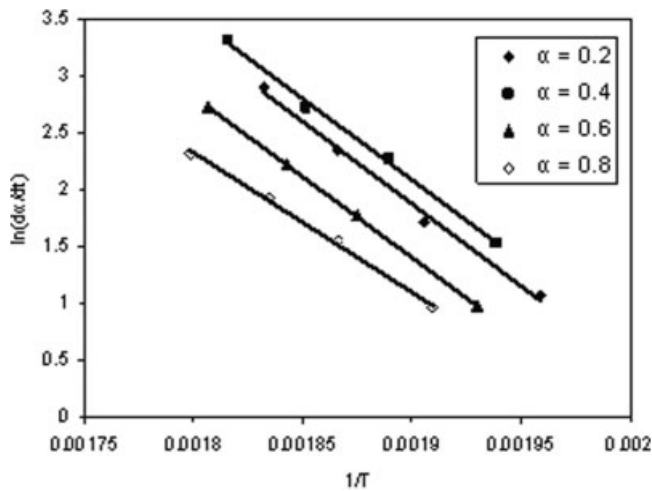
There are only primary amine groups in the structure of complexes (CuLH<sub>4</sub> and NiLH<sub>4</sub>) which reacts with the epoxide groups. The exothermic peak characteristics (*T<sub>i</sub>* and *T<sub>p</sub>*) of the cure reaction of DGEBA with the complex curing agents NiLH<sub>4</sub> and CuLH<sub>4</sub> occur at 217–249°C/min and 224–259°C, respectively, while for DGEBA/LH<sub>6</sub> system, it occurs at 140–180°C at the same heating rate (10°C/min). This comparison indicates the lower reactivity of the complexes than the ligand toward reaction with the epoxide groups. This shows that the basic property of the primary amine in the structure of the curing agents decreased because of formation of a complex with the electro-positive elements as shown in Scheme 1.

From DSC curves (Fig. 1) obtained from the two complex curing agents, it can be clearly observed that the initial curing temperature (*T<sub>i</sub>*) and the exothermic peak temperature (*T<sub>p</sub>*) increase with increasing heating rate. The data are also listed in Table III. The *T<sub>i</sub>* values of the DGEBA/NiLH<sub>4</sub> system at different heating rates are lower than those of the DGEBA/CuLH<sub>4</sub> system, indicating that NiLH<sub>4</sub> has a higher reactivity toward epoxy than CuLH<sub>4</sub> at the beginning of the curing reaction.

The original DSC data were transformed into the  $\alpha_i$  versus temperature curves at various heating

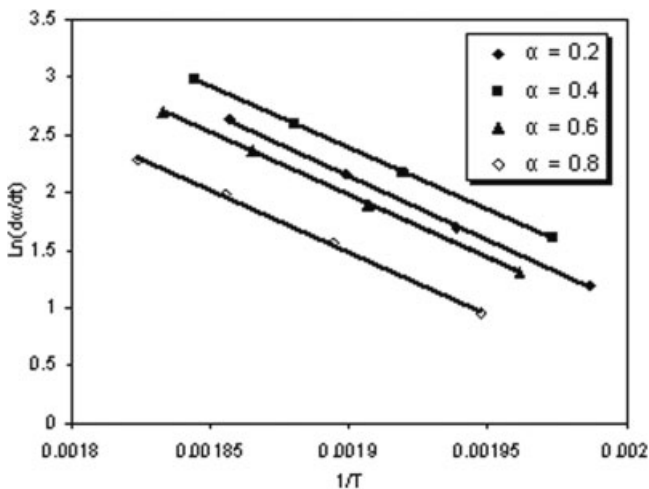


**Figure 4** Degree of conversion of the epoxy groups versus temperature at different heating rate with (a) CuLH<sub>4</sub> at 40 phr, (b) CuLH<sub>4</sub> at 30 phr, (c) NiLH<sub>4</sub> at 40 phr, and (d) NiLH<sub>4</sub> at 30 phr.

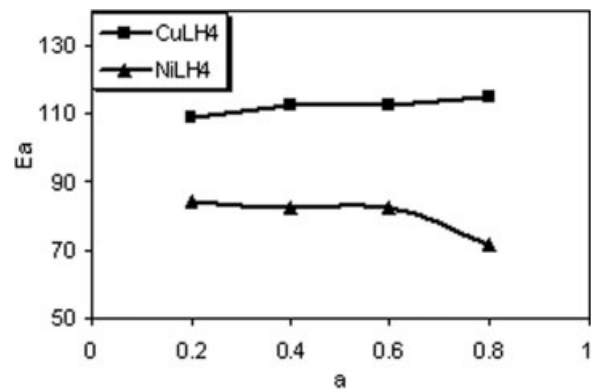


**Figure 5** Arrhenius plots for DGEBA/40 phr CuLH<sub>4</sub> in a range of  $0.2 \leq \alpha \leq 0.8$ .

rates, and the corresponding plots are shown in Figure 4 for different concentrations of curing agent complexes. The data from DSC measurement were also analyzed by using eq. (5). At the same  $\alpha$  value, the Arrhenius plot is a straight line, which gives the  $E_a$  values of a cured resin. Figures 5 and 6 show the Arrhenius plots for the DGEBA/CuLH<sub>4</sub> and DGEBA/NiLH<sub>4</sub> systems in a range of  $0.2 \leq \alpha \leq 0.8$ . Figure 7 shows the variation of the  $E_a$  values versus conversion for the DGEBA/CuLH<sub>4</sub> and DGEBA/NiLH<sub>4</sub> systems. The average value of activation energy for DGEBA/NiLH<sub>4</sub> system is 85.6 kJ/mol and for DGEBA/CuLH<sub>4</sub> system is 114.3 kJ/mol for the conversion range of  $\alpha = 0.2$ – $0.8$ . It can be seen that the  $E_a$  values of the NiLH<sub>4</sub> system are lower than the corresponding ones of the CuLH<sub>4</sub> system. This further demonstrates that NiLH<sub>4</sub> has a higher reactivity toward epoxy than CuLH<sub>4</sub>, which confirm



**Figure 6** Arrhenius plots for DGEBA/40 phr NiLH<sub>4</sub> in a range of  $0.2 \leq \alpha \leq 0.8$ .



**Figure 7** Variation of  $E_a$  values versus conversion of DGEBA for 40 phr complex curing agents.

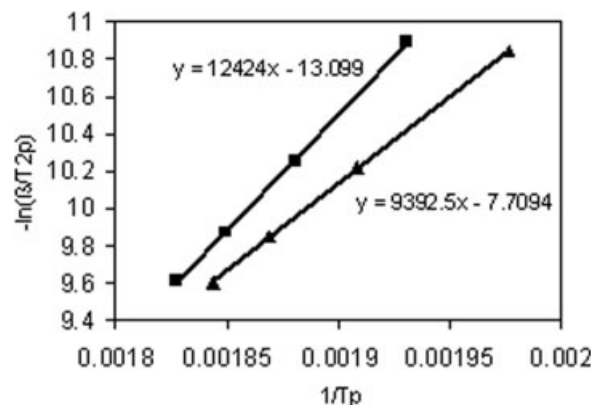
the result obtained by  $T_i$  and  $T_p$  analysis. Moreover, their  $E_a$  values determined from DSC measurements are nearly constant, except that there is for an unknown reason a slight decrease in  $E_a$  of DGEBA/NiLH<sub>4</sub> system above 60% conversion.

We have also applied Kissinger and Ozawa's methods to analyze the cure kinetics of the mentioned systems. These methods were used because it is not necessary to have a prior knowledge on the reaction mechanism, especially in new epoxy/Ni and Cu chelate composites, to quantify kinetic parameters.

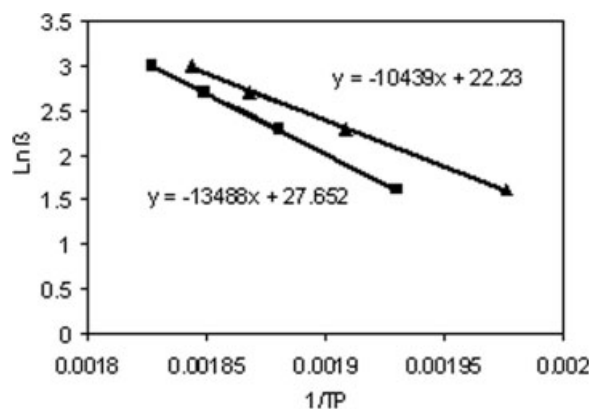
According to the method of Kissinger, the  $E_a$  is obtained from the maximum reaction rate where  $d(d\alpha/dt)/dt$  is zero under a constant heating rate reaction. The multiple curve method of Kissinger can be expressed as

$$\ln(\beta/T_p^2) = -E_a/RT_p \quad (7)$$

Thus the plot of  $\ln(\beta/T_p^2)$  versus  $1/T_p$  yield the apparent activation energy as shown in Figure 8, even if the analytical expression of the velocity equation is unknown.



**Figure 8** Plots for determination of  $E_a$  using Kissinger method for 40 phr: ■ CuLH<sub>4</sub>, ▲ NiLH<sub>4</sub>.



**Figure 9** Plots for determination of  $E_a$  using Ozawa method for 40 phr: ■  $\text{CuLH}_4$ , ▲  $\text{NiLH}_4$ .

The Ozawa-Flynn-Wall method based on Doyle's approximation<sup>24</sup> is an alternative method for the calculation of activation energy and is expressed as follows:

$$\log \beta = \log(AE_a/R) - \log[g(\alpha)] - c - l(E_a/RT) \quad (8)$$

where  $g(\alpha)$  is integrated form of the conversion-dependence function.

The main problem of the Ozawa method consists in the accurate setting of the coefficients  $c$  and  $l$ . For our systems,  $E_a/RT$  was in the range of 18–30; thus we considered  $c = 2.000$  and  $l = 0.4667$ .<sup>26</sup> The activation energy can be calculated from the slope of the linear plot of  $\ln \beta$  against  $1/T_p$ , as shown in Figure 9.

The obtained values of activation energies for the complex curing agents from eqs. (5), (7), and (8) are given in Table IV. It is noteworthy that, as shown in Table IV, there are good agreements between the values of  $E_a$  obtained by using three kinetic methods for each system.

## CONCLUSIONS

The influence of the type of metal ion and structure of complex formation with the ligand, in two complex curing agents, on the mechanism and cure kinetics of an epoxy system have been studied. It was shown that the presence of primary and secondary amine groups in the structure of curing agent

**TABLE IV**  
Values of  $E_a$  for Complex Curing Agents at 40 phr

Curing agent	$E_a$ (kJ/mol)		
	Malek's method	Kissinger's method	Ozawa's method
$\text{NiLH}_4$	85.6	79.45	81.99
$\text{CuLH}_4$	114.3	116.8	116.86

produces an exothermic peak, with a shoulder at higher temperatures due to contribution of the secondary amine in the cure reaction. It was also shown that formation of complex between the ligand and the metal ion can decrease the basic property of the amine groups and results in the higher temperature curing. Different kinetic models on multistep heating rate methods (Kissinger, Ozawa, and Málek) and single-step heating rate method were applied to DSC data to calculate kinetic parameters of curing reaction with the complexes. The activation energies obtained by these methods are close. The  $T_i$ ,  $T_p$ , and  $E_a$  values show the order of reactivity of  $\text{LH}_6 > \text{NiLH}_4 > \text{CuLH}_4$  toward epoxy. We can describe the mentioned results by a higher complexation ability of nickel toward oxygen of epoxy ring than copper. Thus, nickel can facilitate ring opening of epoxy ring during cure reaction.

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