

Structure and Metal Type Effects on Cure Kinetics of DGEBA with Benzil Bisthiosemicarbazone Complexes

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ABSTRACT: The curing reaction kinetics of the diglycidyl ether of bisphenol A- (DGEBA) based epoxy was investigated according to the change of curing agents. Complex curing agents based on Ni(II) and Cu(II) chelates with benzil bisthiosemicarbazone (LH₆) as a ligand was studied using differential scanning calorimetry. The curing reaction was characterized by high-activation energies (E_a), cure onset (T_i), and peak maximum (T_p) temperatures. Dynamic kinetic parameters were calculated by using Kissinger and Ozawa methods. For the NiLH₆Cl₂, CuLH₆Cl₂, and LH₆ the average values of E_a were calculated to be 165.16, 165.92, and 115.75 kJ/mol, respectively. For the

NiLH₆Cl₂ systems, their activation energies at 40 and 30 phr are equal. The T_i and T_p of the DGEBA/NiLH₆Cl₂ system are lower than those of DGEBA/CuLH₆Cl₂ system. These results indicate that NiLH₆Cl₂ has a higher reactivity toward epoxy resin at the beginning of the curing reaction. 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* 107: 4021–4028, 2008

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

INTRODUCTION

In recent years, the need for novel materials with improved specific properties has strongly affected the research and production of composite and organic–inorganic hybrid materials. It is expected that increased interaction between phases in hybrid materials, where inorganic phase is often covalently bonded with the organic polymer, will result in superior properties as compared with classical composites.^{1–6} Metal-containing polymers possess a variety of different, sometimes unique, properties which predetermine their applications. These properties can stem directly from the presence of a metal (e.g., catalytic, ion removal, and biological activities) or from the structural metal-containing monomer characteristics (enhancement of resistance, physicochemical and operating characteristics, etc.).

Among the different polymers utilized as a matrix in the compounding of composites and hybrid materials, thermosets guarantee good dimensional stability and noticeable environmental resistance. Epoxy resins are the most important thermosetting polymers, widely used as adhesives, insulating materials, composites, etc.⁷ The diglycidyl ether of bisphenol A (DGEBA) has been the most important epoxy resin system in industry because of its fluidity, physical

strength after curing, and cost advantage. Curing of the most commonly used epoxy resin, DGEBA, with a variety of aromatic and aliphatic diamines, was extensively studied.^{8–12} Extensive work has been carried out, over the last 30 years, into the use of metals and their salts in the formulation of epoxy resin systems, and this has included the use of organo-transition metal complexes as catalysts for epoxy resins when co-cured with amines, anhydrides, and phenolics. Organo-transition metal complexes have also been added to improve physical properties such as adhesion, flexural strength, fracture resistance, water adsorption, and thermal stability.^{13–15}

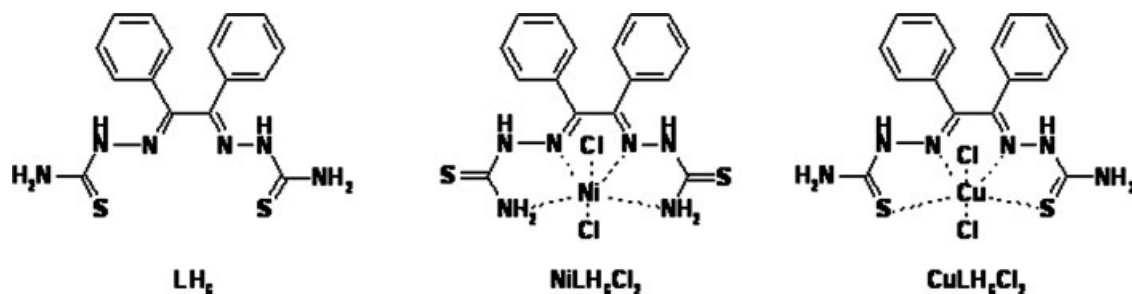
The main object of this work is to study kinetics of curing reaction of DGEBA with Ni(II) and Cu(II) complexes. Different nonisothermal kinetic methods such as Kissinger^{16,17} and Ozawa-Flynn-Wall^{18,19} were applied to DSC data to test their applicability in these new epoxy-hardener systems. The effects of hardener concentration, heating rate, and type of metal ion on the cure kinetic parameters were also investigated. The synthesized metal containing thermosets in this study could be used for selective sorbents for metal ions.

EXPERIMENTAL

Materials

Benzil, thiosemicarbazide, nickel chloride, and copper chloride were purchased from Fluka (Germany)

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Scheme 1 Structures of the curing agents.

and used without purification. The epoxy compound used in the study was a DGEBA-based epoxy, Epidian5: epoxide equivalent 196–208, clear liquid, viscosity (at 25°C) 25,000 mPas, provided by Iran Petrochemical Industry (Iran, Khuzestan). Scheme 1 displays the structure of the curing agents used in this work.

Apparatus

A Mettler Toledo differential scanning calorimeter (DSC 822^e), a Bruker vector 22 FTIR spectrometer, a Bruker AM 100 MHz ¹H NMR spectrometer, and an elemental analyzer of Themofinnigan Flash EA 1112.

Preparation of ligand

Benzil bisthiosemicarbazone LH₆²⁰

A solution of benzil (4.2 g, 20 mmol) in 20-mL ethanol was added to a boiling ethanol–water (4 : 1 v/v) suspension of thiosemicarbazide (3.64 g, 40 mmol), followed by the addition of 1-mL concentrated hydrochloric acid. The reaction mixture was refluxed for 6 h with stirring. The pale-yellow solid formed was filtered off, washed with aqueous ethanol and dried in vacuum oven at 80°C. The melting point was 241°C and the yield 75%. IR/cm⁻¹ 3420, 3330, 3250, and 3150 (NH + NH₂), 1610 (C=N), 1585 (NH₂), 848 (C=S). ¹H NMR (CDCl₃): δ 8.8 (2H, s), 7.6 (6H, m), 7.4 (4H, m), 6.6 (4H, s).

Preparation of complex curing agents

CuLH₆Cl₂²¹

A solution of copper(II) chloride dehydrate (0.24 g, 1.40 mmol) and 50-mL concentrated hydrochloric acid in 50-mL methanol was added to LH₆ (0.5 g, 1.40 mmol) in 100-mL methanol. The mixture was refluxed for 3 h with stirring. The green solid formed was filtered off, washed with methanol and dried in vacuum oven at 80°C. The melting point was 230°C and the yield 85%.

NiLH₆Cl₂²²

A solution of nickel(II) chloride (0.20 g, 0.8 mmol) in 10-mL methanol was added to a suspension of LH₆ (0.30 g, 0.8 mmol) in 20-mL methanol and 10-mL concentrated hydrochloric acid. The mixture was refluxed for 3 h with stirring. The reddish-brown solid formed was filtered off, washed with methanol and dried in vacuum oven at 80°C. The melting point was >260°C and the yield 58%.

Preparation of epoxy-complex curing agents

The complex curing agents were well dried in vacuum oven and were completely powdered by grinding to obtain fine particles. The epoxy resin was completely mixed with the complex curing agents and, to facilitate the mixing, a small amount of acetone was added to the mixing composition. The stoichiometric of the curing agents were calculated through the number of active amino hydrogens. Based on this calculation, we have used concentration of 30 and 40 phr of complex curing agents to study the effect of concentration. The ligand LH₆ was also used in four different concentrations of 10, 15, 20, and 30 phr to investigate the effect of concentration on curing.

DSC measurement

The curing thermal data were obtained using a Mettler Toledo instrument (DSC 822^e), which was heated from 30 to 350°C with 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 small quantity of sample (5–8 mg) well-mixed and uniform viscous liquid was put into a DSC sample pan and closed tightly under pressure with an aluminum lid. An identical empty cell was taken as reference.

The rate of reaction, $d\alpha/dt$, as a function of time was obtained from the rate of heat flow measured in DSC experiments, dH/dt , by:

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

The average value of the total heat developed during DSC tests, ΔH_{Tot} , was taken as a measure of ultimate fractional conversion. By partial integration of the area under $d\alpha/dt$ versus time curve, dependence of the fractional conversion, α_t , on time was obtained as follows:

$$\alpha_t = \Delta H_t / \Delta H_{Tot} \quad (2)$$

The rate of the kinetic process can be described by eq. (3)^{23,24}:

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

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

An Arrhenius type dependence between $k(T)$ and temperature according to eq. (4):

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

where A is the preexponential factor and E_a is the apparent activation energy.

Therefore, the E_a value can be determined by an iso-conversional method under the assumption of the $f(\alpha)$ being the same at different heating rates (β) when the value of α is the same, i.e., in eq. (5) $f(\alpha)$ do not depend on the heating rate at a fixed value of the variable α . From the logarithmic form of eq. (3), we can have

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

For nonisothermal conditions, when the temperature varies with time with a constant heating rate $\beta = dT/dt$, eq. (3) is modified as follows:

$$d\alpha/dt = A/\beta \exp(-E_a/RT) \cdot f(\alpha) \quad (6)$$

An integrated form of the conversion-dependence function $g(\alpha)$ often appears as²⁵:

$$g(\alpha) = \int_0^\alpha d\alpha/f(\alpha) = A/\beta \int_{T_0}^T \exp(-E_a/RT) dT \quad (7)$$

The integral term of right side of eq. (7) can be written by the following polynomial function:

$$E_a/R \cdot P(E_a/RT) = \int_0^T \exp(-E_a/RT) dT \quad (8)$$

The function $P(E_a/RT)$ is the Doyle's approximation, and the above equation can be expressed as follows²⁶:

$$\log(P \cdot E_a/RT) = -2.315 - 0.4567E_a/RT \quad (9)$$

To determine the kinetic parameters, the eqs. (7) and (9) can be combined and rearranged as follows:

$$\ln\beta = -1.052E_a/RT_p + \ln AE_a/R - \ln f(\alpha) - 5.331 \quad (10)$$

RESULTS AND DISCUSSION

IR and elemental analysis of curing agents

Benzil bithiosemicarbazone (LH₆) and its complex with copper (CuLH₆Cl₂) and with nickel (NiLH₆Cl₂) were prepared according to the procedures given in the literatures.^{20–22} IR and elemental analysis data for the curing agents of this study are in good agreement with the results reported in the literature. The results of elemental analysis are given in Table I. The most significant IR bands, useful for determining the ligand mode of coordination, are listed in Table II. The most important bands of the ligand were assigned to published data.²⁷ Figure 1(a–c) shows the IR spectra of the ligand LH₆ and the complexes of CuLH₆Cl₂ and NiLH₆Cl₂, respectively. The absence of any bands in the 2600–2800 cm⁻¹ region of the IR spectra of LH₆ and its complexes suggests the absence of any thiol tautomer in solid state.²⁸ The IR spectra of both complexes show that the band assigned to azomethine nitrogen has been shifted to lower wave number.²⁹ Coordination of these nitrogen is confirmed with the presence of new bands assigned to $\nu(M-N=C)$ in the spectra of complexes.³⁰ In addition, the IR spectrum of complexes show several bands between 3398 and 3098 cm⁻¹ corresponding to N–H stretching vibrations, which indicates that the ligand is present in its neutral form according to the analytical data. The IR spectra of both complexes show two additional bands

TABLE I
Elemental Analysis Results for Ligand and Complex Curing Agents

Complex	% C	% H	% N	% M
LH ₆	54.15 (53.93)	4.49 (4.59)	23.29 (23.08)	–
NiLH ₆ Cl ₂	39.53 (39.51)	3.53 (3.29)	17.25 (17.28)	11.24 (12.08)
CuLH ₆ Cl ₂	38.82 (39.14)	3.59 (3.33)	16.74 (17.12)	11.53 (12.94)

TABLE II
Selected IR Data for the Curing Agents

Complex	$\nu(\text{NH}_2) + \nu(\text{NH})$	$\nu(\text{C}=\text{N})$	$\nu(\text{N}-\text{M}), \nu(\text{S}-\text{M})$	$\nu(\text{M}-\text{Cl})$
	3000–3500 cm^{-1}	1500–1700 cm^{-1}	420–490 cm^{-1}	
NiLH_6Cl_2	3398, 3387, 3273, 3098	1615, 1599, 1583, 1570	487, 432	313, 324
CuLH_6Cl_2	3333, 3240, 3084	1609, 1575	427, 297	284

assignable to $\nu(\text{M}-\text{Cl})$ with respect to ligand, which confirm the Ni—Cl and Cu—Cl bonds.

In the IR spectrum of CuLH_6Cl_2 , in which the ligand acts in its neutral form, the band assigned to $\nu(\text{NH}_2)$ remains in the same position as in the free ligand, so the primary amines are not bonded to copper ion. In addition, coordination via sulfur atoms is indicated by a decrease in the frequency of the thioamide band. The presence of a new band assignable to

$\nu(\text{Cu}-\text{S})$ confirms that the sulfur atoms are involved in the coordination.

In the IR spectrum of NiLH_6Cl_2 , the band corresponding to the thioamide group appears in the same position as the free ligand, but the band assigned to azomethine nitrogen shifted toward lower wave number. These data support both azomethine and the primary amines being bonded to the nickel ion.³¹

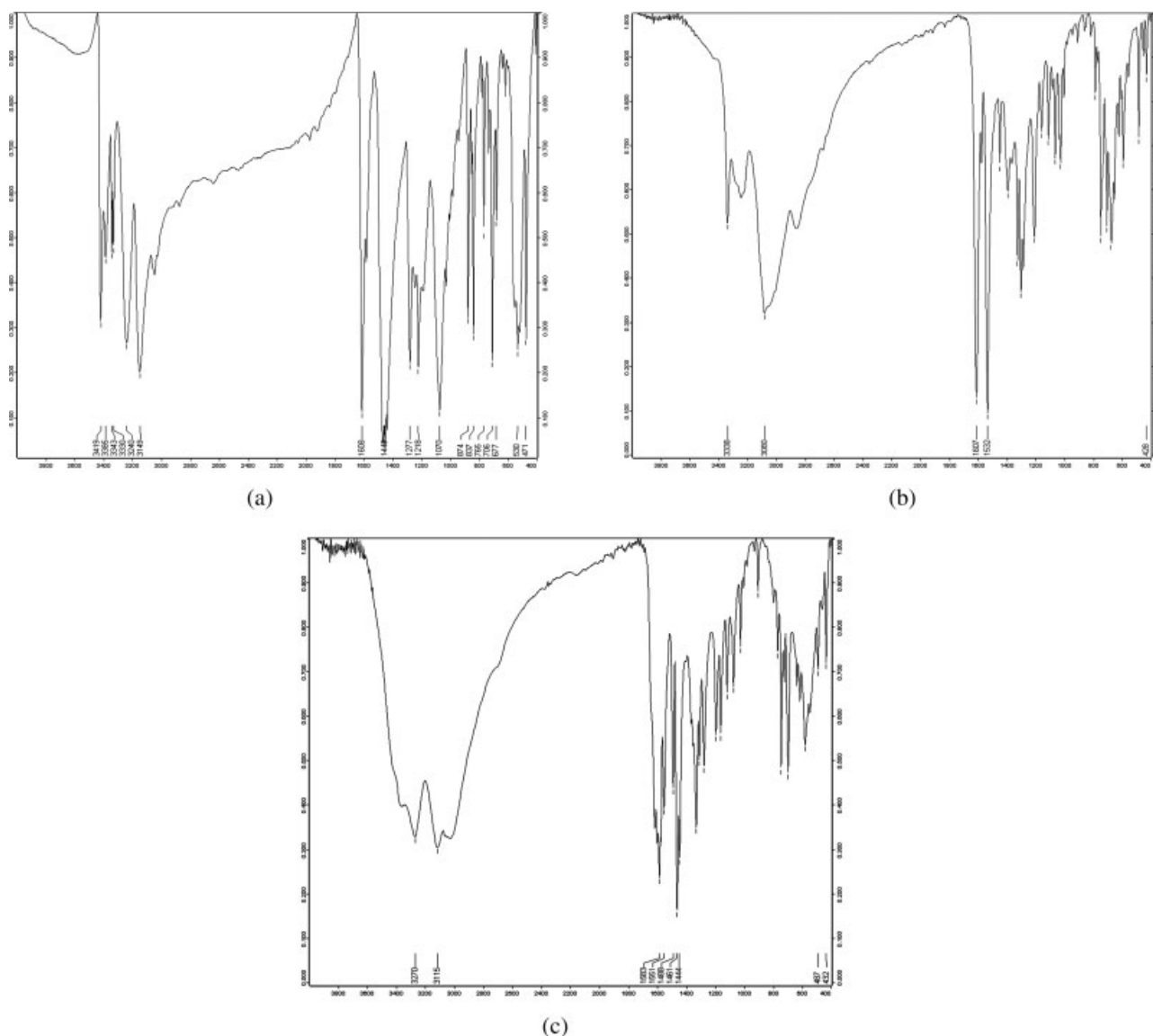


Figure 1 FTIR spectra of curing agents: (a) LH_6 , (b) CuLH_6Cl_2 , and (c) NiLH_6Cl_2 .

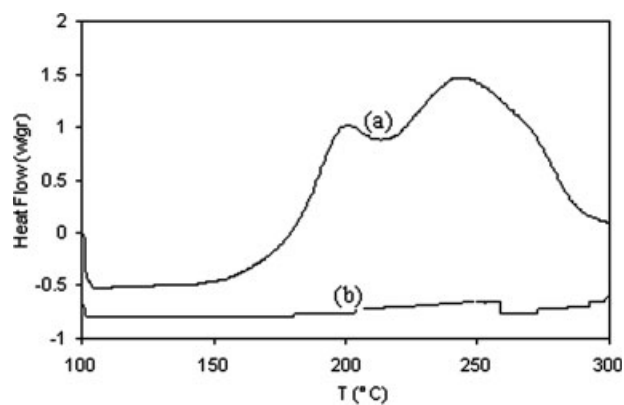


Figure 2 DSC thermograms of DGEBA/20% LH₆ system: (a) first run (b) second run.

Curing behavior

The curing behavior of the DGEBA/CuLH₆Cl₂, DGEBA/NiLH₆Cl₂, and DGEBA/LH₆ systems was studied by DSC at different heating rates (5, 10, 15, and 20 °C/min). The curing behavior of DGEBA with the LH₆ was carried out with dynamic DSC up to 300 °C as shown in Figure 2. The exothermic peak is because of polymerization and etherification reactions of the epoxide groups with the amine groups of the curing agent and hydroxyl groups present and also subsequently formed along the polymer main chains during polymerization. The first DSC scan of curing reaction of DGEBA with LH₆ shows two exothermic peaks (curve a). The first exotherm step starts about 140 °C and reaches its maximum at 190 °C. The second exothermic peak appears at 240 °C and drags on above 300 °C. The second DSC scan of the same sample has not shown any thermal transition up to 300 °C (curve b) which confirms complete curing reaction. DSC thermograms of curing reaction of DGEBA/LH₆ system at different concentrations of the curing agent are shown in Figure 3. The height of first exothermic peak

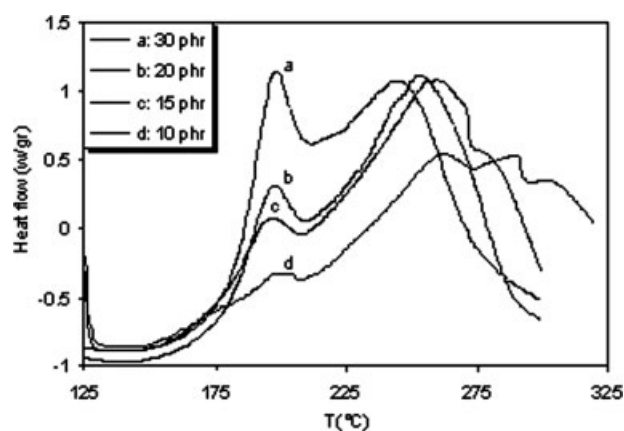


Figure 3 DSC thermograms of curing DGEBA/LH₆ system at different concentrations.

increases and becomes sharper without shifting with the increasing amount of curing agent from 10 to 30 phr, while the second exothermic peak becomes narrower and shifts slightly toward lower temperatures. The first exothermic peak can be related to the polymerization reaction of epoxy resin with the primary amine groups of the ligand. The continuation of curing reaction exhibits a second exothermic peak around 240 °C which can be attributed to contribution of reactions such as etherification, epoxide groups with secondary amine, sulfide, and other species which are probably formed at higher temperatures. Although we have not observed the characteristic absorption band of thiol (—SH) in the FTIR spectrum of the ligand at room temperature, there is also the possibility of tautomerization and formation of thiol group at high temperature which can contribute in reaction with the epoxide group and responsible for the second exothermic peak.

DSC thermograms of curing reaction of DGEBA with 40 phr NiLH₆Cl₂ and CuLH₆Cl₂ complexes at different heating rates are shown in Figure 4(a,b), respectively. The reproducibility of the DSC analysis was found to be excellent as evidenced by scanning

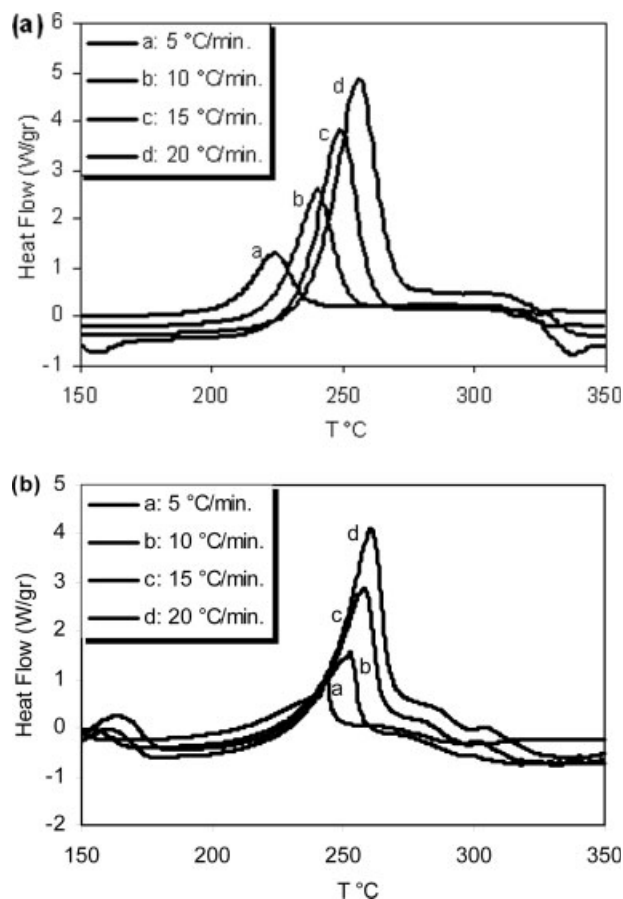


Figure 4 DSC curves of DGEBA cured at different heating rates with: (a) NiLH₆Cl₂ and (b) CuLH₆Cl₂ at 40 phr.

TABLE III
Curing Characteristics for Two Systems Evaluated from DSC Thermograms

Heating rate (°C/min)	DGEBA/NiLH ₆ Cl ₂			DGEBA/CuLH ₆ Cl ₂		
	<i>T_i</i> (°C)	<i>T_p</i> (°C)	Δ <i>H_t</i> (J/g)	<i>T_i</i> (°C)	<i>T_p</i> (°C)	Δ <i>H_t</i> (J/g)
5	206.58 (208.86)	224.36 (224.68)	406.7	219.3 (221.29)	243.61 (245.58)	426.2
10	219.56 (221.05)	240.74 (240.76)	398.5	227.2 (229.27)	252.84 (252.87)	476.2
15	226.4 (226.87)	249.08 (250.8)	435.5	231.88 (233.32)	257.92 (258.2)	449.4
20	230.64 (234.04)	255.97 (259.43)	410.8	238.75 (240.01)	261.4 (264.2)	459.5

Values inside and outside of parenthesis are related to 30 and 40 phr of complex, respectively.

three samples each from two different curing complex systems. As can be seen in this typical thermogram, there is one main exotherm peak for curing reaction of DGEBA with complex representative of polymerization and etherification reactions. The exothermic peak becomes larger, and *T_p* shifts to higher temperature with increasing heating rate. Formation of complex with Ni(II) and Cu(II) has a significant effect on the mechanism of curing reaction of LH₆ with the epoxide group. As can be seen in this figure, there is only one exothermic peak for the curing reaction of DGEBA with the complexes which appears at higher temperature than that of the first exothermic peak of the curing reaction with LH₆ appeared. This can be attributed to the lower reactivity of the primary amine because of coordination with the metal ion. This is consistent with the complex structures given in Scheme 1.

From DSC curves obtained from the two curing systems, it can be clearly observed that the initial curing temperature (*T_i*) and the exothermic peak temperature (*T_p*) increase with increasing heating rate. The data in Table III shows that with increasing curing agents concentration *T_i* and *T_p* decreased (data in parenthesis are for 30 phr). The *T_i* values of the DGEBA/NiLH₆Cl₂ system at different heating rates are lower than those of the DGEBA/CuLH₆Cl₂ system, indicating that NiLH₆Cl₂ has a higher reactivity toward epoxy than CuLH₆Cl₂ at the beginning of the curing reaction. LH₆ as a neutral tetradentate ligand can form two types of complex with Ni and Cu. It acts as a tetradentate ligand of the type of N₂S₂ with Cu, where the primary amines are free or of the type of N₄ with Ni and the primary amines are also chelated with the metal. As reported in our previous work,¹⁵ Ni complex (NiLH₄) shows lower *E_a* and more reactivity toward epoxide groups than copper complex (CuLH₄), while in these complexes due to differences in chemical structure and in the way of chelating, see Scheme 1, the two complexes have almost similar *E_a*.

Cure kinetics

To evaluate the kinetic parameters of mentioned systems, Kissinger and Ozawa methods were also

applied to calculate activation energy (*E_a*) because they are very simple ways to deal with the dynamic cure process of new epoxy/Ni and Cu chelate complexes. The kinetic parameters obtained from these methods do not require a prior knowledge on the reaction mechanism, considering the heating rate, and side reactions as well as the choice of the baseline.

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

$$\ln(\beta/T_p^2) = -E_a/RT_p \quad (11)$$

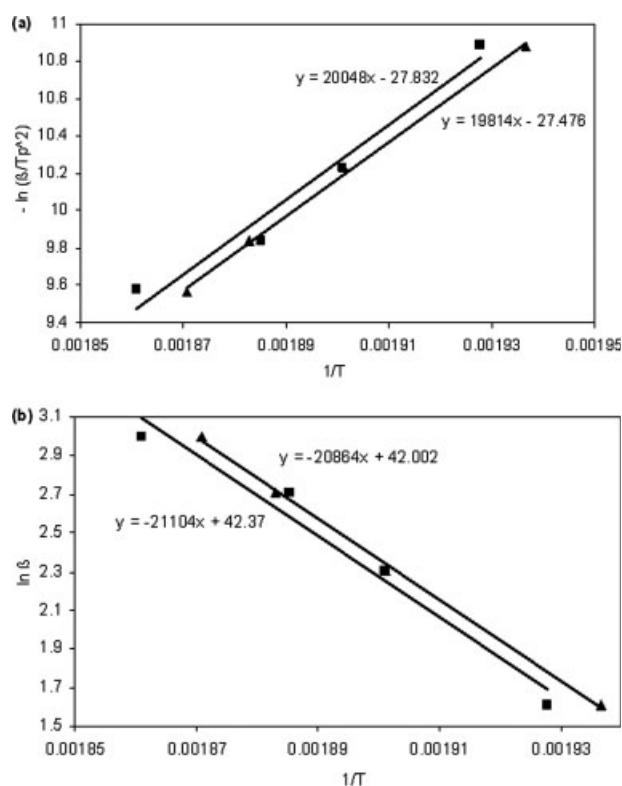


Figure 5 Plots for calculation of *E_a* for curing DGEBA with CuLH₆Cl₂: ■ 30 phr, ▲ 40 phr using: (a) Kissinger and (b) Ozawa methods.

Thus the plot of $\ln(\beta/T_p^2)$ versus $1/T_p$ yield the apparent activation energy as shown in Figure 5(a) for DGEBA/CuLH₆Cl₂ system at two different concentrations and in Figure 6(a) for comparing NiLH₆Cl₂ and DGEBA/LH₆ systems, even if the analytical expression of the velocity equation is unknown.

The Ozawa-Flynn-Wall method based on Doyle's approximation is an alternative method for the calculation of activation energy and is expressed by eq. (10). The activation energy can be calculated from the slope of the linear plot of $\ln \beta$ against $1/T_p$, as shown in Figure 5(b) for DGEBA/CuLH₆Cl₂ system at two different concentrations and in Figure 6(b) for comparing DGEBA/NiLH₆Cl₂ and DGEBA/LH₆ systems. For the DGEBA/NiLH₆Cl₂ system, the calculated activation energies at 30 and 40 phr of curing agents are equal. The obtained values of activation energy are given in Table IV. The calculated values of activation energy by two kinetic models are almost similar.

CONCLUSION

The incorporation of transition metals and their derivatives in epoxy resin have been examined by

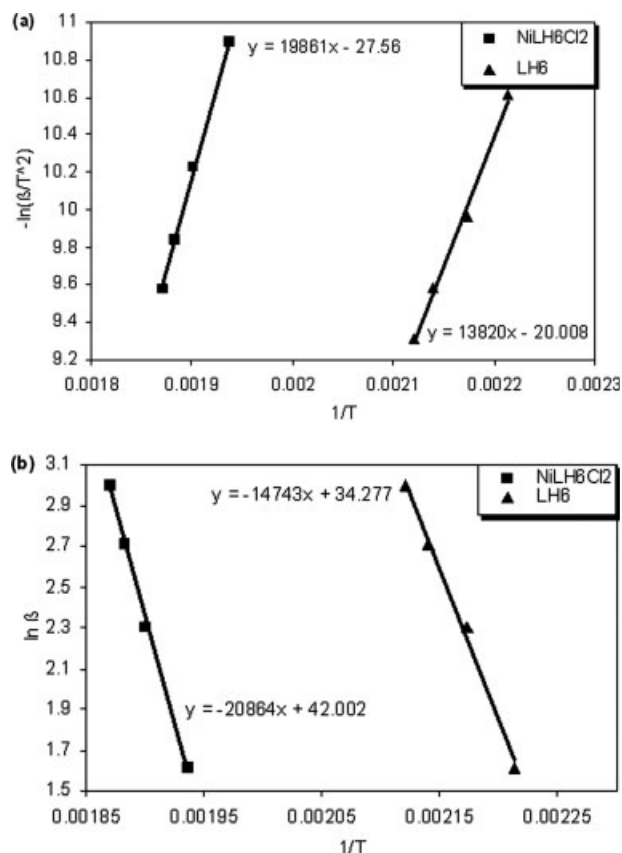


Figure 6 Plots for calculation of E_a for curing DGEBA with NiLH₆Cl₂ and LH₆ using: (a) Kissinger and (b) Ozawa methods.

TABLE IV
Values of E_a for Curing DGEBA with Three Systems

Curing agent	E_a Kissinger's method (kJ/mol)	E_a Ozawa's method (kJ/mol)
LH ₆	114.9 ^a	116.5 ^a
NiLH ₆ Cl ₂	165.12 ^{a,b}	165.2 ^{a,b}
CuLH ₆ Cl ₂	164.73 ^a , 166.67 ^b	165.2 ^a , 167.1 ^b

^a 30 phr.

^b 40 phr.

other researchers¹³ indicating that the final properties of cured epoxy can be controlled by the change of composition of curing agent.

The influence of the type of metal ion, in two complex curing agents on the cure kinetics of an epoxy system has been studied and the results are reported in this article. Formation of complex with Ni(II) and Cu(II) had a significant effect on the mechanism of curing reaction of LH₆ with the epoxide group. There was only one exothermic peak for the curing reaction of DGEBA with the complexes, which appeared at higher temperature than the first exothermic peak of the curing reaction with LH₆ appeared. Two different kinetic models on multistep heating rate methods (Kissinger and Ozawa) were applied to DSC data to calculate kinetic parameters of curing reaction. The activation energies obtained by these methods were close. The T_i and T_p of the DGEBA/NiLH₆Cl₂ system were lower than those of DGEBA/CuLH₆Cl₂ system, indicating that NiLH₆Cl₂ has a higher reactivity toward epoxy than CuLH₆Cl₂. The activation energy of the DGEBA/LH₆ system is lower than those of DGEBA/CuLH₆Cl₂ and DGEBA/NiLH₆Cl₂ systems, indicating that ligand has a higher reactivity toward epoxy than complex curing agents.

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