

Study of Reaction Kinetics of Epoxy and a Nickel(II) Complex Using Dynamic DSC Technique

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ABSTRACT: The curing reaction kinetics of an epoxy based on the diglycidyl ether of bisphenol A (DGEBA) with an inorganic complex based on nickel(II) chelate with ethylenediamine (en) as a ligand were studied using DSC in dynamic mode. The complex curing agent was synthesized and characterized by the elemental analysis, FT-IR, and ICP-Plasma techniques. Thermal dissociation behavior of curing agent was also studied using thermogravimetric (TG) analysis in isolated form. Three kinetic models, Kissinger, Ozawa-Flynn-Wall, and Expanded Freeman-Carrolle, were

used to determine the kinetic parameters. The effect of hardener concentration on the kinetic parameters and the shape of DSC thermograms of the DGEBA/Ni(en)₃Br₂ system were investigated. Finally, the previous proposed mechanism by another researcher was used to explain the DSC data in detail. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 97: 265–271, 2005

Key words: curing of polymers; resins; kinetics; differential scanning calorimetry (DSC)

INTRODUCTION

A great number of compounds have been screened for their suitability as curing agents for epoxy resins. For the thermosetting materials such as amine-cured epoxy resins, the solidification behavior during cure both defines the processing window and determines the properties of the final material. The diglycidyl ether of bisphenol A (DGEBA) has been the most important epoxy system because of its fluidity, physical strength after curing, and cost advantages. There are several factors on which the choice of curing agent to be used with an epoxy resin will depend:¹ 1) handling characteristics; 2) cure, postcure time, and temperature requirements; 3) properties of the cured system; and 4) cost of curing agent. The extent and nature of the intermolecular crosslinking will, therefore, be determined in part by the correct choice of curing agent. The differential scanning calorimeter (DSC), which measures the heat flow from the reacting systems, is a very convenient tool to study the cure reaction of epoxy-amine systems.^{2–13} The incorporation of transition metals and their derivatives in epoxy resin have been examined in recent years. For example, acrylates of Zn, Cr, and Cu have been shown to improve the electrical, thermal, and chemical properties.^{14–16} Kurnoskin^{17,18} reported using metal chelates

of different structures to cure epoxy oligomers of DGEBA. It was shown that the final properties of cured epoxy can be controlled by the change of composition of curing agent. Hamerton and coworkers^{19–21} have recently published articles concerning curing properties of epoxy resin with several Ni and Cu complex curing agents.

The main object of the present work was to study kinetics of curing reaction of epoxy DGEBA with a Ni(II) complex. Different nonisothermal kinetic methods such as Kissinger,^{22,23} Ozawa-Flynn-Wall,^{24,25} and a mechanistic model²⁶ were applied to DSC data to test their applicability in this new epoxy-hardener system. We have also investigated the effects of concentration of hardener and heating rate on the kinetic parameters of the curing system.

EXPERIMENTAL

Materials

The epoxy resin studied was based on a commercial DGEBA, Epon 828 from Shell Co., with an epoxy equivalent weight (eew) of 185. Ethylenediamine, from Fluka, was distilled twice before use. All other components were provided from Fluka and used without further purification. All solvents used were always degassed with nitrogen prior to use.

Apparatus

Fourier transform infrared (FT-IR) spectra were obtained using a NICOLET 550 Magna IR system and

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TABLE I
Elemental Analysis Results for Complex Curing Agent^a

| Complex | %C | %H | %Ni |
|-------------------------------------|--------------|------------|---------------|
| Ni(en) ₃ Br ₂ | 16.4 (16.57) | 6.8 (6.44) | 13.67 (13.51) |

^a requested values are in parentheses.

samples were presented as KBr disks. Elemental analysis (carbon and nitrogen) was performed with CHN-600 Leco. The nickel ion content in the curing agent was also determined by means of the ICP-plasma technique based on a standard calibration method using BYJE ICP-Plasma model JY 138 ultrace sequential. Thermogravimetric (TG) analysis was performed with the Du Pont Instruments (TGA 951) analyzer well equipped with a PC at a heating rate of 10°C/min under nitrogen atmosphere (40 cm³/min) and in the temperature range of 50–800°C. The weight of samples was about 5 mg. Finally, DSC thermograms were recorded using a DuPont instruments (DSC 910) system supported by a DuPont computer for data analysis on samples (ca 3 mg) over the temperature range of 50–350°C at different heating rates (5, 10, 15, and 20°C/min) under nitrogen atmosphere (40 cm³/min).

Preparation of complex curing agent Ni(en)₃Br₂

The general method for preparation of nickel(II) complexes with aliphatic diamine such as ethylenediamine was reported in the literature.²⁷ NiCO₃·3H₂O (1.19 g, 0.01 mol) was smoothly added to concentrated HBr (3.8 cm³, 0.03 mol) in a 250-cm³ reaction vessel. 100 cm³ of absolute ethanol was added to the mixture while the solution was stirred with a magnetic stirrer. Twice distilled ethylenediamine (4.2 cm³) was then added to the solution contents slowly and carefully. The mixture was stirred continuously until the formation of participation was completed, which was indicated by the disappearance of blue color related to the formation of the nickel(II)–ethanol complex. Finally, the complex was filtered and washed twice with absolute ethanol (25 cm³) and dried in an oven at 50°C.

Preparation of the epoxy–nickel chelate composition

The epoxy resin was completely mixed by stirring with the complex curing agent and, to facilitate the mixing, a small volume of acetone was added to the mixing composition. The level of curing agent incorporation can be based on the number of active amino hydrogen atoms in the complex and epoxy equivalent weight. Therefore, for the Ni(en)₃Br₂ complex with a molar mass of 435.5 g/mol and active hydrogen atoms of 12, 36.2 g of this complex was required for 185 g of DGEBA (or 19.4 g for 100 g DGEBA). Based on these

TABLE II
Selected IR Data for the Curing Agent

| Complex | Characteristic bands in mid-IR | | |
|-------------------------------------|--------------------------------|-------------------------------|-------------------------------|
| | 3500–3000 cm ⁻¹ | 1700–1400 cm ⁻¹ | 1290–1220 cm ⁻¹ |
| en | 3356,3278 | 1597,1458 | — |
| Ni(en) ₃ Br ₂ | 3482,3128 | 1582,1460 | 1240,1282 |

calculations, we have used concentrations of 10, 15, 18, 20, and 30 phr of complex curing agent to study the effect of concentration. The complex curing agent was well dried in a vacuum oven and must be powdered carefully to create a homogenous blend and prevent of formation of aggregate region in the epoxy matrix. 3 mg of this composition was put into an aluminum DSC sample pan and covered with an aluminum lid and closed tightly under pressure. The DSC apparatus was calibrated by means of standard high purity prior to any DSC experiment. The DSC apparatus was run dynamically at several heating rates from room temperature to a maximum of 350°C.

RESULTS AND DISCUSSION

IR spectroscopy was used extensively to determine whether complex had been achieved. IR spectra and elemental analysis data for the complex curing agent of the present to work are in good agreement with the results reported in the literature.^{27,28} The results of elemental analysis are given in Table I.

Two main areas within the IR spectra were monitored: 3000–3500 cm⁻¹ (NH₂ asymmetric and symmetric stretch) and 1590–1650 cm⁻¹ (NH₂ deformation). Owing to the complexity of the spectra, it was difficult to characterize the 1220–1290 cm⁻¹ region (C–N stretch) with certainty. FT-IR spectra of the hardener showed no evidence of the presence of free N–H

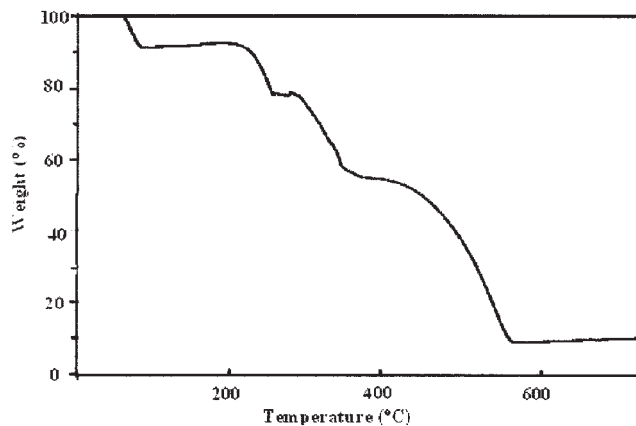


Figure 1 Dynamic TGA data (10°C/min) obtained under nitrogen for the Ni(en)₃Br₂ complex.

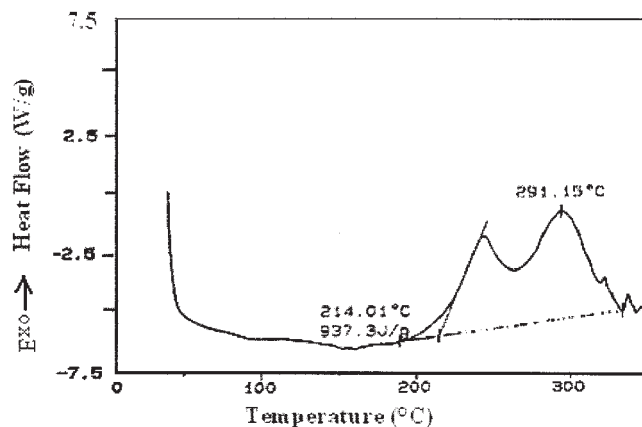
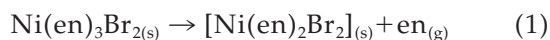


Figure 2 DSC thermogram of DGEBA cured with 10 phr $\text{Ni}(\text{en})_3\text{Br}_2$ at the heating rate of $20^\circ\text{C}/\text{min}$.

stretch. Table II lists the characteristic bands that are indicative of the formation of complex.

The thermal dissociation behavior of the complex curing agent was analyzed in isolated form by means of TGA technique. TGA measurements provide some information regarding thermal stability and pattern of degradation behavior of the complex. However, these studies were carried out on isolated complex that does not resemble the exact environments of the curing reaction. TGA measurement of $\text{Ni}(\text{en})_3\text{Br}_2$ complex, in Figure 1, showed multistep dissociation above 200°C . This result is consistent with the results reported by other researchers^{29,30} for the multistep dissociation process of cobalt and chromium ethylenediamine chelates. A loss of 15% in the mass of the original sample in the first step at about 100°C can be related to the removal of water molecules. The second step in TGA thermogram with a loss of about 23% in mass can be related to the removal of one ligand molecule:

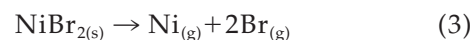


This step was initiated and ended within the temperature range of $200\text{--}250^\circ\text{C}$. The next thermal event

occurred in a temperature range of $280\text{--}350^\circ\text{C}$ with a loss of about 26% in mass and is probably related to the removal of the remaining two ligand molecules:



The final step shows a 36% loss of mass, which is described by the complete dissociation of the complex:



A typical DSC thermogram of the DGEBA/ $\text{Ni}(\text{en})_3\text{Br}_2$ system was shown in Figure 2. The data obtained from these thermograms at different heating rates and concentrations are presented in Table III.

Kinetic analysis of the DSC data for the epoxy/hardener system was performed using two kinetic models: Kissinger and Ozawa's methods.^{22,24} These methods were used because it is not necessary to have a prior knowledge of the reaction mechanism, especially in new epoxy/Ni-chelate composite, to quantify kinetic parameters. If one assumes that the extent of reaction, α , is proportional to heat generated during reaction, the reaction rate ($d\alpha/dt$) can be expressed by means of the general law

$$d\alpha/dt = K(T)f(\alpha) \quad (4)$$

where $f(\alpha)$ is a conversion-dependence function. An integrated form of the conversion-dependence function $g(\alpha)$ often appears as

$$g(\alpha) = \int d\alpha/f(\alpha) = K(T)t \quad (5)$$

According to the method of Kissinger, the activation energy is obtained from the maximum reaction rate where $d(d\alpha/dt)/dt$ is zero under a constant heating rate condition. The resulting relation, for the analysis of DSC data, can be expressed as

TABLE III
DSC Data for DGEBA Cured with $\text{Ni}(\text{en})_3\text{Br}_2$ as Curing Agent at Different Concentrations and Different Heating Rates

| Concentration (phr) | β ($^\circ\text{C}/\text{min}$) | Cure onset ($^\circ\text{C}$) | Maximum temperature of 1st peak ($^\circ\text{C}$) | E_a Kissinger's method (kJ/mol) | E_a Ozawa's method (kJ/mol) |
|---------------------|---|---------------------------------|--|-----------------------------------|-------------------------------|
| 10 | 5 | 143 | 218.0 | | |
| 10 | 10 | 149.8 | 229.0 | | |
| 10 | 15 | 164.2 | 234.0 | 119.6 | 121.6 |
| 10 | 20 | 165.4 | 241.3 | | |
| 15 | 20 | 166.7 | 239.6 | | |
| 18 | 20 | 170.4 | 237.7 | | |
| 20 | 20 | 178.3 | 239.3 | | |
| 30 | 20 | 182.8 | 236.7 | | |

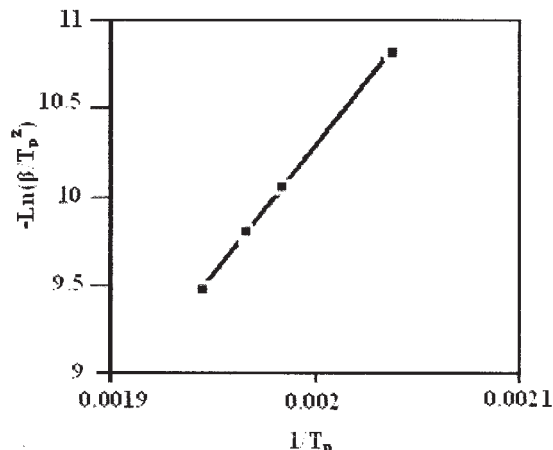


Figure 3 Plot for determination of E_a using Kissinger's method.

$$d[\ln(\beta/T_p^2)] = -E_a/Rd(1/T_p) \quad (6)$$

where T_p is the maximum rate temperature and β is a constant heating rate.

The activation energy (E_a) can be calculated from the slope of the linear plot of $-\ln(\beta/T_p^2)$ against $(1/T_p)$, as shown in Figure 3. The obtained value of activation energy was 28.6 kcal/mol where T_p of the first peak, as shown in Table III, was used for calculations. We have used T_p of the first maximum because it is related to the initial curing reaction taking place between epoxy oligomers and the complex hardener. TG thermogram of pure DGEBA was also obtained to confirm that thermal degradation is not competing with polymerization of epoxy resin at the initial stage of curing reaction (Fig. 4). This thermogram shows that only 2 and 10% loss in mass will occur at temperatures 300 and 350°C, respectively. All DSC thermograms of the DGEBA/ $\text{Ni}(\text{en})_3\text{Br}_2$ systems are ended at less than 330°C. Therefore, the contribution of thermal degradation on the final stage of the cured sample is less than 10% and on the initial stage (first exotherm), which occurs at temperature less than 250°C, is negligible.

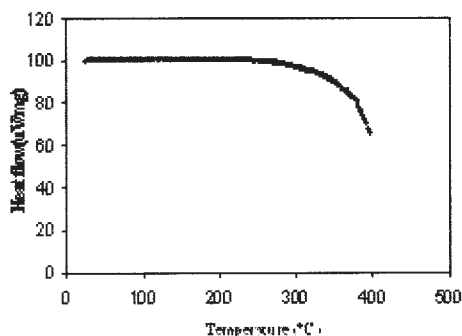


Figure 4 TG thermogram of pure DGEBA.

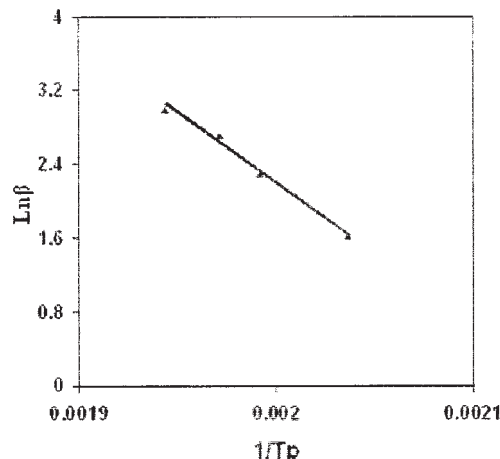


Figure 5 Plot for determination of E_a using Ozawa's method.

It must be noted that multih heating rate methods such as Kissinger and Ozawa's are isoconversional methods and assume that the conversion value, α_p , is constant at the peak exotherm temperature and is independent of the heating rate.^{31,32} This makes it equally effective for both the n th order and the autocatalytic reactions.

The Ozawa-Flynn-Wall method based on Doyle's approximation³³ is an alternative method for the calculation of activation energy and is expressed as follows:

$$\begin{aligned} \log \beta = 1/2.303 \ln \beta = & -0.4567E_a/RT_p \\ & + (\log AE_a/R - \log f(\alpha) - 2.315) \quad (7) \end{aligned}$$

A plot of $\ln(\beta)$ versus $(1/T_p)$ should give a straight line with a slope of $1.052E_a/R$, as shown in Figure 5. This can provide activation energy for different levels of conversion, but at the present study it was only applied to the maximum rate where the peak appears and it was assumed that when the peak of exotherm is reached the degree of conversion is independent of the heating rate. The calculated activation energy based on Ozawa's method was 29 kcal/mol and given in Table III. The activation energies obtained by Kissinger and Ozawa methods were very close and is higher than that reported for the same resin cured with aliphatic and aromatic diamines.³⁴⁻³⁶

The effect of $\text{Ni}(\text{en})_3\text{Br}_2$ concentration on the shape of DSC thermograms as well as kinetic parameters have also been investigated. DSC thermograms for different levels of hardener were shown in Figures 2 and 6(a-d).

Nonisothermal kinetic analysis can be performed both by single and multiple heating rate methods. However, there are several methods to determine the kinetic parameters of thermosetting materials based

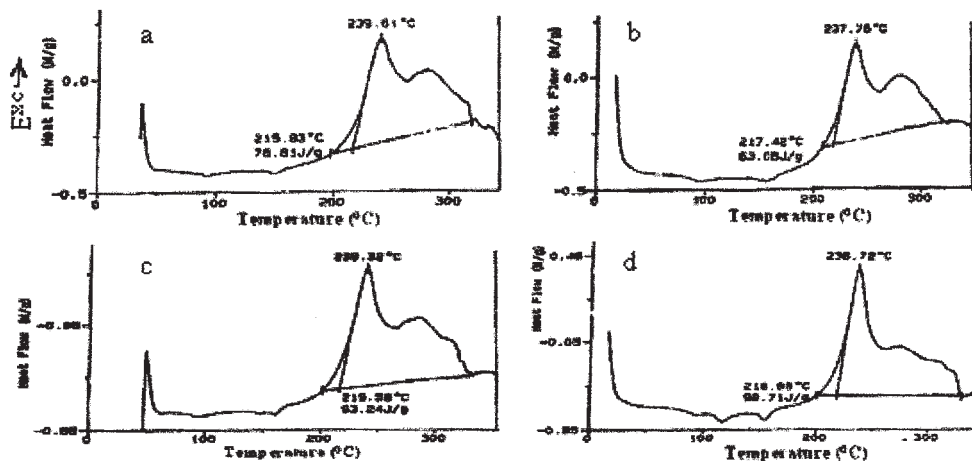


Figure 6 DSC thermograms for DGEBA cured with $\text{Ni(en)}_3\text{Br}_2$ at different concentrations: (a) 15, (b) 18, (c) 20, and (d) 30 phr, heating rate of $20^\circ\text{C}/\text{min}$.

on single heating rate with a single dynamic DSC experiment³⁷ or with two dynamic DSC experiments.³⁸ We have also applied the Expanded Freeman-Carrole method³⁹ for the single dynamic DSC experiment to analyze the curing reaction of DGEBA with 10 phr $\text{Ni(en)}_3\text{Br}_2$ complex. This method, which is also known as a mechanistic model, is expressed in the following form:

$$\text{Ln}(d\alpha/dt) = \text{Ln}[A f(\alpha)] - E_a/RT \quad (8)$$

According to eq. (8), a plot of the $\text{Ln}[(d\alpha/dt)/(1 - \alpha)^n]$ versus $1/T$ should give a straight line with a slope of $-E_a/R$ for a suitable reaction order. Several values of n (0.5, 1, 1.5, and 2) were tried and found that the best linear fitting of experimental results have been obtained by using a reaction order of 2. Figure 7 shows a typical Arrhenius type behavior for DGEBA cured with 18 phr $\text{Ni(en)}_3\text{Br}_2$. The calculated activation en-

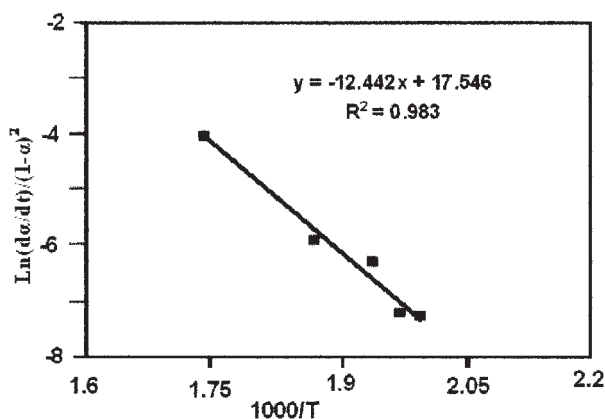


Figure 7 A typical plot using the mechanistic model for determination of E_a , DGEBA cured with 18 phr of $\text{Ni(en)}_3\text{Br}_2$.

ergies using this method are listed in Table IV. It can be seen from this table that the activation energy for the DGEBA/ $\text{Ni(en)}_3\text{Br}_2$ system decreases with increasing rate of heating at a specific concentration and increases with decreasing concentration of hardener at a specific rate of heating. The value of activation energy of the present system reached to the value of activation energy of the cure process of DGEBA with common diamines⁴⁰ when the rate of heating increased from 5 to $20^\circ\text{C}/\text{min}$. These changes in the value of activation energy can be an indication of change in the mechanism of curing reaction of epoxy oligomers with the complex curing agent.

The preexponential factor (A) was calculated using E_a from Table IV and T_p from Table III, according to the following equation:³⁷

$$A = [\beta E_a \exp(E_a/RT_p)] / RT_p^2 [n(1 - \alpha_p)]^{n-1} \approx \beta E_a [\exp(E_a/RT_p)] / RT_p^2 \quad (9)$$

The calculated values of $\text{Ln}A$ were also given in Table IV. The collision frequency increased with decreasing rate of heating and/or increasing concentration of hardener.

The mechanism of curing reaction of DGEBA with several transition metal-chelates was given in the literature.¹⁷ It was established that change in concentration of the complex hardener in the epoxy composition causes significant changes in the polymerization mechanism, structure, and properties of epoxy-metal chelate matrices. The temperature of the beginning of the active reaction between the metal chelate and epoxy oligomer is almost the same as the temperature of decomposition of the complex curing agent. The useful information from this point of view is attainable from TGA thermograms. However, for the $\text{Ni(en)}_3\text{Br}_2$ complex, as shown in Figure 1, the first dissociation of

TABLE IV
Kinetic parameters were calculated using mechanistic method.

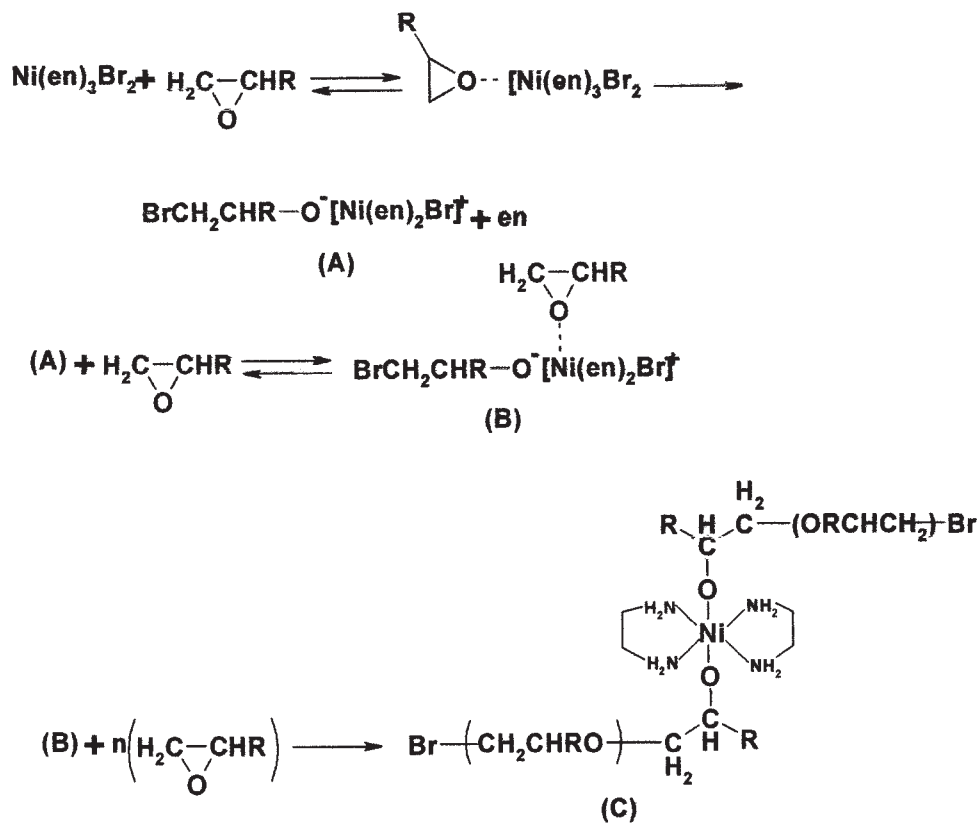
| Complex | Conc. (phr) | β (°C/min) | Ea(kJ/mole) | LnA(min ⁻¹) |
|-------------------------------------|-------------|------------------|-------------|-------------------------|
| Ni(en) ₃ Br ₂ | 10 | 5 | 74.6 | 16.7 |
| Ni(en) ₃ Br ₂ | 10 | 10 | 61.3 | 13.5 |
| Ni(en) ₃ Br ₂ | 10 | 15 | 56.7 | 12.6 |
| Ni(en) ₃ Br ₂ | 10 | 20 | 53.6 | 11.9 |
| Ni(en) ₃ Br ₂ | 15 | 20 | 80.9 | 18.8 |
| Ni(en) ₃ Br ₂ | 18 | 20 | 103.4 | 24.4 |
| Ni(en) ₃ Br ₂ | 20 | 20 | 143.9 | 34.2 |
| Ni(en) ₃ Br ₂ | 30 | 20 | 159.1 | 38.1 |

the complex took place around 200°C and another main loss in mass that was related to the release of two remaining amine molecules was observed on the temperature ranges of 280–350°C. On the other hand, the main exotherm peak for the DGEBA/Ni(en)₃Br₂ system was initiated and ended at about 175 and 330°C, respectively. The expanded DSC thermogram with two shoulders can probably be related to simultaneous occurrence of two mechanisms: catalytic polymerization through complex curing agent and cure process by the amine, which is delivered in the system through dissociation of the complex. With the increase of temperature more values of amine are delivered

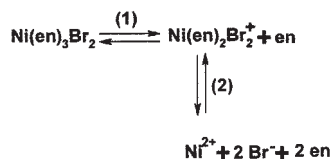
gradually, which caused an expanded DSC exotherm in this new system in comparison with the relatively sharp exotherm in common diamine systems. The catalytic ionic polymerization that is the main polymerization path at low temperatures and low concentrations of curing agent has been proposed by another researcher¹⁷ and can be displayed by Scheme 1.

It is also necessary to take into consideration that the dissociation of chelate is most probably an equilibrium process and depends not only on the temperature but also on the concentration of complex curing agent dissolved in the epoxy oligomers. If we consider an equilibrium behavior for dissociation of curing agent in epoxy media the incorporation of the additional amounts of hardener would shift the chemical equilibrium to the right side as is shown in Scheme 2.

The mechanism of polymerization is affected by the rate of heating, concentration of curing agent, and curing temperature. Evidence for this is seen in Figures 2 and 6(a–d), which show DSC thermograms for different concentrations of hardener at the heating rate of 20°C/min, and also the kinetic parameters in Table IV, which show the effect of the heating rate and concentration of hardener on the activation energy of the initial curing reaction. As shown in these DSC thermograms, the first peak of the exotherm, which appeared at ~ 237°C, became sharper and its area



Scheme 1



Scheme 2

changed with increasing concentration of hardener. From these observations and according to the equilibrium process in Scheme 2, it is suggested that the contribution of the cure process by the free diamine in the initial reaction between epoxy oligomers and the hardener increases with increasing concentration of the complex. The activation energy, as was seen in Table IV, also increased with increasing concentration of the complex, which is also an indication for the contribution of both mechanisms in the initial reaction between epoxy oligomers and the hardener. Supplementary experimental data are required for complete understanding of the curing reaction mechanism.

CONCLUSIONS

Curing of epoxy oligomers DGEBA with complex curing agent based on an aliphatic diamine with Ni(II) was studied using dynamic DSC technique from 25 to 350°C under nitrogen atmosphere. Several instrumental techniques were used to characterize the structure of the complex hardener. TGA showed multistep dissociation of the complex curing agent above 200°C. TG thermogram of pure DGEBA showed that only 2% thermal degradation may occur in the temperature range of 250–300°C. Three different kinetic models based on multistep heating rate methods (Kissinger and Ozawa-Flynn-Wall) as well as a single heating rate method were applied to DSC data to calculate kinetic parameters for the initial polymerization reaction. The activation energies obtained by Kissinger and Ozawa methods were very close (28.8 kcal/mol) and higher than those reported for the epoxy/diamine system. The activation energy obtained by the single heating rate method showed changes with changing heating rate and concentration of curing agent. It was attempted to explain DSC data of the present system based on the proposed mechanism. It was suggested that the expanded DSC thermograms with shoulders in the temperature ranges of 200–330°C can probably be due to simultaneous occurrence of two mechanisms: catalytic polymerization by the complex and curing process by the amine that is released from the complex. Both mechanisms are under influence of

heating rate, curing temperature, and concentration of curing agents.

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