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Thermosetting polymers from epoxy resin and a Nickel catalyst of diethylenetriamine

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Abstract The kinetics and mechanism of cure reaction of DGEBA using a chelate of Ni(II) with diethylenetriamine (dien), $Ni(dien)_2I_2$, as a curing agent was studied by DSC. TG curve of the complex curing agent showed mass loss in two region of temperature: 200–320 and 450–550 °C. Dynamic DSC measurements showed only one exothermic peak with a maximum about 250 °C depending on the heating rate. According to the methods of KAS and Ozawa–Flynn–Wall the values of E_a were 92.5 and 96.2 kJ/mol, respectively. The isoconversional kinetic analysis in whole range of conversion, $\alpha = 0.02$–0.95, showed small changes in the E_a values in the region of $\alpha = 0.04$–0.6 and most likely represent some average values ($E_a = 110$ kJ/mol) between the values of E_a of non-autocatalyzed and autocatalyzed reactions. Using the sole dependence of E_a on α, the time required to reach fully cured materials under isothermal conditions were also predicted and compared with the experimental results.

Keywords Epoxy resin · Curing mechanism · DSC · Nickel catalyst · Kinetics

Introduction

The full characterization of the cure process of an epoxy system involves many factors which are all dependent on the type of epoxy resin, curing agent, and the curing conditions were applied. By selecting distinct kinds of curing agents, a large variety of epoxy based thermosetting materials may be produced with specific mechanical, physical, and chemical properties. It has been found that the incorporation of metal chelates of transition metals with amines as curing agents of the DGEBA, made it possible to prepare metal-containing epoxy polymers possessing improved strength, deformation temperature and heat resistance [1–3]. The structure of this type of curing agents which are so called controllable curing agents is regarded as the combination of three components, namely, metal cation, nitrogen ligand and counterion which are nickel, dien, and iodine in the present work, respectively. Some researches regarding the development of these kinds of curing agents based on inorganic complexes for epoxy resins have been carried out from different aspect of views [4–8]. Among various methods that have been used to the monitoring of thermoset cure, DSC frequently was used to study the cure process of epoxy resins [4–16]. In this work, the kinetic of curing reaction of DGEBA using an inorganic complex of nickel was examined by dynamic DSC technique.

Experimental

Materials

The epoxy resin used was a commercial DGEBA (Epon 828) from Shell Chemicals with EEW = 185. The complex curing agent was a chelate of Ni(II) with diethylenetriamine (dien), $Ni(dien)_2I_2$, that was synthesized according to the procedure [17]. All chemicals were used without any further purification except diethylenetriamine that was distilled twice before use. All solvents used were always degassed with nitrogen. The chemical structures of DGEBA and the complex curing agent are shown in Fig. 1.

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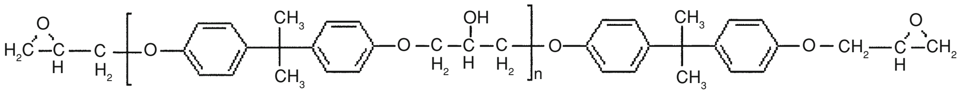
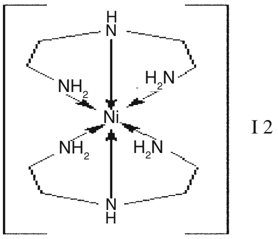
Fig. 1 Chemical structure of the reactants



(DGEBA)



$Ni(dien)_2I_2$

Apparatuses

Differential scanning calorimeter (DSC-SP) from Rheometric Scientific. Thermogravimetric analyses (TGA $1000M^+$) from Rheometric Scientific. FTIR: Nicolet Magna-IR model 550. Elemental analyzer: CHN-600 Leco instrument. The amount of nickel in curing agent was obtained through ICP-Plasma technique using JY 138 Ultrace apparatus from Jobin Yvon.

Preparation of epoxy composite

The curing agent was dried completely in vacuo and powdered prior to preparation of epoxy composition. The amount of curing agent used was 10 phr. Epoxy resin was fully mixed by stirring with $Ni(dien)_2I_2$ to achieve a complete homogenous mixture.

Kinetic methods

DSC heat flow is proportional to the heat released as well as to the cure rate:

$$dH/dt = \Delta H_T \times d\alpha/dt = \Delta H_T K(T) f(\alpha) \quad (1)$$

Where dH/dt is the heat flow, ΔH_T is the total enthalpy of cure reaction, $d\alpha/dt$ is the cure rate, $K(T)$ is the rate constant, and $f(\alpha)$ is the conversion dependence function. The explicit temperature dependence of the rate constant is introduced by an Arrhenius type equation as follows:

$$d\alpha/dt = A\ \exp(-E_a/RT) f(\alpha) \quad (2)$$

where A is the pre-exponential factor and E_a is the activation energy. For dynamic curing, Eq. 2 may be rearranged as follows:

$$d\alpha/dT = A/\beta \exp(-E_a/RT) f(\alpha) \quad (3)$$

where $\beta = dT/dt$ is the heating rate. Epoxy cure are known to include multiple steps that are tended to generate different values of activation energy. It must be noted that curing of DGEBA with metal chelates is also a complex process including different kinetic mechanisms that may take place individually or simultaneously with the progress of curing reaction [2].

According to the method of Kissinger–Akahira–Sunose (KAS) [18], E_a is obtained from the maximum reaction rate where $d(d\alpha/dt)/dt$ is zero under a constant heating rate condition. The basic equation of the method is:

$$Ln(\beta_i/T_{p,i}^2) = Ln(AR/E_a) - E_a/RT_{p,i} \quad (4)$$

where β_i is the heating rate and $T_{p,i}$ is the peak temperature at different heating rates. E_a can be calculated from the slope of the linear plot of $-Ln\left(\beta_i/T_p^2\right)$ against $(1/T_p)$. The value of E_a obtained in Eq. 4 is an overall value representing all complex reactions that occur during curing.

The Ozawa–Flynn–Wall method [19, 20] based on Doyle's approximation [21] is an alternative method for the calculation of E_a and is expressed as follow:

$$Ln(\beta_i) = Const. - 1.052E_a/RT_p. \quad (5)$$

A plot of $Ln\beta$ versus $1/T_p$ should give a straight line with a slope of $1.052E_a/R$.

The above methods (Eqs. 4 and 5) have a limitation because they produce a single value of the E_a for the whole process which is a sign of a single-step process. A more complete determination of the E_a at any selected conversion can be calculated by the most popular isoconversional Equation 6 [22, 23] of Ozawa–Flynn–Wall, where $T_{\alpha,i}$ is the temperature at different conversions at different heating rates:

$$Ln(\beta_i) = Const. - 1.052E_a/RT_{\alpha,i}. \quad (6)$$

The isoconversional methods allow complex processes to be detected by a variation of E_α with α.

The idea of predicting the isothermal behavior of a substance from non-isothermal data usually reduces to inserting non-isothermally estimated A, E_a, and $g(\alpha)$ into Eq. 7 which is the integral form of Eq. 1 [24]:

$$t = g(\alpha)/A \exp(-E_a/RT) \qquad (7)$$

.

There have been several methods proposed [25–27] for the estimation of isothermal behavior for the cure progress of a substance from non-isothermal data. Each of these methods shows one or more pitfalls. We have used the technique which has been developed by Vyazovkin [22, 27] assuming that the reaction model, g(α), and Arrhenius parameters related to a specific conversion remain constant with the change of temperature. Under this assumption they have equated the following Eq. 8 that enables one to calculate, at an arbitrary temperature, the time at which a given conversion will be reached.

$$t_\alpha = [\beta \exp(-E_a/RT_0)]_0^{-1} \mathrm{T}\alpha \exp(E_a/RT) \mathrm{d}T. \qquad (8)$$

Results and discussion

Elemental analysis results of the curing agent listed in Table 1 and are in good agreement with the requested values. The infrared absorption spectral bands of the chelate hardener show that the stretching vibration frequencies $v(NH_2)$ of the complex lie near 3250–3270 cm^{-1} and are decreased by 40 cm^{-1} in comparison with $v(NH_2)$ of the ligand, which testifies to the coordination of the amines with the metal through the amine nitrogen atoms. The aliphatic amine in coordination with a metal results in the formation of a chelate ring. The stability of the chelate depends on the size of the ring, the number of amino groups in a ligand, coordination and steric factors, and the metal cation type [28]. The deactivation of the amino groups of the ligand caused by chelate formation significantly prolongs the pot life of DGEBA. The pot life of this compound at 20 °C was found to be more than a month, whereas the original aliphatic amines are known as hardeners for 'cold' curing that harden bisphenol based epoxy resins at room temperature in less than 24 h [29].

A sample mass of 5 mg of the complex curing agent in TG measurements at a heating of 20 °C/min, Fig. 2 shows decomposition of the complex taking place in two steps over the range of 50–600 °C in isolation form. There is about 33% loss in mass in the first step over the temperature range of 200–320 °C, and about 50% loss in the second step from 450–550 °C. Therefore, the major mass loss of the complex occurs at temperature around 450 °C. It is suggested that the complex curing agent dissociates to form active cation species during the first step mass loss. With further increase in temperature, the complex cation is dissociated completely and is responsible for the second major mass loss. It was also suggested [2, 3] that the dissociation equilibrium of the complex curing agent dissolved in epoxy resin at high temperatures may be as shown in Scheme 1.

Table 1 Elemental analysis data for $Ni(dien)_2I_2$

Complex	%C	%H	%Ni
$Ni(dien)_2I_2$	18.43 (*18.52*)[a]	5.06 (*5.05*)	11.28 (*11.32*)

[a] Calculated values in parenthesis

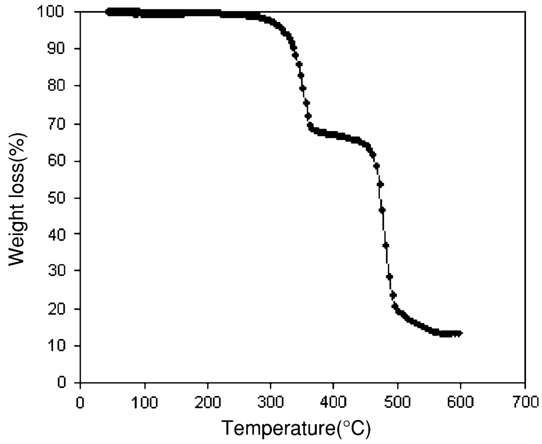
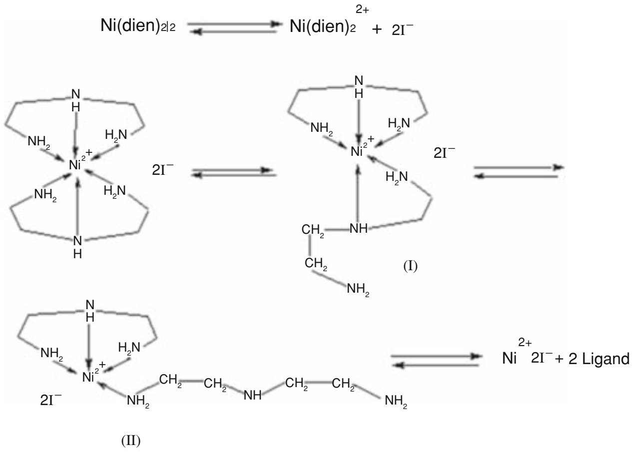


Fig. 2 TG curve of $Ni(dien)_2I_2$ at 20 °C/min in air

DSC curves of curing reaction of DGEBA with the complex were shown in Fig. 3, and the data were listed in Table 2. DSC instrument was calibrated by high purity Indium prior to any DSC test. DSC experiments were carried out by heating 3 mg of the mixture in a temperature range from 30 °C to 320 °C in air at various heating rates of 5, 10, 15, and 20 °C/min.

The maximum exothermic temperature raised 30 °C when the heating rate increased from 5 °C/min to 20 °C/min. The curing temperature is within the temperature range of the



Scheme 1

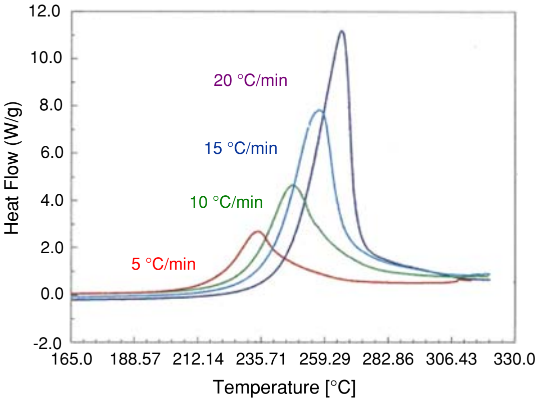


Fig. 3 DSC curves of DGEBA cured with Ni(dien)$_2$I$_2$ at different heating rates

Table 2 Dynamic DSC data at various heating rates for DGEBA/Ni(dien)$_2$I$_2$ system

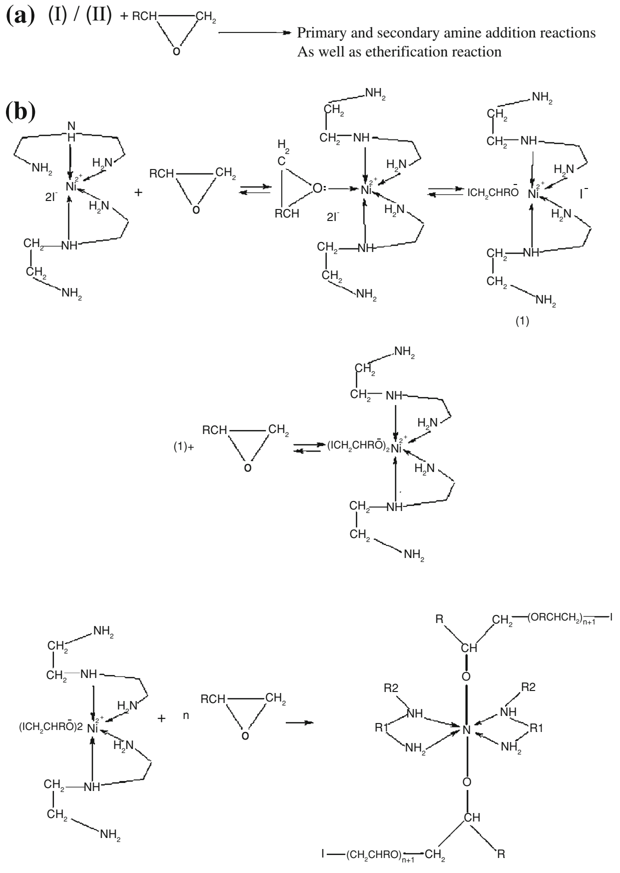
Curing agent	Heating rate/°C/min	Cure onset/°C	Peak Max/°C	Δ*H* (J/g)/°C
Ni(dien)$_2$I$_2$	5	201	234.64	744.8
Ni(dien)$_2$I$_2$	10	212	246.93	677.7
Ni(dien)$_2$I$_2$	15	219	257.68	673.3
Ni(dien)$_2$I$_2$	20	227	264.76	638.6

first step decomposition of the complex shown in TG curve in Fig. 2. Aliphatic amines such as diethylenetriamine are usually used as room temperature curing agent of epoxy resins. Deactivation of the amine groups due to formation of complex with the nickel caused no curing of epoxy resin occurs at temperature below 200 °C. Ring opening polymerization of epoxide groups occurs when the free amine groups are available. It can be seen from DSC data in Table 2 that the cure onset temperatures lay above 200 °C. This temperature corresponds to the beginning of complex dissociation and the formation of active particles, free dien ligands, able to react with the epoxy oligomers. As the reaction of complex dissociation is endothermic, the heat of reaction of this hardener with DGEBA must be less than that of the pure amine. The two diens ligand lose their linkage with nickel and are released almost simultaneously and, therefore there are no different interactions between the loose amine groups and the epoxide groups resulting in a single exotherm peak to be observed in DSC experiment. Our previous observations [30] on the curing of epoxy resin with a nickel chelate of ethylenediamine showed two exothermic peaks, due to different interactions between the epoxide groups and the active particles of the complex hardener. The same results have been reported in the literature on hardening of epoxy resin with metal-ethylenediamine chelates [2].

It is clear that complex curing agent is not capable of having an interaction with the epoxy groups due to deactivation of the amine groups, steric hindrance, and coordination number restriction. This means that other active species must be created in the reaction media to start the curing reaction. With raising the temperature, the active species such as (I) and (II) are produced owing to dissociation of the complex, that is more Ni–N, donor–acceptor, linkages are broken and more active amine sites will be available as shown in Scheme 1.

It is interesting to note that both species (I) and (II) are able to commence effective interactions with the epoxy groups by the amine addition reactions, Scheme 2a and/or catalytic polymerization reaction (due to reduction of the coordination number of nickel to 4), Scheme 2b.

It seems that there is a competition between catalytic polymerization reaction and amine addition reactions at the initial step of the curing reaction. However, the complex cation (II) is dissociated completely at elevated temperatures, as suggested in Scheme 1, and the polymerization is preceded by the amine addition reactions. It can be seen in Table 2 that the curing reaction of DGEBA with the complex curing agent is accompanied with changes in the enthalpy of reaction which is similar to the results reported by other researchers [31] for different curing systems.



Where R_1= CH_2-CH_2 and R_2= CH_2-CH_2-NH_2

Scheme 2

The values of E_a of curing were obtained by using dynamic DSC data and the methods discussed in previous section. According to the method of KAS, Eq. 4, the slope of the linear plot of $-Ln\left(\beta/T_p^2\right)$ versus $1/T_p$ produced a value of $E_a = 92.5$ kJ/mol. By using Ozawa method, Eq. 5, plot of $Ln(\beta)$ versus $(1/T_p)$ gave slope of $1.052E_a/R$ and the value of E_a = 96.2 kJ/mol. The values of conversion which is based on the ratio of heat released at a special temperature (H_T) to the total heat, $\alpha = H_T/\Delta H_{total}$, were obtained from DSC curves in Fig. 3 for different heating rates. Figure 4 shows the conversion versus temperature plots at various heating rates for the studied epoxy system.

The reaction rate, $d\alpha/dt = dH/dt/\Delta H_{total}$, versus conversion plots are also shown in Fig. 5 displaying a maximum value of reaction rate at the conversion range of $\alpha = 0.3$–0.5, which is a character of autocatalytic reaction.

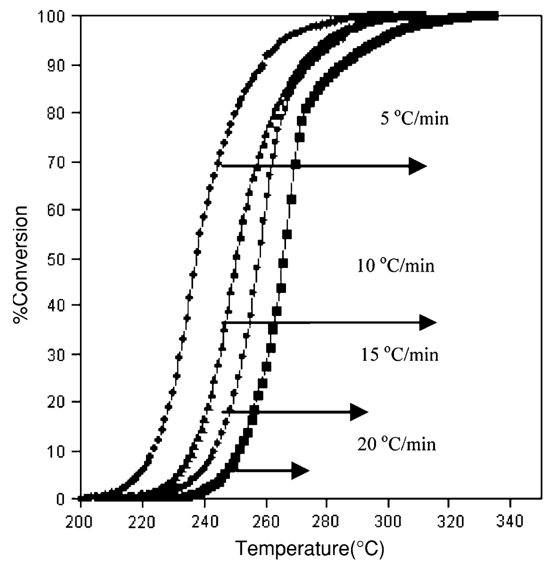


Fig. 4 Degree of conversion versus temperature plots at various heating rates

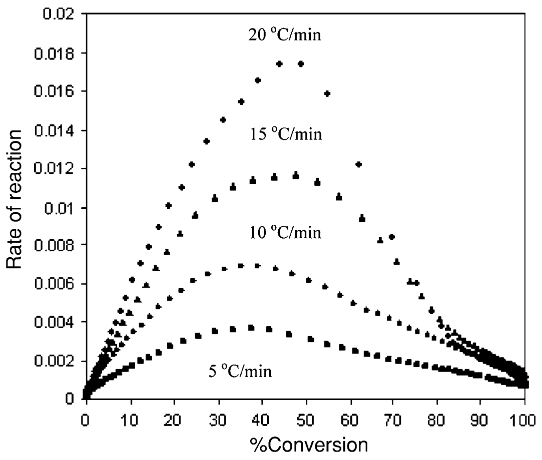


Fig. 5 Reaction rate versus conversion plots at different heating rates

In order to understand E_a-conversion dependence, we applied the isoconversional method to dynamic data at different conversions and E_a values were obtained by using Eq. 6.

The calculated values of E_a from the slope of the linear plots of $Ln_{\beta i}$ versus $1/T_\alpha$ are shown at various conversions in Fig. 6. It can be seen that the curve corresponding up to $\alpha = 0.6$ exhibits a relatively straightforward line, indicating that there are not changes on the main process taking place in this range of conversion. This range may be considered as the propagation step of polymerization reaction. The average value of the E_a for this interval is 110 kJ/mole.

On the other hand, applying the Ozawa method [18] to the initial step of the studied curing reaction leads to a value of $E_a = 107.8$ kJ/mole at $\alpha = 0.02$. The initial values of E_a in the conversion region of up to $\alpha = 0.6$ most likely represent some average values between the activation energies of non-autocatalyzed and autocatalyzed reactions. We have observed an increase in the value of E_a in the conversion degree higher than $\alpha > 0.6$. This can be described by the change in the reaction mechanism from kinetic control to diffusion control regime. With completing the cure process, the activation energies decreased in the conversion range of $\alpha > 0.8$.

The dynamically cured sample in the DSC (up to 320 °C) was allowed to cool to room temperature at a heating rate of 20 °C/min and rescanned at 10 °C/min for measuring any residual heat of reaction. The sample did not show any exothermic peak but there was a stepwise transition at about 87 °C that presumably is the glass transition temperature (T_g).

By knowing the dependence of E_a on conversion and the experimental values of T_α, we have calculated the time required to reach a practically complete curing (typically 95% of conversion) at different selected temperatures of

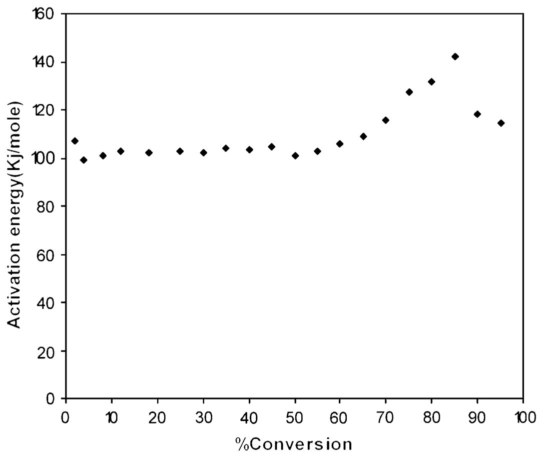


Fig. 6 Energy of activation as a function of conversion for the cure reaction of DGEBA with $Ni(dien)_2I_2$ complex curing agent

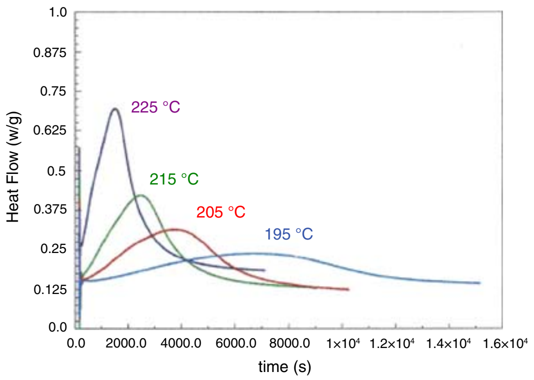


Fig. 7 DSC curves are recorded for DGEBA/Ni(dien)$_2$I$_2$ system at different isothermal temperatures

195, 205, 215, and 225 °C by using Eq. 8. We have also carried out isothermal DSC experiments on DGEBA/Ni complex samples at the above temperatures to measure the actual time needed for the samples to reach a complete curing. The isothermal DSC curves were shown in Fig. 7. The predicted times of curing (using Eq. 8) were compared with the experimental values in Table 3. As can be seen, there is a good concordance between theoretical and experimental values.

A cured sample of epoxy with 10 phr of Ni(dien)$_2$I$_2$ at 195 °C for 4.5 h was tested for thermal stability by using TG. As can be seen from the Fig. 8, a reasonable thermally stable epoxy similar to that cured with an aliphatic diamine can be achieved by using nickel chelate as a hardener. Thermal stability of the cured sample was determined by char yield measurement at 700 °C and has been found to be 19.6% in air.

Table 3 Predicted and measured times (h) to reach practically complete cure

System		195 °C	205 °C	215 °C	225 °C
DGEBA/Ni(dien)$_2$I$_2$	Predicted	5.80	3.34	1.94	1.17
	Measured	4.02	2.71	1.95	1.02

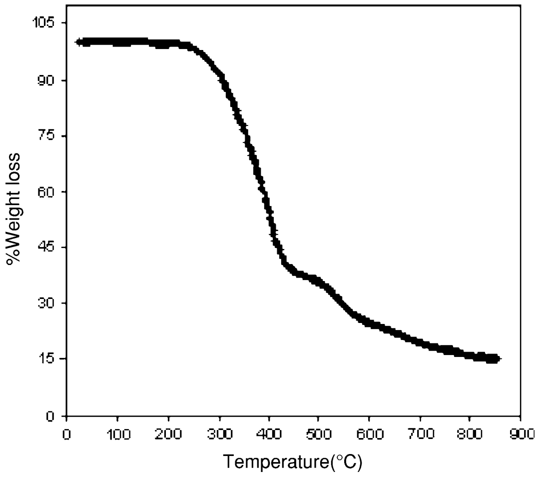


Fig. 8 TG curve of isothermally cured DGEBA with Ni(dien)$_2$I$_2$ sample was recorded at 15 °C/min in air

Conclusions

The deactivation of the aliphatic amino groups of the ligand caused by chelate formation significantly prolongs the pot life of the epoxy compound based on DGEBA. The pot life of this compound at 20 °C was found to be more than a month.

TG tests for the isolated form of the complex showed two steps mass loss: 33% in the region of 200–320 °C and 50% in the region of 450–550 °C. These were related to the partial and complete dissociation of the ligands from the metal, respectively.

DSC measurements of the cure reaction of DGEBA with the complex showed only one exotherm peak with a maximum >200 °C depending on the heating rate. It was suggested that the main mechanism of cure reaction is primary amine addition to the epoxide groups, although catalytic polymerization reaction of epoxide groups with the complex cation can also occur at the lower temperatures. According to the methods of KAS and Ozawa–Flynn–Wall, the values of E_a were 92.5 and 96.2 kJ/mol, respectively. The experimental dependence of activation energy on conversion by isoconversional method showed small changes in the E_a values in the conversion region of $\alpha = 0.04$–0.6 and most likely represent some average values ($E_a = 110$ kJ/mol) between the activation energies of nonautocatalyzed and autocatalyzed reactions. Vyazovkin model-free-kinetics algorithm was applied to predict the practically complete isothermal cure times at different selected temperatures. The time values obtained by theoretical method were in good agreement with the values obtained by isothermal DSC measurements.

References

1. Kurnoskin AV. Diane oligomers: heat resistance increase by metal ions. Polym Plast Technol Eng. 1991;30:737–50.
2. Kurnoskin AV. Reaction mechanisms of the metal chelates with epoxy oligomers and the structures of the epoxy – chelate metal-containing matrixes. J Appl Polym Sci. 1992;46:1509–30.
3. Kurnoskin AV. Metalliferous epoxy chelate polymers: Part 1. Synthesis and properties. Polymer. 1993;34(5):1060–7.
4. Hamerton I, Hay JN, Howlin BJ, Jepson P, Mortimer S. The development of controllable complex curing agents for epoxy resins. I. Preparation, characterization, and storage behavior of transition metal-diamine complexes. J Appl Polym Sci. 2001;80: 1489–503.

5. Hamerton I, Hay JN, Herman H, Howlin BJ, Jepson P, Gillies DG. The development of controllable complex curing agents for epoxy resins. II. Examining the dissociation and thermal behavior of transition metal-diamine complex-epoxy blends. J Appl Polym Sci. 2002;84:2411–24.
6. Ghaemy M, Rostami AA, Omrani A. Isothermal cure kinetics and thermodynamics of an epoxy-nickel-diamine system. Polym Int. 2006;55:279–84.
7. Omrani A, Rostami AA, Ghaemy M. Kinetics and thermal properties of epoxy resin cured with Ni(II)-tris-(O-pheneylendiamine) bromide. J Appl Polym Sci. 2006;101:1257–65.
8. Omrani A, Ghaemy M, Rostami AA. Curing behavior of epoxy resin using controllable curing agents based on nickel complexes. Macromol Mater Eng. 2006;291:181–93.
9. Toda A, Arita T, Hikosaka M. Kinetic response of an epoxy thermosetting system observed by TMDSC. J Therm Anal Calorim. 2000;60:821–7.
10. Prolongo SG, Prolongo MG. Epoxy/poly(4-vinylphenol) blends crosslinked by imidazole initiation. J Therm Anal Calorim. 2007;87:259–68.
11. Liu G, Zhang L, Qu X, Li Y, Gao J, Yang L. A new curing kinetic model and its application to BPSER/DDM epoxy system. J Therm Anal Calorim. 2001;65:837–46.
12. Vinnki RM, Roznyatovsky VA. Kinetic method by using calorimetry to mechanism of epoxy-amine cure reaction. J Therm Anal Calorim. 2004;76:285–93.
13. Macan J, Brnardi I, Ivankovi M, Mencer HJ. DSC study of cure kinetics of DGEBA-based epoxy resin with poly(oxypropylene) diamine. J Therm Anal Calorim. 2005;81:369–73.
14. Sheng X, Akinc M, Kessler MR. Cure kinetics of thermosetting bisphenol E cyanate ester. J Therm Anal Calorim. 2008;93(1): 77–85.
15. Nigam V, Setua DK, Mathur GN. Characterization of rubber epoxy blends by thermal analysis. J Therm Anal Calorim. 2001;64:521–7.
16. dell'Erba IE, Williams RJJ. Epoxy networks modified by multifunctional polyhedral oligomeric silsesquioxanes (POSS) containing amine groups. J Therm Anal Calorim. 2008;93:95–100.
17. Ruff JK, Wold A. Inorganic synthesis, vol 14. New York: McGraw-Hill, Inc.; 1973. pp. 57–67.
18. Kissinger HE. Reaction kinetics in differential thermal analysis. Anal Chem. 1957;29:1702–6.
19. Ozawa T. Kinetic analysis of derivative curves in thermal analysis. J Therm Anal. 1970;2:301–24.
20. Omrani A, Simon LC, Rostami AA, Ghaemy M. Cure kinetics, dynamic mechanical and morphological properties of epoxy resin-Im_6NiBr_2 system. Eur Polym J. 2008;44:769–79.
21. Doyle CD. Kinetic analysis of thermogravimetric data. J Appl Polym Sci. 1961;5:285–92.
22. Vyozovkin S, Sbirrazzuoli N. Mechanism and kinetics of epoxy—amine cure studied by differential scanning calorimetry. Macromolecules. 1996;29:1867–73.
23. Vyozovkin S, Sbirrazzuoli N. Isoconversional kinetic analysis of thermally stimulated processes in polymers. Macromol Rapid Commun. 2006;27:1515–32.
24. ANSI/ASTM E698–79. Standard test method for Arrhenius kinetic constants for thermally unstable materials. Philadelphia: ASTM; 1979.
25. Fava RA. Differential scanning calorimetry of epoxy resins. Polymer. 1968;9:137–51.
26. Barton JM. Polymer characterization by thermal methods of analysis. New York: Marcel Dekker; 1976. p. 25.
27. Vyazovkin S, Lesnikovich AL. Practical application of isoconversional methods. Thermochim Acta. 1992;203:177–85.
28. Irving H, Williams RJ. The stability of transition-metal complexes. J Chem Soc. 1953; 3192–210.
29. Lee H, Neville K. Handbook of epoxy resins. New York: McGraw Hill; 1967. p. 386.
30. Ghaemy M, Omrani A, Rostami AA. Study of reaction kinetics of epoxy and a nickel(II) complex using dynamic DSC technique. J Appl Polym Sci. 2005;97:265–71.
31. Ooi SK, Cook WD, Simon GP, Such CH. DSC studies of the curing mechanisms and kinetics of DGEBA using imidazole curing agents. Polymer. 2000;41:3639–49.