European Polymer Journal 46 (2010) 1158–1162

Contents lists available at ScienceDirect

European Polymer Journal

journal homepage: www.elsevier.com/locate/europolj

Short communication

Investigation of curing kinetics of various cycloaliphatic epoxy resins using dynamic thermal analysis

Myong Jae Yoo [a,b], Sang Hyun Kim [a], Seong Dae Park [a], Woo Sung Lee [a], Jong-Woo Sun [b], Jae-Hong Choi [b], Sahn Nahm [b,*]

[a] *Electronic Materials & Device Research Center, Korea Electronics Technology Institute, Seongnam 463-816, Republic of Korea*
[b] *Department of Materials Science and Engineering, Korea University, Seoul 136-701, Republic of Korea*

ARTICLE INFO

Article history:
Received 17 August 2009
Received in revised form 29 December 2009
Accepted 1 February 2010
Available online 11 February 2010

Keywords:
Cure kinetics
Cycloaliphatic epoxy resin
Differential scanning calorimetry
Activation energy

ABSTRACT

Curing reactions of three cycloaliphatic epoxy resins with methyltetrahydrophthalic anhydride (MTHPA) was investigated by differential scanning calorimetry at different heating rates. Activation energy was calculated based on Kissinger method and varied in the range of 67–72 kJ/mol depending on sample. The curing kinetic behavior was well described by Sestak–Berggren (SB) model and the order of the curing reaction is observed to be from 0.02 to 2.11 according to sample.

1. Introduction

Epoxy resins are one of the most widely used thermosetting polymers in aerospace, automobile industries and electronic applications as adhesives, coatings and matrices of high performance composite materials. These advanced applications demand outstanding material properties which are dependent on the chemical structure of the epoxy resin as well as the curing agent and ultimately on the network achieved after curing process [1–3]. The processing of thermosetting epoxy resins with curing agent involves the exposure of the materials to varying levels of curing profiles which are dependent on the curing kinetics. Therefore knowledge of the curing kinetics is of great importance to achieve optimum material properties.

Cure kinetics of epoxy resins can be studied by various techniques, such as differential scanning calorimetry (DSC), infrared spectroscopy, dielectric spectroscopy [4] and dielectric thermal analysis [5]. Of these techniques DSC is the least complicated and can measure the heat of polymerization directly and requires only small quantities of samples (normally below 20 mg) and can obtain kinetic data in a relatively short period of time. The use of DSC to investigate the cure kinetics of thermosetting polymers was previously reported [6–10]. Isothermal DSC analysis have been utilized but pre heating of samples to required temperatures involve considerable reaction which might lead to erroneous interpretation of the kinetics of reaction therefore in this study dynamic DSC analysis was utilized [11,12].

Cycloaliphatic epoxy resins have low viscosity properties comparable to bi-functional type epoxy resins which enable incorporation of large amounts of fillers while achieving high glass transition temperature properties with appropriate curing agents. This enables fabrication of various composite materials for high temperature applications [13,14]. As such the use of cycloaliphatic epoxy resins has a long history in the electronic industry for applications such as electric insulation and encapsulation but not much information is available on their cure kinetics [15,16]. In the present work the dynamic DSC technique

---

* Corresponding author. Tel.: +82 2 3290 3715; fax: +82 2 928 3584.
E-mail address: snahm@korea.ac.kr (S. Nahm).

0014-3057/$ - see front matter © 2010 Elsevier Ltd. All rights reserved.
doi:10.1016/j.eurpolymj.2010.02.001

is applied to study the curing kinetics of various cycloaliphatic epoxy resins with methyltetrahydrophthalic anhydride (MTHPA) as curing agent and their curing kinetic properties are investigated.

2. Kinetic models

Most curing kinetics studied by dynamic DSC analysis can be described by Eq. (1) [17].

$$d\alpha/dt = Ae^{-E_a/RT}f(\alpha) \tag{1}$$

where α is the fraction of conversion, t is the curing time, $d\alpha/dt$ is the rate of conversion, A is the preexponential factor, E_a is the activation energy, R is the gas constant, T is the absolute temperature and $f(\alpha)$ the function representing the kinetic model. The most frequently cited basic kinetic models are summarized in Table 1. As can be seen in Table 1 there are various kinetic models describing the curing kinetics. In order to determine the most suitable kinetic model knowledge of the activation energy (E_a) is prerequisite [22–24]. The E_a can be obtained by Kissinger [24] method shown in Eq. (2).

$$[d(\ln \Phi/T_p^2)]/d(1/T_p) = -E_a/R \tag{2}$$

where Φ is the heating rate (°C/min) and T_p is the maximum point from the dynamic DSC analysis curve. From the slope of the plot of $\ln \Phi/T_p^2$ versus $1/T_p$, E_a can be estimated.

Once the activation energy has been determined it is possible to find the kinetic model which best describes the measured set of dynamic DSC analysis. For this purpose a $y(\alpha)$ function was employed as defined by Malek [25].

$$y(\alpha) = Af(\alpha) = (d\alpha/dt)e^{E_a/RT} \tag{3}$$

$$d\alpha/dt = H/\Delta H_T \tag{4}$$

where H is heat flow (mW/mg) which is the measured data from dynamic DSC analysis curve, ΔH_T is the total heat of reaction of curing which is the total area of the dynamic DSC analysis curve. As shown in Eq. (3) the function $y(\alpha)$ is proportional to $f(\alpha)$ therefore by determining the shape of the function $y(\alpha)$ it is possible to identify the shape of the $f(\alpha)$ which leads to selection of the most suitable kinetic model.

In order to determine the shape of the function $y(\alpha)$ with respect to α calculation of α is needed. By integrating dynamic DSC analysis curve peaks with respect to time α can be calculated. Basis for calculation is that the measured heat flow is proportional to the extent of conversion of the epoxide group in the epoxy resin or the reactive group in the curing agent. Values of $y(\alpha)$ value can be calculated by determining the $d\alpha/dt$ value from measured data as shown in Eq. (4) and multiplying by $e^{E_a/RT}$ where predetermined E_a value is substituted. After determination of the shape of $f(\alpha)$ the most suitable kinetic model can be selected and the kinetic parameters such as n, m and A are calculated by the methods described in Ref. [25].

3. Experimental

3.1. Materials

Three types of cycloaliphatic epoxy resins were used in this study. EHPE3150 (Daicel, molecular weight of 2234), CEL2021P (Daicel, molecular weight of 252.3) and YDH184 (Epotec, epoxide equivalent weight of 165–177). The curing agent used was methyltetrahydrophthalic anhydride (MTHPA), (Sigma–Aldrich) and catalyst was *N*,*N*-dimethyl benzylamine (BDMA), (Sigma–Aldrich). The materials were used as received from the manufacturers. Table 2 shows the chemical structures of the cycloaliphatic epoxy resins used in this study.

3.2. Sample preparation

Three samples were prepared. Sample A is a mixture of EHPE3150, MTHPA and BDMA. Sample B is a mixture of CEL2021P, MTHPA and BDMA. Sample C is a mixture of YDH184, MTHPA and BDMA. The mass ratio of cycloaliphatic epoxy resin to curing agent was set at 100:75 and the amount of catalyst was set at 1wt% of curing agent. Cycloaliphatic epoxy resin and curing agent were well mixed until a homogeneous mixture was obtained. The catalyst was added to the homogenous mixture and stirred for additional 20 min to obtain uniform mixture.

3.3. Measurements

Dynamic DSC analysis was done by DSC 200F3 model (Netzsch, Germany) which was calibrated with high purity indium and zinc standards. Samples of 7.5–10.5 mg were added to aluminum pans and analyzed dynamical with heating rates varying from 5 °C/min to 40 °C/min, respectively in a nitrogen atmosphere. Measurements were always carried out with an empty cell as reference from 25 °C up to 300 °C.

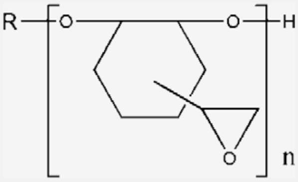
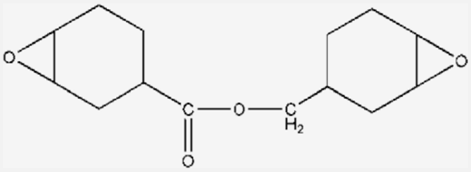
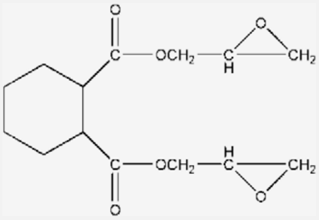
4. Results and discussion

Fig. 1 shows a dynamic DSC analysis curve measured for sample A with four heating rates (Φ) 5, 10, 20, 40 °C/min in

Table 1
The basic kinetic models.

Models	Symbol	$f(\alpha)$	Shape of function
Johnson–Mehl-Avrami [18]	JMA(n)	$n(1-\alpha)[-\ln(1-\alpha)]1^{-1/n}$	When $\alpha_{max} = 0$, concave for $n < 1$, linear for $n = 1$, when $0 < \alpha_{max} < \alpha_p$ maximum for $n > 1$
Jander equation [19]	D3	$3/2(1-\alpha)^{2/3}/[1-(1-\alpha)^{2/3}]$	When $\alpha_{max} = 0$, concave
Reaction order [20]	RO(n)	$(1-\alpha)^n$	When $\alpha_{max} = 0$, convex for $n < 1$, concave for $n > 1$
Sestak-Berggren [21]	SB(m,n)	$\alpha^m(1-\alpha)^n$	When $0 < \alpha_{max} < \alpha_p$, maximum

Table 2
Cycloaliphatic epoxy resin chemical structures.

Product name	Chemical structure	Supplier
EHPE3150		Daicel
CEL2021P		Daicel
YDH-184		Epotec

the temperature range 50–300 °C. For samples B and C similar curves were obtained. The main characteristics of the dynamic DSC analysis taken into consideration in obtaining information about the curing kinetics were as follows, the initial curing temperature T_i, peak temperature T_p, finishing temperature T_f, the area under the curve (total and partial) and the cure time.

Using Eq. (2) the activation energies for the three samples were calculated. Obtained E_a values were 67, 70 and 72 kJ/mol for sample A, sample B and sample C accordingly. This difference in activation energy value is attributed to the difference of the epoxide ring in the chemical structure. From the calculated values of activation energy it was determined that the reactivity of the cycloaliphatic epoxy resin EHPE3150 with MTHPA as curing agent was higher than the other two types of cycloaliphatic epoxy resins.

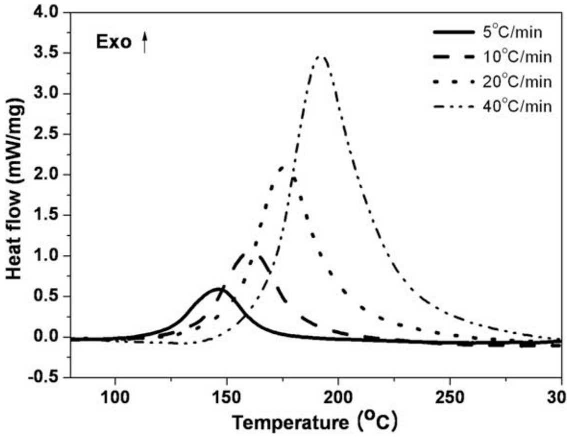


Fig. 1. Dynamic DSC curve for sample A at different heating rates of 5, 10, 20, and 40 °C/min.

Fig. 2 shows the shape of function $y(\alpha)$ with respect to α for the three samples. From the shape of the $y(\alpha)$ it was determined that a maximum α_{max} exists. The α_{max} is the maximum point in degree of conversion. As can be seen from Table 1, two kinetic models JMA($n > 1$) and SB(m,n) fit the given condition. Furthermore as described by Malek [22] for the case of JMA($n > 1$) kinetic model the condition of $\alpha_p = 0.632$ must be met where α_p is the calculated value of the maximum point from the dynamic DSC analysis curve. In our experiment this condition was not satisfied. Therefore it was determined that the autocatalytic model SB(m,n) is the most suitable to describe the curing kinetic behavior. For SB(m,n) model the curing kinetic parameters m, n are expressed as in Eq. (5)

$$\alpha_{max} = m/(m+n) \tag{5}$$

where α_{max} is the maximum point of α from Fig 2. Rewriting Eq. (1) using Eq. (5) and SB(m,n) kinetic model function gives the following equation.

$$\ln[(d\alpha/dt)e^{E_a/RT}] = \ln A + n\ln[\alpha^{(\alpha_{max}/(1-\alpha_{max})}(1-\alpha)] \tag{6}$$

Using Eq. (6), kinetic parameter n can be estimated from the slope of $\ln[(d\alpha/dt)e^{E_a/RT}]$ versus $\ln[\alpha^{(\alpha_{max}/(1-\alpha_{max})}(1-\alpha)]$. From the estimated n value kinetic parameter m value can be calculated from Eq. (5). The kinetic parameters m, n and $\ln A$ using the SB(m,n) model for each sample are shown in Table 3. According to sample different kinetic behavior was observed. For sample A with increasing heating rate (Φ), a maximum value shows for m parameter whereas n parameter remains nearly unchanged. The other two samples saw increased value of m parameter with

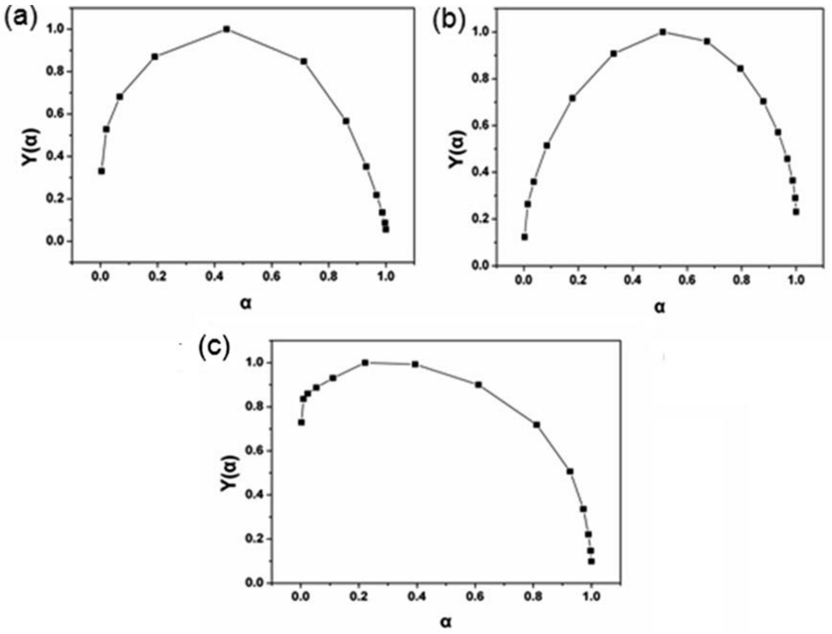


Fig. 2. The $y(\alpha)$ functions for the three samples at heating rate of 10 °C/min with conversion degree α. (a) Sample A, (b) Sample B, (c) Sample C.

increasing heating rate (Φ). The different change trend of kinetic parameter is probably due to the reactivity difference of the cycloaliphatic epoxy resin with curing agent and also to the decrease of the concentration and the mobility of the unreacted chemical groups of the cured resin which in turn affect the curing kinetics.

The validity of the chosen kinetic model SB(m,n) was evaluated by plotting in the curves of heat flow versus temperature using the calculated data in Table 3 to Eq. (1) and compared with the curves obtained by measured data. A compared result for sample A is shown in Fig. 3. A good fit was obtained up to the peak temperatures with various heating rates. Re-plotting the computed curves with lower values of activation energy than the calculated values results in more optimal fit with measured thermal data especially for the temperatures over the peak temperature. This agrees with the fact that the activation energy has a dependence on conversion as mentioned by various authors [26,27]. The cause of the decrease of the activation energy can be attributed to complex chemical reaction at the near end of conversion by mass transfer processes such as viscous relaxation and vitrification. That is the monomer molecules become immobile in their positions in the glassy state that results in the virtual cessation of polymerization which would lead to the decrease of the activation energy with increasing temperature.

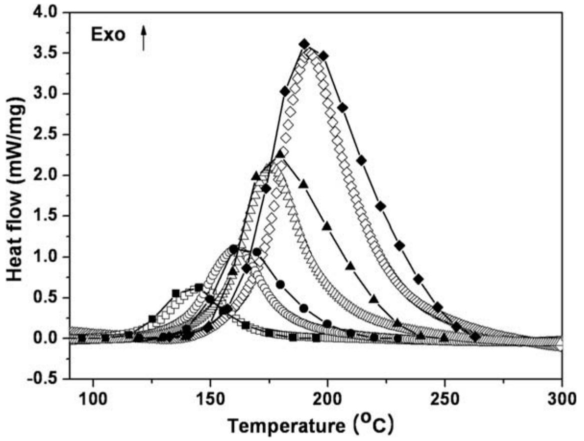


Fig. 3. Comparison of experimental values (empty symbols) and calculated values (full symbols with lines) for sample A at various heating rates (Φ). (□) 5 °C/min, (○) 10 °C/min, (△) 20 °C/min, (◇) 40 °C/min.

Table 3
Calculated kinetic parameters for each sample.

Heating rate (°C/min)	Sample A			Sample B			Sample C		
	m	n	ln A	m	n	ln A	m	n	ln A
5	1.35	1.41	25.54	1.01	0.97	22.47	0.02	1.18	24.67
10	1.14	1.45	24.2	1.08	1.04	21.19	0.33	1.04	24.34
20	1.63	1.46	23.26	1.32	1.08	21.31	1.01	1.46	24.62
40	0.73	1.37	22.87	2.11	0.95	20.68	1.03	1.43	24.49

5. Conclusion

The dynamic thermal analysis has been applied to study the curing kinetics of cycloaliphatic epoxy resin with MTHPA curing agent. Kinetic parameters determined for the three types of sample showed great influence of the heating rate on the curing kinetics. With the calculated E_a value all the kinetic behavior of the three samples were well described with SB(m,n) kinetic model. Slight deviations in the temperature region above the peak temperature were attributed to reduced E_a due to complex mass transfer process. Fitting of calculated kinetic parameters (E_a, m, n and A) with measured values obtained good agreement for all the samples.

Acknowledgements

This research was supported by a grant from the Fundamental R&D Program for Core Technology of Materials funded by the Ministry of Knowledge and Economy, Republic of Korea [M2007010011, 3-D Integrated Ceramic Technology by Nano-dispersion and Non-sintering Process, sub title: Development of Nano-materials for Multilayer Interconnection and High Integration Processing Technology].

References

[1] Cizmecioglu M, Gupta A, Fedors RF. Influence of cure conditions on glass transition temperature and density of an epoxy resin. J Appl Polym Sci 1986;32:6177–90.
[2] Meyer F, Sanz G, Eceiza A, Mondragon I. The effect of stoichiometry and thermal history during cure on structure and properties of epoxy networks. Polymer 1995;36(7):1407–14.
[3] Naito Christine, Todd Michael. The effects of curing parameters on the properties development of an epoxy encapsulant material. Microelectron Reliab 2002;42:119–25.
[4] Prime RB. In: Turi EA, editor. Thermal characterization of polymeric materials. New York: Academic press; 1981.
[5] Shigue CY, Rafaela GS, Baldan CA, Ruppert-Filho E. Monitoring the epoxy curing by the dielectric thermal analysis method. IEEE Trans Appl Superconduct 2004;4(2):1173–6.
[6] Sourour S, Kamal MR. Differential scanning calorimetry of epoxy cure: isothermal cure kinetics. Thermochim Acta 1976;14:41–59.
[7] Montserrat S, Flaque C, Andreu Mcalafell G, Malek J. Influence of the accelerator concentration on the curing reaction of an epoxy-anhydride system. Thermochim Acta 1995;269/270:213–29.
[8] Han Seung, Kim Whan Gun, Yoon Ho gyu, Moon Tak jin. Curing reaction of biphenyl epoxy resin with different phenolic functional hardeners. J Polym Sci A 1998;36:773–83.
[9] Rosu D, Mustata F, Cascaval CN. Investigation of the curing reactions of some multifunctional epoxy resins using differential scanning calorimetry. Thermochim Acta 2001;370:105–10.
[10] Thomas R, Durix S, Sinturel C, Omonov T, Goossens S, Groeninckx G, et al. Cure kinetics, morphology and miscibility of modified DGEBA-based epoxy resin – effects of a liquid rubber inclusion. Polymer 2007;48:1695–710.
[11] Fernandez Xavier, Ramis Xavier, Salla Josep M. Cationic copolymerization of cycloaliphatic epoxy resin with an spirobislactone with lanthanum triflate as initiator kinetics of the curing process. Thermochim Acta 2005;438:144–54.
[12] Montserrat S, Flaque C, Pages P, Malek J. Effect of the crosslinking degree on curing kinetics of an epoxy-anhydride system. J Appl Polym Sci 1995;56(11):1413–21.
[13] Wang Jinlin, Chen Tim. The effect of flow properties on filler settling of underfill in the flip chip package. Elect Comp Tech Conf 2004:761–6.
[14] Wong CP, Shi Songhua H, Jefferson G. High performance no flow underfills for low cost flip chip applications: material characterization. IEEE Trans Comp Package Manuf Technol 1998;21(3):450–8.
[15] Wu S, Soucek MD. Crosslinking of acrylic latex coatings with cycloaliphatic diepoxide. Polymer 2000;41:2017–28.
[16] Voytekunas Vanda Yu, Ng FL, Abadie Marc JM. Kinetics study of the UV initiated cationic polymerization of cycloaliphatic diepoxide resins. Eur Polymer 2008;44:3640–9.
[17] Criado JM, Malek J, Ortega A. Applicability of the master plots in kinetic analysis of non-isothermal data. Thermochim Acta 1989;147:377–85.
[18] Avrami M. Kinetics of phase change, granulation, phase change and microstructure. J Chem Phys 1941;9(2):177–84.
[19] Sestak J. Thermophyscial properties of solids. In: Svehla G, editor. Comprehensive analytical chemistry. Amsterdam: Elsevier; 1984.
[20] Bamford CH, Tipper CFH, editors. Comprehensive chemical kinetics. New York: Elsevier; 1980.
[21] Sestak J, Berggren G. Study of the kinetics of the mechanism of solid state reactions at increasing temperatures. Thermochim Acta 1971;3:1–12.
[22] Ozawa T. Kinetic analysis of derivative curves in thermal analysis. J Therm Anal 1970;2:301–24.
[23] Crane LW, Dynes PJ, Kaelable DH. Analysis of curing kinetics in polymer composites. J Polym Sci Polym Lett Ed 1973;11:533–40.
[24] Kissinger Homer E. Reaction kinetics in differential thermal analysis. Anal Chem 1957;29(11):1702–6.
[25] Malek J. The kinetic analysis of non isothermal data. Thermochim Acta 1992;200:257–69.
[26] Stutz H, Mertes J, Neubecker K. J Polymer Sci A 1993;31:1879.
[27] Sbirrazzuoli N, Vyazovkin S. Learning about epoxy cure mechanisms from isoconversional analysis of DSC data. Thermochim Acta 2002;388:289–98.