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Curing kinetics study of epoxy resin/flexible amine toughness systems by dynamic and isothermal DSC

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ABSTRACT

Curing kinetics of two epoxy resin/flexible amine systems was studied by dynamic and isothermal differential scanning calorimetry (DSC). In dynamic experiments, the activation energy at different curing degree was computed under nonisothermal condition by using isoconversion method. At the same time, the isothermal experimental data was simulated by nonlinear least-squares fitting (NLSF). The results showed that the Arrhenius activation energy (E) increased with the increasing curing degree of diglycidyl ether of bisphenol A (DGEBA)–Jeffamine (T403) system, while in the DGEBA–D230 system activation energy decreased in the initial stage, and then increased when the value of α (the curing degree) was within the range of 0.1–0.4, and afterwards decreased. Under the isothermal condition, the Kamal's model was suitable to simulate two systems in the whole curing process.

1. Introduction

Renewable energy sources such as wind energy are indigenous and can help in reducing the dependency on fossil fuels. Wind energy provides a variable and environmental friendly option and national energy security at a time when the reduction of global reserves of fossil fuels threatens the long-term sustainability of global economy [1]. Wind energy could be generated from the wind turbine, in which wind turbine blades were one of the important sections. When the size of wind turbine blades was less than 25 m, hand lay-up has been used to manufacture the blades. When the size of wind turbine blades was more than 40 m, liquid composites molding (LCM) could be employed. In such method, the formulated resin matrix should provide low viscosity, adjustable reactivity and high flexibility, and be cured at moderate temperature. With the increasing size of wind turbine blades, higher flexible resin matrix would be required. Thermoplastic [2,3], rubber-elastic [4,5] and core–shell rubber (CSR) particles [6] were usually used to improve the toughness of epoxy matrix. However, the curing temperature and viscosity of these systems were too high to meet the requirements of LCM. The flexible curing agents may be explored to enhance the toughness of the resin matrix suitable for LCM.

Jeffamines, which was a polyether oligomers of different molecular weight terminated at each end with an amine group, has been reported it would improve the toughness of epoxy resin [7,8]. It is well known that the physical properties of the cured epoxy resin depended on the structure of crosslinking network, the curing extent, and the time and temperature of curing [9–12]. Such kinetic parameters related to network formation could provide substantial information concerning the final structure and properties of epoxy network, and the processability of epoxy resin. Therefore, kinetic analysis of epoxy resin is essential to understand structure/property/processing relationships for the preparation of high performance composites. However, there were few reports on the kinetic of Jeffamine, such as T403 and D230. It is required to understand the knowledge of the curing rate and kinetics of the flexible curing agents.

In this work, dynamic and isothermal DSC was used to study the curing kinetics of diglycidyl ether of bisphenol A (DGEBA) with two kinds of Jeffamine, T403 and D230. Detailed kinetic study has been preformed using nonlinear isoconversion analysis. The influences of activation energy on the curing degree were discussed in DGEBA–T403 and DGEBA–D230 system, respectively. In order to illustrate the toughness of T403 and D230, iso-phorone diamine (IPDA) was selected as a co-hardener, the mechanical

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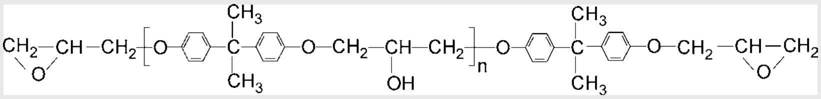
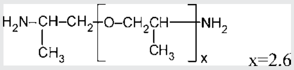
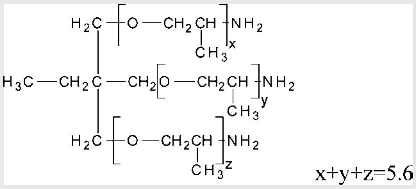
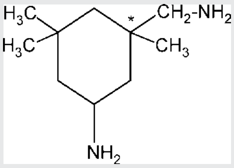
Table 1
Chemical structures of epoxy and curing agents

Materials	Chemical structures
Epoxy resin (DGEBA)	
Curing agent (D230)	 x=2.6
Curing agent (T403)	 x+y+z=5.6
Curing agent (IPDA)	

properties of resin casts were studied in DGEBA/T403/IPDA and DGEBA/D230/IPDA systems.

2. Experimental

2.1. Materials

The diglycidyl ether of bisphenol A type (Mw 380) epoxy resin was used in this study, which was provided by Wuxi resin plant, China (epoxy value 0.51). Curing agents were IPDA (Ahew 42.6), Jeffamine T403 (Ahew 81) and D230 (Ahew 60), supplied by BASF, Germany. The chemical structures of these materials are shown in Table 1.

2.2. DSC measurements

Studies on curing kinetics of epoxy resin were carried out using differential scanning calorimeter (DSC, Pyris 1, American). Resin and agents (DGEBA, T403 and D230) were mixed at a stoichiometric epoxide/amine ratio at room temperature, respectively. For dynamic DSC scans, samples (5–8 mg) were sealed in aluminum pans, and heating up to 300 °C from room temperature at rates of 5 °C/min, 10 °C/min, 15 °C/min and 20 °C/min, respectively.

For isothermal curing, small quantities of the samples (5–8 mg) were sealed aluminum pans, measured at constant temperature of 70 °C, 80 °C, and 90 °C, respectively.

Nitrogen was purged at rate of 20 ml/min to minimize oxidation of the sample during the curing. Before the curing of the samples, two standard materials, indium (99.999% pure) and zinc (99.999% pure), were used to calibrate the temperature and energy axis of the DSC apparatus. Thermal equilibrium was regained within 1 min of sample insertion, and the exothermic reaction was considered to be complete when the recorder signal leveled off to the baseline. The final baseline was extrapolated to determine the total area under the exothermic curve and the heat of curing.

2.3. Resin casts preparation and testing

The agent IPDA was first mixed with flexible amine agent and the relative flexible amine content in the mixed system varied from 0 to 100% in weight. The mixtures of two agents served as the agent. Then the equal equivalent amount of epoxy resin was added. Namely, the stoichiometric ratio of epoxy/amine was 1. Formulae employed in this study are listed in Table 2. The resultant materials were completely mixed by a mechanical stirrer and degassed with a vacuum pump to eliminate air bubbles. The bubble free mixtures were then poured into the preheated steel mold in an oven, and then cured at 80 °C/4 h + 120 °C/1 h when the curing agent was T403/IPDA and at 60 °C/1 h + 80 °C/2 h + 120 °C/1 h when the curing agent was D230/IPDA.

Tensile properties were measured by using tensile testing machine (Instron 1121) with a crosshead speed of 2 mm/min. Flexural properties were measured by three-point bending test with a crosshead speed of 2 mm/min using tensile testing machine (Instron 1121). The dimension of a specimen was 80 mm × 10 mm × 2 mm. The specimens were tested with a span of 64 mm. Impact properties were measured by using RESIN IMPACTOR (P/N 6957.000) according to ISO 180. At least five specimens were tested for each resin casts.

3. Results and discussion

3.1. Dynamic DSC analysis

In general, the heat evolution recorded by DSC is assumed to be proportional to the extent of consumption of the reactive groups.

Table 2
Formulas of the epoxy resins used for resin casts testing

Relative amines	flexible content (wt%)	DGEBA (g)	T403 (g)	D230 (g)	IPDA (g)
T403	0	100	0.0	–	24.0
	32	100	8.8	–	18.7
	58	100	18.1	–	13.2
	81	100	28.8	–	6.7
	100	100	40.0	–	0.0
D230	0	100	–	0.0	24.0
	32	100	–	8.3	17.8
	58	100	–	16.3	11.8
	81	100	–	24.2	5.7
	100	100	–	32.0	0.0

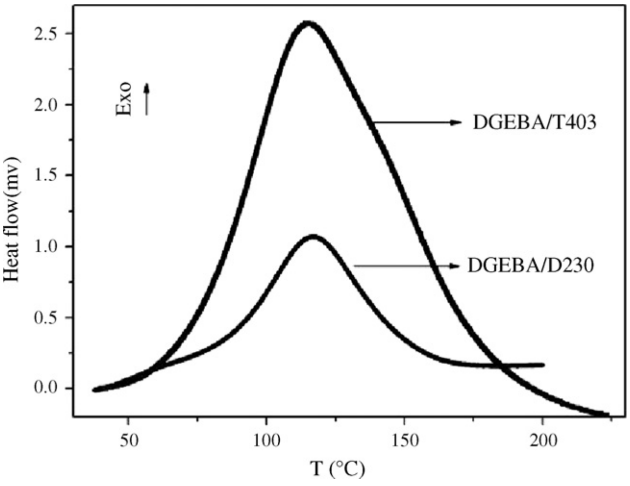


Fig. 1. DSC curves of DGEBA/T403 and DGEBA/D230 systems at 5 °C/min heating rates.

Thus the conversion rate and curing rate during the curing process can be described as follows:

$$\alpha = \frac{H_t}{H_u} \tag{1}$$

$$\frac{d\alpha}{dt} = \left(\frac{1}{H_u}\right)\frac{dH}{dt} \tag{2}$$

where α is the conversion rate, $d\alpha/dt$ is the cure rate, H_t is the reaction heat within time t, dH/dt is the heat flow rate, and H_u is the total heat of reaction.

The typical DSC curve displaying heat flow dH/dt against temperature T is shown in Fig. 1. The informations which could be obtained directly from the DSC curve were the onset temperature T_i, the peak temperature T_p, the terminal temperature T_f, and the values of dH/dt.

Fig. 1 shows the DSC curves of DGEBA/T403 and DGEBA/D230 systems. From DSC thermograms of the two studied systems, the curing reaction information, such as: the peak temperature (T_p), the onset temperature (T_i), the terminal temperature (T_{end}) and the curing range of the studied systems can be obtained. Some data on the curing reaction are listed in Table 3.

The exothermic heat of DGEBA–D230 system was higher than those of DGEBA–T403 system; however, the curing range was contrary. The reason for these phenomena might be the different structure of T403 and D230, which led to the different reactivity [13]. Though their amine groups are located on secondary carbon atoms at the ends of an aliphatic polyether chain, T403 is a kind of branched Jeffamine, whose steric hinderance was stronger than that of D230. Therefore, the reactivity of D230 is better than that of T403.

In this study, nonlinear isoconversional method [Eq. (3)] [14,15] was used to analyze the dynamic DSC data

$$\sum_{i=1}^{n}\sum_{j\neq i}^{n}\frac{I(E_\alpha, T_{\alpha,i})\beta_j}{I(E_\alpha, T_{\alpha,j})\beta_i} \tag{3}$$

where β is the heating rate, T is the temperature, E is the activation energy, i, j are ordinal numbers of DSC runs performed at different heating rates. The activation energy can be determined at any particular value of α by finding the value of E_α for which the Eq. (3) is a minimum. In Eq. (3), the temperature integral

$$I(E, T_\alpha) = \int_0^{T\alpha} \exp\left(\frac{-E}{RT}\right) dT \tag{4}$$

is determined by with the help of a Doyle's approximation [16]

$$I(E, T) \cong \frac{E}{R}\exp\left(-5.331 - 1.052\frac{E}{RT}\right) \tag{5}$$

The application of Eq. (3) to nonisothermal data, give rise to the dependencies of E_α on α as is shown in Fig. 3.

The activation energy increased with the increasing of the curing degree in DGEBA–T403 system, and the value of activation energy ranged from 20 kJ/mol to 50 kJ/mol, which was typical for epoxy-amine reaction [17,18]. At early stages ($\alpha < 0.3$), the viscosity increased with the increase of the curing degree, thus more energy was required to overcome the motion among molecule chains. With the curing reaction proceeding, the curing degree increased, and the free volume only allowed local motions of the chain segments. Therefore, a great degree of cooperatives among the chain segments were required to initiate translational motion of the segments. This would results in a large energy barrier of the segment motion, which was reflected through activation energy at later curing stages.

For DGEBA–D230 system, at early stages ($\alpha \leq 0.1$) activation energy decreased. This could be attributed to the cooperative motion of the chain segments [19]. The packing was loose at early stages, which allowed the chain segments moving independently. At later stages ($\alpha \leq 0.4$) activation energy increased. With the increase of the curing degree, the viscosity of epoxy system increased, which required more energy to achieve the motion of molecule chains. When $\alpha \geq 0.4$, activation energy decreased, which was attributed to the high reactivity of D230, resulting in sufficient molecular mobility from the thermal energy during the curing process of diffusion controlled [20,21].

The different activation energies of two systems could be attributable to the structure of monomer [18]. D230 was a linear molecular and terminated at each end with an amine group, however, T403 is a branch molecular, as shown in Table 1.

3.2. Isothermal curing analyses

In general, the curing reaction of thermosetting resin can proceed over a wide temperature range. However, owing to the sensitivity and response of heat changes, the DSC apparatus is generally operated in a moderate curing temperature which determines the isothermal curing reaction heat. In order to study the isothermal curing reaction of DGEBA–T403 and DGEBA–D230 systems, the first step was to choose the optimum curing temperatures, by analyzing dynamic cure DSC curves (Fig. 2). Then, a series of measurements of isothermal curing reaction was performed (Fig. 4). Finally, the isothermal curing kinetics data could be obtained from the isothermal DSC curves.

Fig. 4 shows that the change of curing degree varies with the curing temperature and time. At a given temperature, the curing degree increased rapidly during the initial reaction stage, then increased slowly, and finally tended to a certain value. This was attributable to the sequence reactions of chain extension, branching and self-crosslinking of epoxy resin during the curing process, and these reactions reduced the mobility of the reacting molecules and slowed down the conversion rate. At the same curing temperature and time, DGEBA–D230 system had short curing time

Table 3
Curing characteristics of the DGEBA/T403 and DGEBA/D230 systems

Samples	T_i (°C)	T_p(°C)	T_{end} (°C)	Curing range (°C)	ΔH (J g^{-1})
DGEBA/T403	42.6	114.1	230	187.4	396.5
DGEBA/D230	32.5	116.6	177.6	145.1	600.6

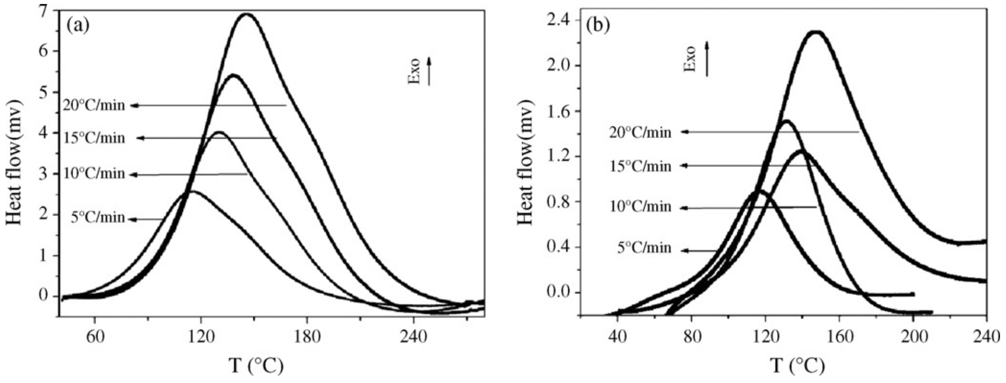


Fig. 2. DSC curve of curing system without IPDA at different heating rates: (a) DGEBA/T403 and (b) DGEBA/D230.

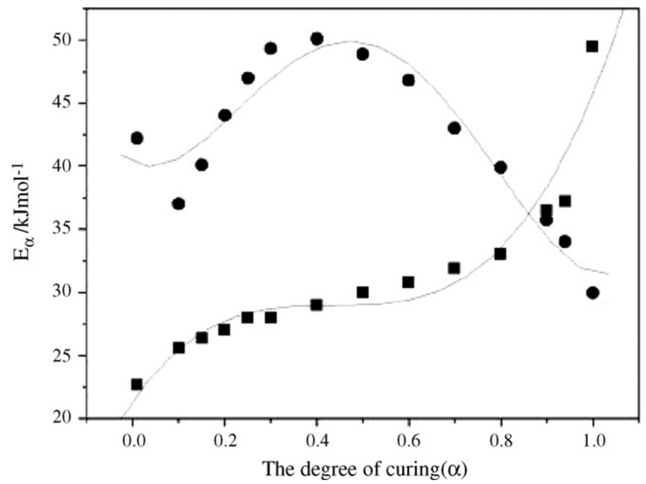


Fig. 3. The influence of activation energy on the curing degree in DGEBA/T403 and DGEBA/D230 systems. ■ represents DGEBA/T403 system and ● represents DGEBA/D403 system.

than DGEBA–T403 system. This was related to their different reactivity.

The methods used to study the curing kinetics could be classified in mechanistic [22] or phenomenological [9–27] terms. Mechanistic models were made from the balance of chemical species involved in the chemical reaction. Since the resin cure reaction was very complex due to the interaction between the chemical kinetics and changes in their physical properties, thus it was difficult to derive a mechanistic model. Phenomenological or empirical models were preferred to study the curing kinetics of these polymers.

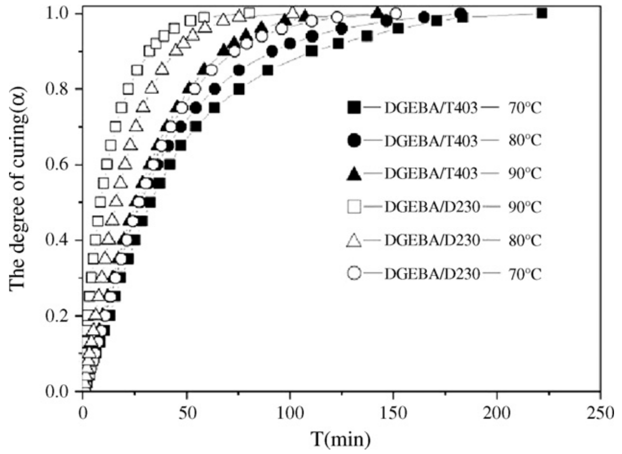


Fig. 4. The curing degree vs. time at different curing temperatures in DGEBA/T403 and DGEBA/D230 systems.

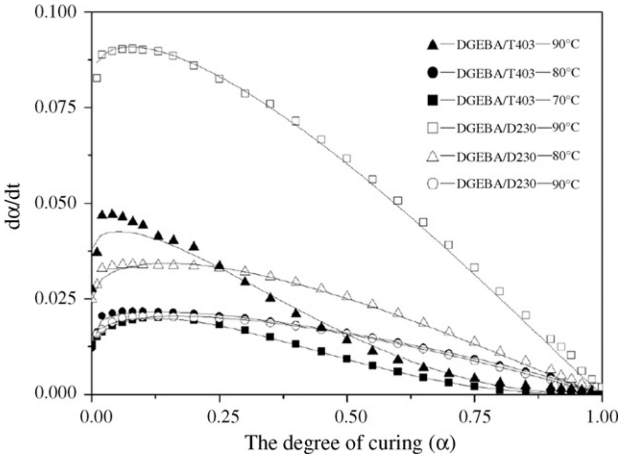


Fig. 5. Comparisons of experimental data with the Kamal's model in DGEBA/T403 and DGEBA/D230 systems.

For the thermosetting resins, $\mathrm{d}\alpha/\mathrm{d}t$ is usually expressed as

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = A \exp\left(-\frac{E}{RT}\right) f(\alpha) \tag{6}$$

where A was the frequency factor, E was the activation energy, $f(\alpha)$ was a function of the degree of curing(α), R was the gas constant and T was the absolute temperature. When a reaction was catalyzed by a proton donor which presented or was produced during the curing process, the reaction mechanism was considered to be autocatalytic.

Table 4
Parameters used in Kamal's model (Eq. (7)) in DGEBA/T403 and DGEBA/D230 systems

Temperature (°C)	k_1 (k^{-1})	K_2 (k^{-1})	m	n	$m+n$	r
T403						
70	0.011	0.058	0.68	2.40	3.08	0.9995
80	0.013	0.060	0.68	2.45	3.13	0.9934
90	0.038	0.062	0.60	2.30	2.90	0.9715
D230						
70	0.014	0.025	0.50	1.02	1.52	0.9981
80	0.025	0.040	0.48	1.09	1.57	0.9954
90	0.081	0.061	0.48	1.05	1.53	0.9988

Table 5
Mechanical properties of resin casts at room temperature according to the formulas of Table 2

Relative amines	Flexible content (wt%)	Tensile strength (MPa)	Flexible strength (MPa)	Impulsive strength (kJ/m^2)
T403	0	73.5 ± 2	130.0 ± 3	26.8 ± 5
	32	66.0 ± 2	131.0 ± 2	33.0 ± 8
	58	63.4 ± 1	117.1 ± 3	37.8 ± 10
	81	61.5 ± 1	115.8 ± 3	47.1 ± 12
	100	55.8 ± 3	92.0 ± 3	53.6 ± 15
D230	0	73.5 ± 2	130.0 ± 3	26.8 ± 5
	32	65.6 ± 2	127.5 ± 5	32.6 ± 4
	58	61.3 ± 3	118.3 ± 4	36.8 ± 6
	81	59.1 ± 2	112.6 ± 5	45.2 ± 8
	100	58.3 ± 4	102.3 ± 4	51.8 ± 12

Generally, the following equation can be expressed as autocatalytic kinetics:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = (k_1 + k_2\alpha^m)(1-\alpha)^n \qquad (7)$$

which was usually called Kamal's model [23], and it modified model:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = k\alpha^m(1-\alpha)^n \qquad (8)$$

Fig. 5 shows that the curing degree varies with the conversion rate. At the same time and temperature, the conversion rate of DGEBA–D230 system was higher than that of DGEBA–T403 system. The conversion rate had a maximum value at some intermediate curing degree, which indicated that the systems obeyed autocatalytic kinetics [24,25]. In this study, the Kamal's model was used to describe the data. The conversional rate constants k_1 and k_2 depended on the temperature and followed the Arrhenius relationship:

$$k = A\exp\left(-\frac{E}{RT}\right) \qquad (9)$$

Several methods [23,26,27] have been used to calculate the parameters in Eq. (7). In our study, a nonlinear least-squares fitting (NLSF) was used to compute the four parameters k_1, k_2, m and n from the experimental data. The results are shown in Fig. 5 and Table 4.

Fig. 5 shows that the model provided an excellent fit to the isothermal curing tests at all temperatures examined and two systems. Table 4 shows that compare to DGEBA–T403 system, DGEBA–D230 system shows higher the value of k_1 and k_2 at the same curing temperature, which lead to that the curing reaction of DGEBA–D230 occurs more quickly than that of DGEBA–T403 system.

3.3. *Mechanics properties of resin cast*

The mechanics properties of resin cast are shown in Table 5. The tensile and flexible strength decreased and the impact strength increased with increasing content of T403 and D230, respectively. The decreased tensile and flexible strength can be related to the reduced crosslinking density after addition of the flexible amine content [28]. The increased impact strength can be attributed to the reduction of internal stress due to the stress relaxation by flexible molecular chains of flexible amines [28], when the samples were subjected to impact.

4. Conclusions

In dynamic experiments, the Arrhenius activation energy (E) increased with increasing the curing degree of diglycidyl ether of bisphenol A (DGEBA)–Jeffamine (T403) system, while in DGEBA–D230 system activation energy decreased in the initial stage, then increased when the value of α ranged from 0.1 to 0.4 and afterwards decreased. In isothermal experiments, the Kamal's model worked very well in the whole curing process. The value of $m+n$ ranged from 2.9 to 3.13 and from 1.52 to 1.57 for DGEBA–T403 and DGEBA–D230 system, respectively. Mechanics properties of resin casts demonstrated that the addition of T403 and D230 could improve the toughness of epoxy resin.

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