Curing Kinetics Study of an Epoxy Resin System for T800 Carbon Fiber Filament Wound Composites by Dynamic and Isothermal DSC

Weiming Chen, Peng Li, Yunhua Yu, Xiaoping Yang

The Key Laboratory of Beijing City on the Preparation and Processing of Novel Polymers, Beijing University of Chemical Technology, Beijing 100029, China

ABSTRACT: Curing kinetics of DGEAC/DDM/DETDA/DGEB epoxy resin system was studied using dynamic and isothermal differential scanning calorimetry (DSC) for the preparation of T800 carbon fiber filament wound composites. In dynamic experiment, four kinds of epoxy resin systems were studied. Curing characteristics, such as curing range and curing temperatures of the epoxy resin system with mixed hardeners (DGEAC/DDM/DETDA), were found lying within those of the two epoxy resin systems with a single hardener (DGEAC/DDM, DGEAC/DETDA). The addition of reactive diluter (DGEB) caused increase in curing range and exothermic heat. In addition, the activation energies calculated by the isoconversional method of all four resin systems decreased to the minimum value in the early stage due to the autocatalytic role of hydroxyl groups in the curing reaction and then increased due to the increased viscosity and crosslink of epoxy systems. The addition of reactive diluter led to the decrease in activation energies on the initial stage (conversion = 0.1–0.3). In isothermal experiment, a series of isothermal DSC runs provided information about the curing kinetics of the DGEAC/DDM/DETDA/DGEB system over a wide temperature range. The results showed that the isothermal kinetic reaction of the epoxy resin followed an autocatalytic kinetic mechanism. The autocatalytic kinetic expression chosen in this work was suitable to analyze the curing kinetics of this system. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 107: 1493–1499, 2008

Key words: epoxy resin; filament wound composites; curing kinetics; DSC

INTRODUCTION

Filament winding is an efficient and viable technique used commonly in the mass production of carbon fiber-reinforced polymer (CFRP) composites such as pressure vessels, pipes, and shafts. These carbon fiber filament wound composites have been widely used in such applications as aviation and spaceflight for their light weight and high strength and stiffness.

T800 carbon fiber is one kind of important reinforcement used in filament wound composites. Like T300 or T700 carbon fibers, the commercial T800 carbon fibers have been taken surface treatment to improve the interfacial adhesion between fibers and resin matrix by increasing the surface-active sites on the fibers.[1–4] However, strong treatment may damage the carbon fiber surface and decrease its mechanical properties.[5,6] In fact, the interface/interphase adhesion of T800 CF composites is one model of ''double interface/interphase adhesion.''[7] One is the adhesion between carbon fiber and sizing, and another is that between the sizing and matrix. In our previous research, it was pointed out that the interface/interphase adhesion formed through the chemical reactions between the sizing and the matrix played a more important role in improving the interfacial adhesion of T800 CF composites than the adhesion between the T800 CFs and sizing. Therefore, an optimized resin matrix is significant for T800 CF filament wound composites.

When compared with T300 or T700 carbon fiber, T800 carbon fiber possesses smaller diameter but higher tensile strength and elongation. When T800 carbon fiber filament wound composites perform well by its best properties, the resin systems with good strength, high toughness, and suitable viscosity for good impregnation must be required. In a previous research, the authors have paid much attention to the study of new epoxy matrix for T800 carbon fiber filament wound composites. A new epoxy resin matrix system (DGEAC/DDM/DETDA/DGEB) with good adherence to T800 carbon fibers in filament winding has been developed by the addition of a reactive diluter (DGEB).[7]

As we know, physical properties of cured epoxy resins are depended on their network structure, curing degree, curing time, and temperatures.[8–11] Kinetic parameters relating to network formation can

Correspondence to: X. Yang (yangxp@mail.buct.edu.cn).

TABLE I
Chemical Formulas of the Materials

Materials	Chemical formula
DGEAC (epoxy resin)	
DDM (hardener)	
DETDA (hardener)	(2,6-isomer) + (2,4-isomer)
DGEB (diluter)	CH_2-CH-CH$_2$O-(CH$_2$)$_4$-O-CH$_2$-CH-CH$_2$

provide substantial information on the final structure of the network, properties, and material processibility. Therefore, kinetic characterization of the epoxy resin system for T800 carbon fiber filament wound composites is essential to understand the structure, properties, and processing of the composites.

As far as epoxy/amine reactions are concerned, experimental studies and modeling of reaction kinetics have been widely carried out by phenomenological or mechanistic kinetic equations,[12–24] but mostly in the case of a single hardener (aliphatic or cycloaliphatic or aromatic diamine) even if the epoxy-amine systems are sometimes modified with an additive (thermoplastics, liquid crystals, or elastomers).[18–22]

In this work, curing kinetics of the epoxy resin system for T800 carbon fiber filament wound composites (DGEAC/DDM/DETDA/DGEB system) was studied by dynamic and isothermal DSC. In the epoxy resin system, diamine DDM and DETDA hardeners were mixed to DGEAC epoxy resin, and a reactive diluter (DGEB) was added to reduce the viscosity and promote the mechanical properties of the resin system and T800 composites. In dynamic experiment, the effects of the mixed hardeners and the reactive diluter on the curing kinetics were studied. In an isothermal experiment, a series of isothermal DSC runs provided information on the curing kinetics of the DGEAC/DDM/DETDA/DGEB system over a wide temperature range and the isothermal kinetic reaction mechanism of the epoxy resin system was analyzed.

EXPERIMENTAL

Materials

Epoxy resin used in this experiment was diglycidyl ester of aliphatic cyclo (DGEAC) resin, supplied by Tianjin Jindong Chem, China (epoxy value, 0.85). Hardener, 4,4′-diaminodiphenylmethane (DDM), was obtained from Tianjin Synthetic Material Research Institute, China. Another hardener, a mixture of diethyl toluene diamines (DETDA, 74–80% 3,5-diethyltoluene-2,4-diamine and 20–26% 3,5-diethyltoluene-2,6-diamine) was purchased from Lonza, Switzerland. Diluter, diglycidyl ether of butanediol (DGEB) (epoxy value, 0.65–0.75; viscosity at 25°C, 15–25 mPa s) was synthesized by authors to reduce the viscosity of DGEAC resin. Table I shows the chemical formulas of the materials. Table II shows various epoxy resin systems with different formulations.

Differential scanning calorimetry

Curing kinetics study of the epoxy resin systems was carried out using differential scanning calorimetry (DSC, Netzsch 204 F1). About 2 mg of each resin system was sealed in aluminum pans and heated from 50 up to 300°C at rates of 5, 10, 15, and 20°C/min for dynamic DSC scanning and heated to 120, 130, 140, 150, 160, 170, and 180°C at a rate of 50°C/min for isothermal DSC scanning. Then, they were kept till the scanning signal leveled off to baseline. After that the cured resin was quenched in liquid nitrogen and reheated from 50 to 300°C at 10°C/min to evaluate

TABLE II
Epoxy Resin Systems with Different Formulations

Resin system	Weight ratio of the components	Stoichiometric amine/epoxide ratio
1 DGEAC/DDM	100/42	1
2 DGEAC/DETDA	100/38	1
3 DGEAC/DDM/DETDA	100/22/18	1
4 DGEAC/DDM/DETDA/DGEB	100/24/19/20	0.8

the residual heat of reaction, H_{res}, which could be calculated from the area under the exothermic peak in a DSC curve. The final baseline was extrapolated to determine the total area and the heat of curing.

RESULTS AND DISCUSSION

Dynamic curing analysis

Figure 1 shows the exothermic heat curves of four resin systems at a heating rate of 5°C/min. Table III lists the curing characteristics of the four resin systems. When compared with DGEAC/DDM system, DGEAC/DETDA system possessed an obviously wider curing range of 49°C because of the lower reactivity of DETDA than DDM, which can be explained by the steric hindrance effect (or, equivalently, the segmental mobility) introduced by the methyl and ethyl groups near to the amine groups in DETDA,[23] while there are no substituted groups beside the amine groups in DDM. When the mixed hardeners (DDM/DETDA) were added to the DGEAC resin, the curing range of DGEAC/DDM/DETDA system became narrower than that of the DGEAC/DETDA system, and the peak temperature was in the range between those of the DGEAC/DDM system and the DGEAC/DETDA system. When the diluter (DGEB) was added to the DGEAC/DDM/DETDA system, the peak temperature of its exothermic heat curve was unchanged. But the exothermic heat increased obviously because of the presence of the reactive diluter, which caused the decrease in viscosity and increase in the number of epoxide groups of the system.[24]

In this study, the following Kissinger [eq. (1)][25–27] and isoconversional [eq. (2)][28–30] equations were used. Kissinger equation is

$$E_a = -R \frac{d\left[\ln(q/T_p^2)\right]}{d(1/T_p)} \quad (1)$$

where q is the heating rate, T_p is the peak temperature of exothermic heat, E_a is the activation energy, and R is the gas constant. The relationship between $\ln\left(q/T_p^2\right)$ and $1/T_p$ can be obtained from the dynamic DSC curves of different heating rates, and activation energy could be calculated from the slope.

The dynamic DSC experiments were performed on the four systems. Table IV lists their activation energies calculated by the Kissinger equation. Figure 2 shows the dynamic DSC curves of different heating rates for the DGEAC/DDM/DETDA/DGEB system. The maximum peak temperature of the DSC curves increased with the heating rate due to the increase in thermal inertia.

When compared with the DGEAC/DDM system, the DGEAC/DETDA system had higher activation energy and a resultant higher shelf life because of the lower reactivity of DETDA with epoxy resin, which also resulted in high onset temperature, peak temperature, and wide curing range, as shown in Table IV. Comparing the activation energies of the DGEAC/DDM/DETDA system and the DGEAC/DDM/DETDA/DGEB system, it was seen that the addition of reactive diluter could slightly reduce the activation energy by increasing the number of epoxide groups in the system,[24] which might be unfavorable to the shelf life requirement for filament winding. However, it should be known that filament winding is a dynamic process with requirements of low viscosity and good wettability to carbon fibers. To satisfy these requirements, the viscosity diluter (DGEB) synthesized by authors was added to the DGEAC/DDM/DETDA system. Furthermore, the
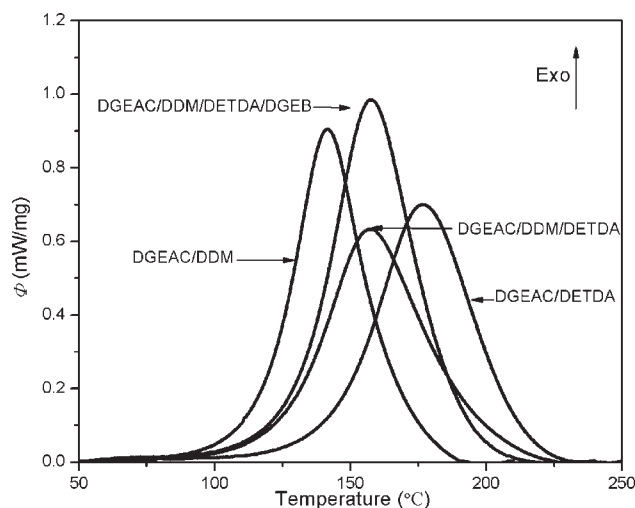

Figure 1 DSC curves of four resin systems at a heating rate of 5°C/min.

	Resin system	T_o (°C)	T_p (°C)	T_f (°C)	Curing range (°C)
1	DGEAC/DDM	117.1	141.5	166.6	38.0
2	DGEAC/DETDA	145.0	176.3	210.0	49.0
3	DGEAC/DDM/DETDA	131.5	157.3	187.6	42.5
4	DGEAC/DDM/DETDA/DGEB	128.3	157.4	192.1	50.8

T_o, the onset temperature; T_p, the peak temperature; T_f, the offset temperature.

addition of the diluter could reduce the viscosity of the epoxy resin and promote the mechanical properties of filament wound composites.[7] These results suggest that the optimum viscosity of matrix is necessary to increase the interfacial properties of T800 CF/epoxy filament wound composites.

More complete accession of activation energies throughout the entire conversion were obtained from the isoconversional equation:

$$E_a = -R \frac{d \ln(q)}{d(1/T)} \qquad (2)$$

where q is the heating rate, E_a is the activation energy, R is the gas constant, and T is the temperature to be a selected conversion at each heating rate. From the slope, activation energies could be obtained.

Figure 3 shows the conversion curves of DGEAC/DDM/DETDA/DGEB system at four different heating rates, which were obtained by integrating the DSC curves in Figure 2. For the conversion curve at a heating rate of 5°C/min, the conversion increased very slowly in the initial stage (conversion < 10%), then rapidly increased in the range of 120–200°C and followed constantly in the final stage (conversion > 90%). The rapid increase in conversion could be explained by autocatalytic curing mechanism.[25,31] All of the curves showed s-shapes and shifted to right hand side with the increase in heating rate. The activation energies at each conversion for the four resin systems can be calculated from the isoconversional equation.

Figure 4 shows the activation energies at each conversion for the four resin systems. The initial E_a at low conversion (conversion < 30%) of the four systems were high then followed by a decrease. This rule was accordance with the hypothesized mecha-

nism of an amino epoxy.[29,32] The decrease in activation energy was due to the autocatalytic role of hydroxyl groups in the curing reaction.[25,31] One hydroxyl group was generated by the reaction between an epoxide group and amine group (Scheme 1), which could continue to participate in the curing reaction as a catalyst (Scheme 2). In the proceeding of curing reaction, the concentration of hydroxyl groups increased, and the conversion rate steeply increased. However, the activation energy increased at final conversion due to the increase in viscosity and crosslink, which could reduce the mobility of the unreacted functional groups.[26] Furthermore, as shown in Figure 4, the DGEAC/DDM/DETDA/DGEB system had lower activation energies on the initial stage (conversion < 30%) than DGEAC/DDM/DETDA system in that DGEB is an aliphatic epoxy and less bulky, which could accelerate the curing reaction as well as reduce viscosity of the resin system.

The reactions of primary and secondary amines can be described by two rate constants, k_1 and k_2. The ratio of the rate constants, k_1/k_2, depends on the electron-donating properties of the amines.[32] When compared with the secondary amine addition, the primary amine addition usually plays a more important role in controlling the overall rate at the begin-

TABLE IV
Activation Energies of the Epoxy Resin Systems Obtained by Kissinger Equation

	Resin system	E_a (kJ/mol)
1	DGEAC/DDM	40.73
2	DGEAC/DETDA	70.81
3	DGEAC/DDM/DETDA	63.04
4	DGEAC/DDM/DETDA/DGEB	60.46

Figure 2 DSC curves of different heating rates for DGEAC/DDM/DETDA/DGEB system.

Figure 3 Conversion curves of DGEAC/DDM/DETDA/DGEB system at various heating rates.

ning of the curing reaction. Therefore, at the beginning of the curing reaction with a conversion about zero, the E_a approaches to the activation energy of the nonautocatalyzed reaction. Although at higher conversions, the E_a can be determined by the k_1/k_2 ratio.[27]

Isothermal-curing analysis

In general, the curing reaction of a thermosetting resin can proceed over a wide temperature range. However, considering the sensitivity and response limitation to heat changes, the isothermal DSC analysis is usually operated in a moderate curing temperature range. In the curing kinetics study of the DGEAC/DDM/DETDA/DGEB system by isother-

Figure 4 Relationship between activation energy and conversion of epoxy resin systems.

Scheme 1 Epoxy/amine reactions.

mal DSC analysis, the optimum curing temperature range (120–180°C) was determined based on the dynamic curing DSC curves (Fig. 2). The isothermal curing kinetics data were obtained from isothermal DSC curves.

The basic assumption underlying the application of DSC to a thermoset curing was that the measured heat flow rate (dH/dt) is proportional to the curing conversion rate ($d\alpha/dt$),

$$\frac{d\alpha}{dt} = \frac{1}{H_u}\frac{dH}{dt} \qquad (3)$$

where α is the conversion and H_u is the total heat of reaction. H_u was determined as the highest value of $H_t + H_{res}$, where H_t is the maximum heat of reaction determined at various isothermal curing temperatures and H_{res} is the residual heat of reaction determined after the isothermal scanning. Therefore, a can be obtained from eq. (4).

$$\alpha = \frac{H_t}{H_u} \qquad (4)$$

where H_t is the reaction heat within time t.

According to eqs. (3) and (4), α and $d\alpha/dt$ could be calculated. Figure 5 shows the conversion (α) versus time t at various temperatures. For the same curing time, the higher the curing temperature was, the higher conversion could be obtained. In addition, at a given temperature, the conversion increased rapidly during the initial reaction stage, then increased slowly, and finally tended to a constant. This was attributed to the sequence reactions of chain propagation, branching, and self-cross-linking of epoxy resin during the curing process, which reduced the mobility of the reacting molecules and slowed down the conversion rate. According to the chemical kinetics and diffusion control theories, the isothermal curing reaction process of the DGEAC/DDM/DETDA/DGEB system can be divided into two

Scheme 2 Ternary intermediate complex of hydroxyl groups with reactants in epoxy system.
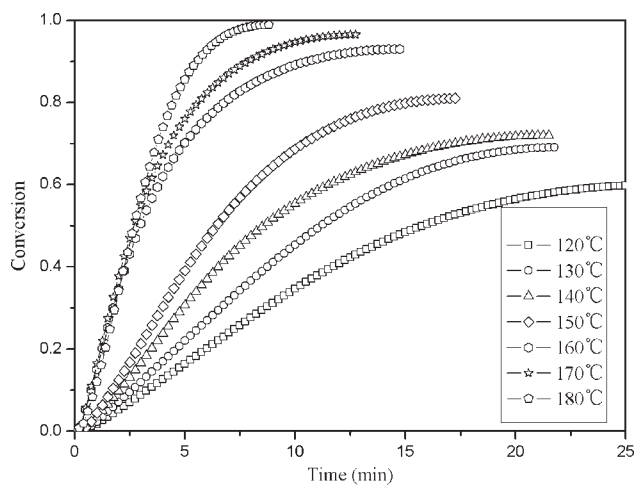
Figure 5 Conversion versus time at various temperatures.

stages: a chemical kinetic controlled stage and diffusion-controlled stage.

Figure 6 shows the conversion rate ($d\alpha/dt$) of the DGEAC/DDM/DETDA/DGEB system versus time at various temperatures. With the increase of curing temperature, the maximum value of conversion rate increased and the time to the maximum value became shorter, indicating that the presence of diluter in the resin system did not vary the autocatalytic curing mechanism of the epoxy/amine system.

To describe the curing kinetics, the autocatalytic kinetic model including diffusion controlled effects by vitrification in the final phase was proposed:[33]

$$\frac{d\alpha}{dt} = (k_1 + k_2 a^m)(a_{\max} - a)^n \qquad (5)$$

where $\alpha_{\max}$ is the maximum conversion in isothermal tests and can be obtained from Figure 5; k_1 and k_2 are the rate constants with two different activation
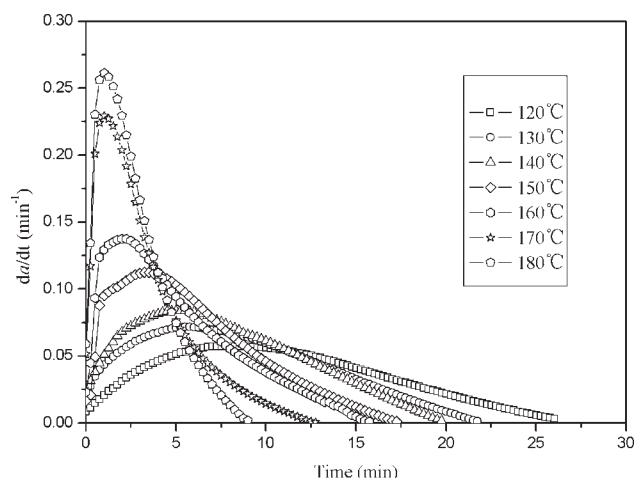

Figure 6 Conversion rate versus time at various temperatures.
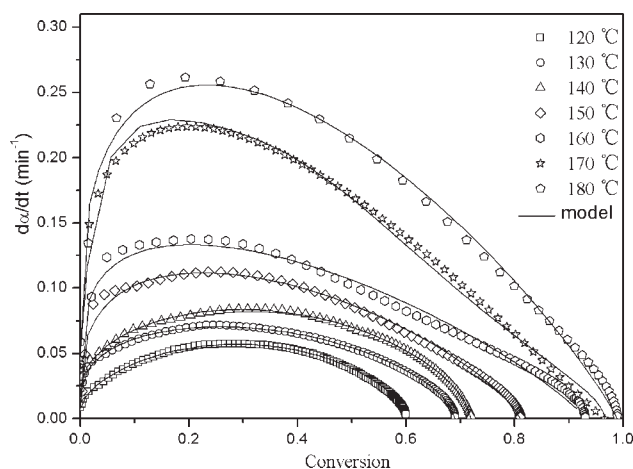
Figure 7 Conversion rate versus conversion with model predictions. The solid lines represent the autocatalytic model.

energies and preexponential factors, and represent the catalytic and the autocatalytic nature of the reaction, respectively; m and n are variables (kinetic exponents), which determine the reaction order and can have different values, with $m + n$ being the overall reaction order. For the maximum degree of reaction, the equation reported below can be applied:

$$\alpha_{\max} = pT + q \qquad (6)$$

where T is the temperature expressed in °C, p and q represent the slope and the intercept of the linear fit of $\alpha_{\max}$ versus the isothermal T data.

The constant rate k_1 in eq. (5) can be simply obtained from DSC data from the initial conversion rate when $\alpha = 0$ since the natural logarithm of eq. (5) is

$$\ln\left(\frac{da}{dt}\right) = \ln(k_1 + k_2 a^m) + n\ln(a_{\max} - a) \qquad (7)$$

It follows that $k_1 = \frac{\frac{da}{dt}\big|_{a=0}}{a_{\max}^n}$.

A closer look at eq. (8) shows that it is possible to determine a preliminary value of n by plotting $\ln(d\alpha/dt)$ versus $\ln(\alpha_{\max} - \alpha)$ for the higher isothermal temperature. When $\alpha_{\max} = 1$, the slope of the curve will be n. The mean value of n given by the different isothermal DSC curves is then used to determine the values of k_2 and m, calculated by rearranging eq. (5) and by using the previously determined k_1 and n values. These values of the kinetic model parameters can be used as a preliminary set in a regression analysis procedure to determine the final kinetic model of the analyzed system.[33]

Figure 7 shows the conversion rate versus conversion at various isothermal scanning temperatures and their corresponding model simulations for the

TABLE V
Kinetic Parameters for Isothermal Curing of
DGEAC/DDM/DETDA/DGEB

Parameters	Value
k_1 (min^{-1})	0.0274
k_2 (min^{-1})	0.2857
m	0.4121
n	0.7778
p	0.0069
q	−0.2158

DGEAC/DDM/DETDA/DGEB system. The values of the kinetic parameters are reported in Table V. A good correlation between experimental and model results was observed in Figure 7, suggesting that the chosen autocatalytic kinetic model could represent the kinetic behavior of the system in the temperature range analyzed.

CONCLUSIONS

Because of the decrease in the viscosity and the increase in the number of epoxide groups, addition of the reactive diluter (DGEB) to the epoxy resin DGEAC/DDM/DETDA system leads to increase in curing range and exothermic heat.

In the isoconversional method, due to the autocatalytic curing reaction and the increasing crosslink density, the activation energy of the four studied systems decreased to minimum value in the initial stage and increased after that value. The addition of diluter has influence on the cure of DGEAC/DDM/DETDA system in the initial stage ($a < 0.3$).

The curing reaction of DGEAC/DDM/DETDA/DGEB system follows an autocatalytic kinetic mechanism and can be described by an autocatalytic kinetic model. The theoretical prediction and experimental data have a good correlation.

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