

Cure Kinetic Study of Carbon Nanofibers/Epoxy Composites by Isothermal DSC

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ABSTRACT: An investigation was carried out into the cure kinetics of carbon nanofibers (CNF)/epoxy composites, composed of tetraglycidyl-4,4'-diaminodiphenylmethane (TGDDM) resin and 4,4'-diaminodiphenylsulfone (DDS) as a curing agent. The experimental data for both neat system and CNF/epoxy composites revealed an autocatalytic behavior. Analysis of DSC data indicated that the presence of carbon nanofibers had only a negligible effect on the cure kinetics of the epoxy. Kinetic analysis was performed using the phenomenological model of Kamal and two diffusion factors were introduced to describe the cure reaction in the

latter stage. Activation energies and kinetic parameters were determined by fitting experimental data. Comparison between the two diffusion factors was performed, showing that the modified factor was successfully applied to the experimental data over the whole curing temperature range. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 96: 329–335, 2005

Key words: curing of polymers; carbon nanofibers; vapor-grown carbon fibers; differential scanning calorimetry (DSC); resins

INTRODUCTION

Carbon nanofibers (CNF), such as vapor-grown carbon fibers (VGCF), have been recognized to be unique forms of carbon materials.^{1–5} VGCF can be produced from a hydrocarbon gas, such as benzene and methane, in the presence of hydrogen, at a temperature around 900–1200°C, with transition metal catalyst particles (usually Fe, Co, Ni) supported on an inert substrate. Because of its unique growth mechanism, the diameter of vapor-grown carbon fibers, approximately 200 nm, is very small compared to that of conventional polyacrylonitrile (PAN) and pitch-based fibers (5–10 μm). VGCF have been characterized in terms of the highly preferred orientation of their graphitic basal parallel to the fiber axis, with an annular ring texture in the cross section. This structure gives rise to excellent mechanical properties and very high electrical

and thermal conductivities for high graphitization degree of the fibers.^{2,4} Because of their physical properties and their potentially low cost of production, vapor-grown carbon fibers have gained interest for their possible applications, principally as fillers and reinforcements in polymer composite materials.^{6–12}

Tetraglycidyl-4,4'-diaminodiphenylmethane (TGDDM) epoxy resin, cured with 4,4'-diaminodiphenylsulfone (DDS), is commonly used as the polymeric matrix in high-performance fiber composites used in the aerospace industry. The attractive features of this thermosetting resin are its low density combined with high tensile strength and modulus, and a very high T_g combined with good thermal and chemical resistance.¹³ There have been a number of experimental studies, using differential scanning calorimetry (DSC), on the influence of reinforced filler, such as glass fibers and carbon fibers, on the cure reactions of TGDDM/DDS systems in the literatures.^{14–17} No pronounced effects of these fibers on the cure kinetics of the TGDDM/DDS system were observed. In our previous study, the effect of carbon nanotubes on the cure behaviors of this thermosetting resin was studied by isothermal DSC.¹⁸ It was found that carbon nanotubes have pronounced effects on the cure reaction of the resin. In this work, the cure kinetics of TGDDM/DDS epoxy, reinforced by carbon nanofibers, was studied by DSC technique.

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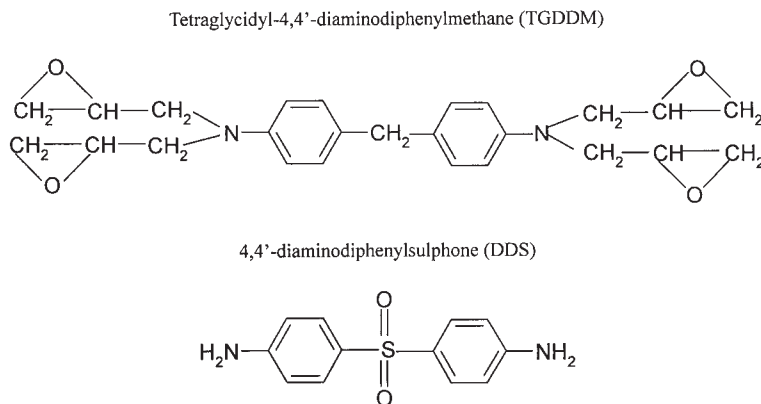


Figure 1 Chemical structures of epoxy resin and curing agent.

EXPERIMENTAL

Materials

The epoxy resin used in this study was tetraglycidyl-4,4'-diaminodiphenylmethane (TGDDM), AG80, with a weight per epoxy equivalent of 120 g equiv^{-1} , from Shanghai Synthetic Resin Institute, China. The curing agent was 4,4'-diaminodiphenylsulphone (DDS), with a molecular mass of 248.31 and purity $> 99\%$ according to the supplier. See Figure 1 for the structures of TGDDM and DDS. Carbon nanofibers were prepared from propylene over Ni–Cu catalyst in a conventional horizontal tube furnace. The diameter of CNF was about 200 nm.

Sample preparation

TGDDM resin/CNF mixture was sonicated for 2 h before curing. Subsequently, the mixture was placed in an oil bath at 120°C and a stoichiometric amount of DDS was slowly added, under continuous mechanical stirring, until a homogeneous mixture was observed, which took about 10 min. Several DSC aluminum pans were filled with the reaction mixture. The samples ($\approx 10 \text{ mg}$) were then cooled and stored in a freezer until required. The weight fractions of CNF in the TGDDM/DDS system were 1 and 5 wt %.

Differential scanning calorimetry

A differential scanning calorimeter [Perkin–Elmer Pyris 1 DSC supported by a Perkin–Elmer computer for data acquisition/analysis (Perkin Elmer Cetus Instruments, Norwalk, CT)] was used for the dynamic and isothermal curing experiments and data analysis under an argon flow of 20 mL/min . The isothermal curing experiments were conducted at four temperatures (180, 190, 200, and 210°C). The reaction was considered complete when the signal leveled off to baseline. The total area under the exotherm curve,

based on the extrapolated baseline at the end of reaction, was used to calculate the isothermal heat of reaction, ΔH_i (J/g), at a given temperature. After each isothermal run the sample was cooled rapidly in the DSC cell to 50°C and then reheated at 10°C/min to 300°C to determine the residual heat of reaction, ΔH_r (J/g).

RESULTS AND DISCUSSION

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

$$\frac{d\alpha}{dt} = \frac{dH/dt}{\Delta H_i + \Delta H_r} \quad (1)$$

where α is the conversion (extent of reaction), ΔH_i is the isothermal heat of reaction, ΔH_r is the residual heat of reaction from subsequent dynamic scan, and $\Delta H_i + \Delta H_r$ constitutes the total heat of reaction.

The conversion is given by

$$\alpha = \frac{\Delta H_t}{\Delta H_i + \Delta H_r} \quad (2)$$

where ΔH_t is the heat generated up to time t in an isothermal experiment.

Figure 2 shows the isothermal reaction rates versus time at 210°C for the neat TGDDM/DDS system and its composites with CNF. Although the isothermal reaction rate peaks and initial reaction rates of the CNF/epoxy composites are slightly lower than those of the neat resin, the maximum conversion does not differ. Furthermore, the isothermal reaction peaks occur practically at the same time for all systems. It can be seen that the presence of CNF has a negligible effect on the reaction rate. This result is identical to that of

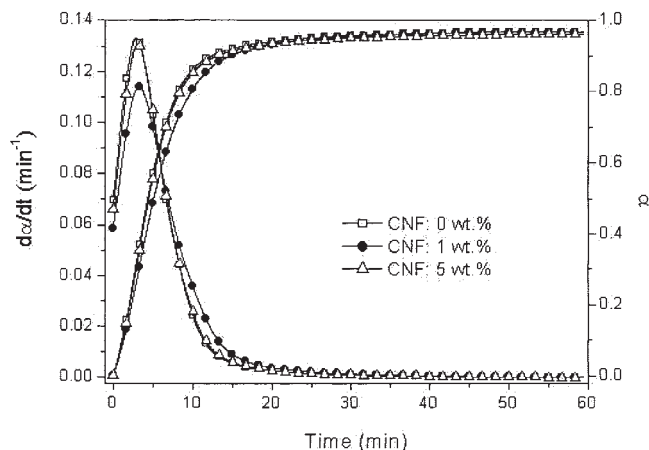


Figure 2 Curves of reaction rate and conversion versus time for neat resin and its CNF composites at 210°C.

the conventional carbon fiber-reinforced TGDDM/DDS system.^{16,17}

Mechanistically, the cure kinetics of thermosets can be divided into two general categories: n th-order and autocatalytic. Because there may be more than one chemical reaction occurring during cure, the kinetics may represent an overall process when these chemical reactions occur simultaneously.¹⁹ For thermosets that follow n th-order kinetics, the reaction rate is proportional to the concentration of the unreacted material, that is

$$\frac{d\alpha}{dt} = k(1 - \alpha)^n \quad (3)$$

where n is the reaction order and k is the rate constant. Autocatalyzed thermoset cure reactions, where one of the reaction products is also a catalyst for further reaction, are characterized by an accelerating isothermal reaction rate, typically reaching a maximum be-

tween 20 and 40% conversion. The kinetics of autocatalyzed reactions are described by the following equation²⁰:

$$\frac{d\alpha}{dt} = (k_1 + k_2\alpha^m)(1 - \alpha)^n \quad (4)$$

where m and n are reaction orders, and $m + n$ is the overall order; k_1 and k_2 are the rate constants. As shown in Figure 2, the cure kinetics of the TGDDM/DDS system and its CNF composites are typically autocatalytic, with the maximum reaction rate after the start of the cure reaction. The constant k_1 in eq. (4) can be calculated from the initial reaction near $\alpha = 0$; Values of k_2 , m , and n were obtained by a least-squares method without any constraints. The kinetic parameters k_1 , k_2 , m , and n for the neat TGDDM/DDS system and its CNF composites are listed in Table I. It can be seen that the values of k_1 and k_2 increase with curing temperatures and k_2 is greater than k_1 . The reaction orders m and n are approximately 0.9–1.2 and 1.4–1.9, respectively, for both the neat system and its CNF composites. The overall order $m + n$ increases with the curing temperature. Furthermore, at the same curing temperature, the value of $m + n$ slightly decreases with the CNF content.

In eq. (4) the rate constants k_1 and k_2 are temperature dependent through an Arrhenius relationship given by

$$k = A \exp(-E/RT) \quad (5)$$

where A is the preexponential factor, E is the activation energy, R is the gas constant, and T is the absolute temperature. Because there are two kinetic constants, k_1 and k_2 , two activation energies, E_1 and E_2 , could be obtained by plotting $\ln k_1$ and $\ln k_2$, respectively, versus $1/T$. The slopes of these curves were then used to

TABLE I
Values of the Parameters k_1 , k_2 ; Reaction Orders m , n ; and Overall Order $m + n$ for Each of the TGDDM/DDS/CNF Composites

CNF (wt %)	Temperature (°C)	k_1 (min ⁻¹)	k_2 (min ⁻¹)	m	n	$m + n$
0	180	0.0158	0.249	1.14	1.89	3.03
	190	0.0243	0.320	1.08	1.79	2.87
	200	0.0381	0.392	1.04	1.67	2.71
	210	0.0697	0.494	0.96	1.48	2.44
1	180	0.0139	0.199	1.01	1.86	2.87
	190	0.0258	0.282	1.03	1.68	2.71
	200	0.0373	0.316	0.93	1.60	2.53
	210	0.0585	0.481	0.91	1.50	2.41
5	180	0.0166	0.223	1.06	1.73	2.79
	190	0.0259	0.288	1.03	1.63	2.66
	200	0.0413	0.399	1.02	1.58	2.60
	210	0.0661	0.468	0.94	1.45	2.39

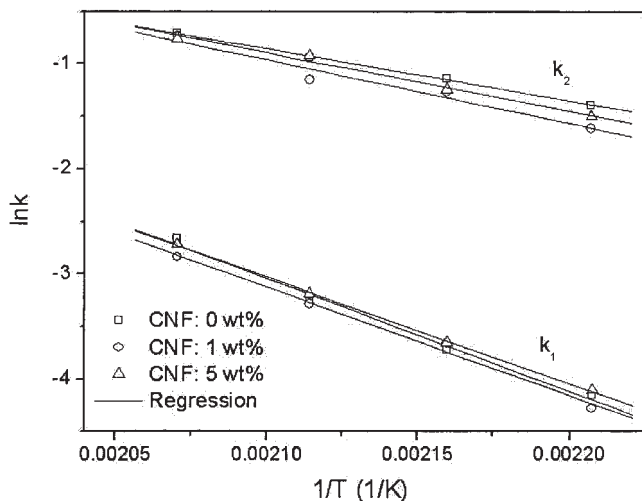


Figure 3 Curves of $\ln k_1$ and $\ln k_2$ versus $1/T$ for neat resin and 1 and 5 wt % CNF/epoxy composites.

estimate the activation energies of these two steps. Figure 3 shows the curves of $\ln k_1$ and $\ln k_2$ versus $1/T$, from which the activation energies for k_1 and k_2 were determined for the neat epoxy and its CNF composites. The values of the activation energies are listed in Table II. Compared with the neat TGDDM/DDS epoxy, the CNF/epoxy composites exhibited slightly lower activation energies for k_1 and slightly greater activation energies for k_2 . Because k_1 governs the early-stage autocatalytic reaction and k_2 affects the reaction after the initial autocatalytic stage,²¹ these results suggest that the presence of carbon nanofibers has only a very small acceleration effect on the reaction of the resin in the initial stage, whereas after the initial autocatalytic stage the filler hinders the reaction. These results are just opposite to the case of the multiwall carbon nanotubes (MWNTs)-modified TGDDM/DDS system, where the MWNTs/epoxy composites exhibited lower activation energies for k_1 and E_1 decreased with increasing MWNTs content compared with the neat TGDDM/DDS epoxy and E_2 does not change with the MWNTs content.¹⁸ In the MWNT/TGDDM/DDS system, hydroxyl groups were found in the surface of carbon nanotubes. Schechter et al.²² found that hydroxyl groups generated during the cure reaction, or provided by the solvent (plus other catalysts), sub-

TABLE II
Activation Energies and Preexponential Factors for CNF/Epoxies Composites

CNF (wt %)	E_1 (kJ/mol)	E_2 (kJ/mol)	$\ln A_1$	$\ln A_2$
0	89.0	41.1	19.4	14.4
1	85.4	50.2	27.8	11.7
5	83.9	46.4	18.2	10.8

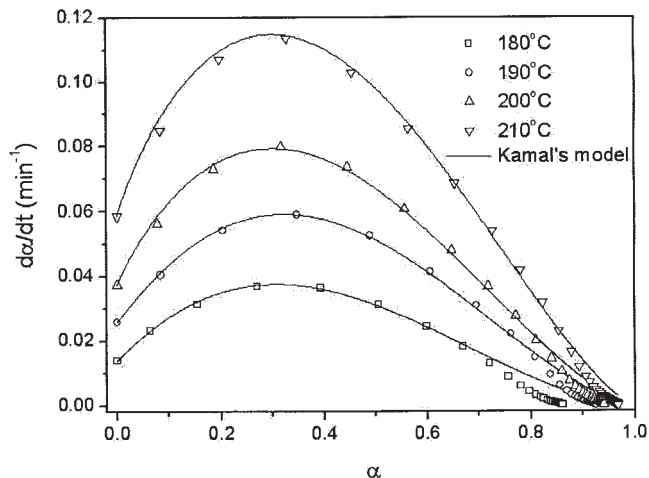


Figure 4 Curves of reaction rate versus conversion with model predictions for 1 wt % CNF/epoxy composites. The solid lines represent the autocatalytic model.

stantially accelerated the amine-glycidyl ether reaction. Unlike traditional carbon fibers, such as polyacrylonitrile (PAN) and pitch-based fibers, the unique growth mechanism of CNF results in fiber with lower concentrations of functional groups (such as $-\text{OH}$) on the surface.^{23,24}

In the curing of thermosetting resins, it is generally accepted that there are two distinct stages during the cure progress: chemically controlled and diffusion controlled. In the early stage of cure (before gel or vitrification), the cure reactions are mainly controlled by the kinetic rate of the chemical reaction. Subsequently, the cure reaction reaches higher conversions, where the reaction gradually becomes diffusion controlled.^{19,25-27} When the system reaches the gel point, a network is gradually formed with an infinite molecular weight and the viscosity of the system would increase significantly, and the system is transformed from a liquid/rubbery state to a glassy state. Generally, formation of macromolecular networks is accompanied by a considerable increase in the T_g of the reacting system. In such a case, segmental motion of the system is slowed down and the chemical reaction is controlled by these mechanisms rather than reactivity. Therefore, to model the reaction or the cure progress, the diffusion control mechanism must be taken into account. Figure 4 shows comparison of experimental data of 1 wt % CNF/epoxy composites and model-fitted results of Kamal's model [eq. (4)]. It can be seen that the results agreed well in the initial stage of reaction, but in the latter stage of the reaction the data from Kamal's model were greater than experimental results. These results show that a deviation of the prediction of the original model will be caused if diffusion control in the latter stage of the reaction is not properly considered.

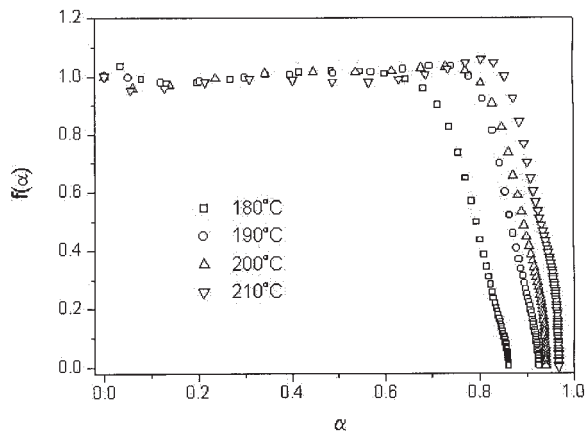


Figure 5 Curve of diffusion factor $f(\alpha)$ from eq. (7) versus conversion α for 1 wt % CNF/epoxy composites.

To consider the diffusion effect, a diffusion factor $f(\alpha)$ was incorporated into the chemically controlled equation^{28–30}:

$$f(\alpha) = \frac{1}{1 + \exp [C(\alpha - \alpha_c)]} \quad (6)$$

where C is a fitted parameter and α_c is the critical conversion. When α is much smaller than the critical value α_c , then $f(\alpha)$ approximates unity, the reaction is kinetically controlled, and the effect of diffusion is negligible. As α approaches α_c , $f(\alpha)$ begins to decrease and approaches zero as the reaction effectively stops.

On the base of Cole's equation,²⁹ Fournier et al.³¹ modified the diffusion factor as

$$f(\alpha) = 2 \left[1 + \exp \left(\frac{\alpha - \alpha_f}{b} \right) \right]^{-1} - 1 \quad (7)$$

where α_f is the final conversion and b is an empirical parameter. If the reaction is chemically controlled, $f(\alpha)$ is unity. In the case of full diffusion control, the reaction is practically interrupted and the diffusion control is zero. The diffusion factor was obtained as the ratio of experimental reaction rate to the reaction rate predicted by the autocatalytic model in eq. (4). Figure 5 depicts the behavior of $f(\alpha)$ from eq. (7) with conversion for 1 wt % CNF/epoxy composites at all curing temperatures. The decrease in $f(\alpha)$ and, consequently, in the effective reaction rate arising from the onset of diffusion at higher conversions is seen.

Application of nonlinear regression to $f(\alpha)$ versus α to eqs. (6) and (7) gives values of critical conversion α_c , parameter C , and parameter b , respectively, which are summarized in Table III. Values of α_c and α_f are seen to increase in the neat system and its composites with increasing curing temperature. No discernible trend is found for the parameter C , in agreement with results

of other studies on TGDDM/DDS systems.^{29,32} According to the theory that the reaction is lowered at low temperature, the empirical constant b was expected to rise as the temperature of the cure was lowered, and the network changes are also slower at the latter stage of the cure. Different from the results of Fournier et al.³¹ the b values obtained from the analysis in Table III follow such behavior very well.

Using the diffusion factor, the effective reaction rate at any conversion can be expressed in the following form:

$$\frac{d\alpha}{dt} = (k_1 + k_2\alpha^m)(1 - \alpha)^n f(\alpha) \quad (8)$$

Figure 6 shows the experimental values of reaction rate and conversion versus time for 5 wt % CNF/epoxy composites for all curing temperatures and the corrected data comparing the data calculated by the autocatalytic model, as well as the modified autocatalytic model with diffusion factor, according to eqs. (6) and (7). Good agreement between experimental data and the modified autocatalytic model from eq. (7) was found over the whole curing temperature range, compared with the model from eq. (6). It should be noted that the critical conversion is not an observable quantity because the transition to the diffusion regime is gradual. Consequently, the difference of fitted results from eqs. (6) and (7) may be attributable to the difficulty of determining the critical conversion with accuracy.³¹

CONCLUSIONS

In this work, the cure kinetics of tetraglycidyl-4,4'-diaminodiphenylmethane (TGDDM)/4,4'-diaminodiphenylsulfone (DDS)/carbon nanofiber (CNF) composites was investigated by isothermal DSC. It was

TABLE III
Values of the Critical Conversion α_c , Parameter C , Final Conversion α_f , and Empirical Parameter b for Each of the TGDDM/DDS/CNF Composites

CNF (wt %)	Temperature (°C)	α_c	C	α_f	b
0	180	0.821	35.1	0.885	0.0549
	190	0.861	47.4	0.912	0.0428
	200	0.914	41.0	0.954	0.0311
	210	0.918	42.8	0.968	0.0284
1	180	0.794	35.4	0.861	0.0587
	190	0.869	41.8	0.925	0.0469
	200	0.893	41.7	0.941	0.0375
	210	0.929	46.5	0.967	0.0284
5	180	0.810	47.0	0.860	0.0431
	190	0.847	38.7	0.913	0.0567
	200	0.891	39.0	0.948	0.0469
	210	0.907	41.1	0.961	0.0446

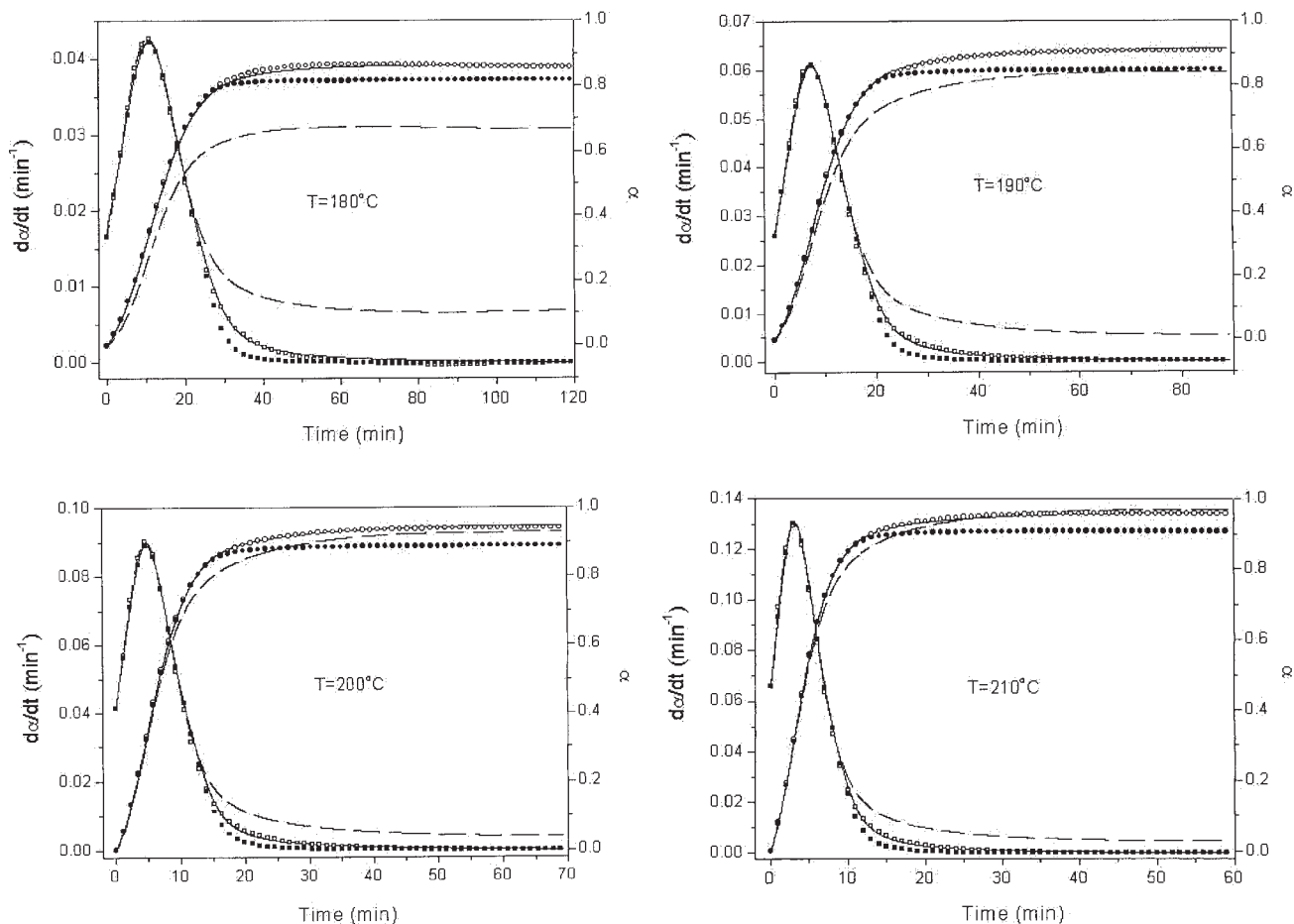


Figure 6 Comparison of experimental data with model predictions: reaction rate, (■) and (□), and conversion, (●) and (○), fitted from eq. (6) and eq. (7), respectively, versus time for 5 wt % CNF/epoxy composites at all curing temperatures. Results from autocatalytic model (dashed line); experimental results (solid line).

observed that the presence of CNF in the composites have only a negligible effect on the initial reaction rates and the time to maximum reaction rate. Kamal's autocatalytic model fitted well with the cure behavior of the neat TGDDM/DDS system and its CNF composites up to the diffusion-controlled reaction. To consider diffusion control in the latter stage of cure, two diffusion factors were introduced into Kamal's model. Good agreement between experimental data and the autocatalytic model with the modified diffusion factor from eq. (7) was found over the whole curing temperature range at all curing temperatures.

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