# Effect of Polyaniline Surface Modification of Carbon Nanofibers on Cure Kinetics of Epoxy Resin

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**ABSTRACT:** Polyaniline (PANI) "nanograss" was grown on carbon nanofibers (CNFs). The cure behavior of an epoxy resin with and without unmodified CNFs or PANI modified CNFs was studied by means of non-isothermal and isothermal differential scanning calorimetry (DSC). CNFs accelerated the reaction of epoxy and diamine. PANI surface modification further increased the reaction rate and the extent of reaction. An autocatalytic cure kinetic model was used to fit the reaction curves. It was found that activation energies of the epoxy reaction decreased in the presence of CNFs and PANI modified CNFs. The observed catalytic effect of CNF and PANI surface coating can be very useful for low temperature cure of large epoxy composite products. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 118: 2328–2335, 2010

**Key words:** carbon nanofibers (CNFs); polyaniline; epoxy resin; cure behavior

## INTRODUCTION

Among all thermoset polymers, epoxy resins provide the best overall performance, such as, good mechanical properties, chemical resistance, and low shrinkage. Hence, it is the most widely used thermoset resin. It is used in paints, electric insulators, printed circuit boards, adhesives, etc.[1] Because of its high specific strength and stiffness, it is also used as the matrix material in composites used for high end applications like airplane fuselage, wind turbine blades, and other high temperature aerospace applications. The epoxy cure reaction is very important in determining the end mechanical properties of the composite.[2] Based on the cure reaction, epoxies can be classified into high and low temperature curing systems. Several researchers have studied the curing kinetics of high temperature epoxy systems.[3,4] However, there have not been many studies regarding low temperature cure of epoxy. Because of their low viscosity and room temperature curing reaction, low temperature epoxies are easy to process. Large composite parts like wind turbine blades are manufac-

tured using soft molding processes like Seeman composite resin infusion molding process (SCRIMP).[5] Therefore, the ease of processing obtained by using low temperature epoxy systems is very important. However, low temperature cure epoxies tend to have their own challenges like incomplete cure, which leads to premature failure of the composite and long cycle times which prevents cost effectiveness. These are particularly serious concerns if the application is as critical as that of a wind turbine blade. To fulfill the immediate needs in wind energy applications, it is desirable to add nanoparticles in the polymer resin to yield nano-reinforced polymer composites for improved resin reaction and mechanical properties.[6] In this study, we investigate the effect of carbon nanofibers (CNFs) on cure kinetics of a low temperature wind epoxy resin system. Further, we modify the surface of the CNFs by growing polyaniline (PANI) "nanograss" and investigate how this physical surface modification affects the curing kinetics of the epoxy resin system.

The detailed cure mechanism of epoxy resins is highly complex as many reactions take place simultaneously and are affected by phenomena, such as, vitrification and gelation. Incorporation of nanoparticles in the epoxy resin makes the curing process even more complicated. Considerable research has been devoted to the cure kinetics of epoxy/nanoparticle systems. Venkata and Avadhanam[7] have recently reviewed the kinetic mechanisms of carbon nanotube (CNT)-modified epoxy-amine systems. Opalicki et al.[4] studied the cure kinetics of neat

epoxy and carbon fiber reinforced epoxy with tetraglycidyl-4,4′-diaminodiphenylmethane (TGDDM) and 4,4′-diaminodiphenyl sulfone (DDS) by differential scanning calorimetry (DSC). They observed that carbon fiber had little effect on the cure kinetics. Xie et al.[8] reported similar results in the CNF/TGDDM/DDS cure system. On the other hand, Wu and Chung[9] used CNF, carbon black (CB), and other manually chopped carbon fibers as fillers and found that the presence of carbon as a filler in the epoxy resin increased the exothermal heat and accelerated the reaction rate. However, some researchers have also reported certain retarding effects of carbon fillers. For example, Bae et al.[10] reported that CNT and CB retarded the cure.

This difference in the results could be attributed to the sample preparation of the epoxy nanocomposites. As reported in one of our earlier studies,[11] epoxy nanocomposites can be prepared in different methods and the resulting dispersion of the nanoparticles and the end properties of the nanocomposites are different. The same could hold true for curing kinetics. Hence, this kinetic study was done using the manufacturing process of the end composite as the reference.[12]

PANI coating on carbon nanoparticles has been studied earlier. Peliskova et al.[13,14] investigated the effect of coating short carbon fiber and graphite particles with nonconducting PANI-base layer on charge transport in epoxy resin composites to provide new materials for various electrical and electromagnetic applications. They used a high concentration (0.2$M$) of aniline hydrochloride solution and got irregular PANI layer on the graphite surface. However, the cure kinetics of PANI/nanoparticle/epoxy system have not been reported.

In this work, we present results of growing PANI nanograss on the surface of CNFs by dilute oxidative polymerization of aniline. The cure kinetics of a wind epoxy resin in the presence of CNFs and PANI modified CNFs is studied.

## EXPERIMENTAL

### Materials

Aniline (Aldrich), ammonium peroxydisulfate (APS; 99.99%, Aldrich), and perchloric acid (HClO$_4$, 70%, Aldrich) were used directly as received without further purification. An epoxy resin, EPIKOTE$^{TM}$ RIM 135 with an epoxy equivalent weight (EEW) about 166–185, and a diamine curing agent, EPIKURE$^{TM}$ RIM H 137 with an amine value about 400–600 mg [KOH]/g, were provided by Hexion Speciality Chemicals (Houston, TX). Highly heat treated CNFs (PR-24-LHT-HHT) were obtained from Applied Sciences (Cedarville, OH).

### PANI nanograss preparation

The growth of the PANI nanograss on CNF was carried out using a method developed in our lab.[15,16] Aniline was dissolved in 100 mL of 1.0$M$ HClO$_4$ solution and carefully transferred to a well-dispersed 1.0$M$ HClO$_4$ solution of APS and CNF in a beaker. The reaction was carried out at room temperature with moderate stirring. The initial concentration of aniline to the total volume of solution was maintained at 8.0 m$M$ and the molar ratio of aniline to APS was 2.0. The CNF concentration was 1.0 g/L. After 24 h, the products was filtered by Buchner funnel and then purified with deionized water until the filtrate became colorless. Then, the final product was dried for 12 h in a vacuum oven at a temperature of 70°C. The CNFs were analyzed by scanning electron microscopy (SEM) and thermo gravimetric analysis (TGA).

### DSC measurement

Cure behavior of the epoxy resin in the presence of unmodified or modified CNFs was analyzed using DSC-2920 (TA Instruments). Typically, the non-isothermal DSC experiments of epoxy/CNF were carried out as follows: 100 g of RIM 135 and 35 g of RIM H 137 were mixed homogeneously with a glass rod in a beaker. Then, 10 g reactive mixture (RIM 135/H 137) was mixed with 0.1 g of CNF homogeneously, and the samples (10–25 mg) were sealed under air in aluminum pans and cured by heating. The calibration of DSC was done using an Indium standard. Non-isothermal experiments were performed with a heating rate of 10°C/min under N$_2$ at 50 mL/min from 30 to 300°C. A second scan with the same heating rate was carried out to determine the residual reaction heat. No residual heat was found after dynamic scanning. Hence, the final degree of conversion after non-isothermal scanning was assumed to be 1.

Similarly, the isothermal DSC experiments were carried out at 45°C, 60°C, and 75°C for 200 min. Then, two dynamic scans with a heating rate of 10°C/min were carried out to measure the residual reaction heat and the glass transition temperature, respectively.

### Kinetic model

The basic assumption for applying DSC to the kinetic study is that the reaction rate, $d\alpha/dt$, is proportional to the measured heat flow, $dH/dt$, as follows:

$$\frac{d\alpha}{dt} = \frac{1}{\Delta H_{total}} \frac{dH}{dt} \qquad (1)$$

where $\Delta H_{total}$ is the total enthalpy of the cure reaction measured by non-isothermal DSC scan from 30 to 300°C with a heating rate of 10°C/min.
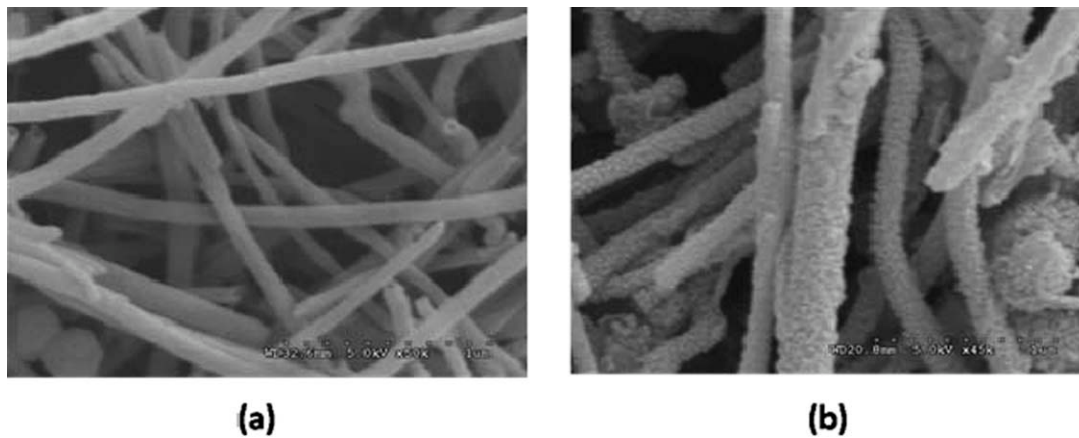
**Figure 1** SEM pictures of CNF with or without PANI nanograss surface modification.

To investigate the effect of CNF on the cure kinetics of epoxy resin, an autocatalytic model with the following generalized expression can be used:

$$\frac{d\alpha}{dt} = (k_1 + k_2\alpha^m)(\alpha_f - \alpha)^n \qquad (2)$$

The parameters $k_1$ and $k_2$ are the $n$th-order and autocatalytic rate constant, respectively, $n$ and $m$ are the respective reaction orders, and $\alpha_f$ is the final conversion. $\alpha_f$ equals 1 in most non-isothermal cases, whereas the final conversion in isothermal case can be obtained by the equation as follows:

$$\alpha_f = \frac{\Delta H_{\text{total}} - \Delta H_{\text{residual}}}{\Delta H_{\text{total}}} \qquad (3)$$

where $\Delta H_{\text{residual}}$ is the residual heat of cure reaction after the isothermal cure, which can be measured by scanning the isothermally cured samples. In some
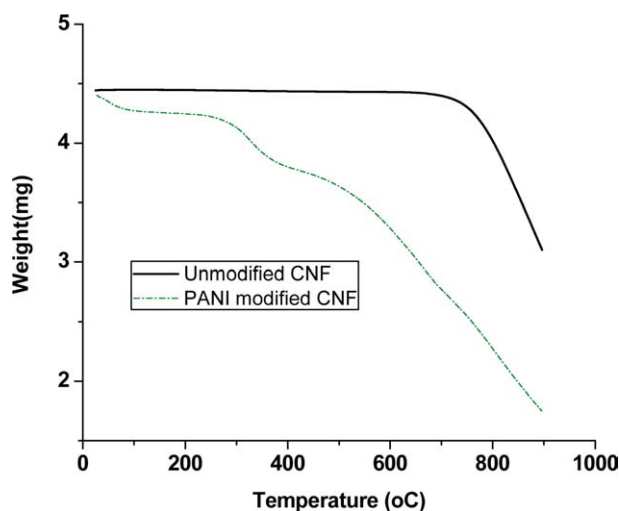
isothermal cases, the initial conversion, $\alpha_0$, is not zero because the cure process starts before the cure system reaches to the specified isothermal temperature. Therefore, a part of reaction heat is missed at the initial stage, so we define as follows:

$$\alpha_0 = \frac{\Delta H_{\text{total}} - (\Delta H_{\text{isothermal}} + \Delta H_{\text{residual}})}{\Delta H_{\text{total}}} \qquad (4)$$

where $\Delta H_{\text{isothermal}}$ is the exotherm of cure reaction during the isothermal cure.

The rate constants, $k_1$ and $k_2$, are the temperature dependent parameters and can be given by an Arrhenius relationship:

$$k_i = A_i \exp(-E_{a,i}/RT), \quad i = 1, 2 \qquad (5)$$

where $E_a$ is the activation energy, $R$ is the gas constant, $T$ is the absolute temperature, and $A$ is the



**Figure 2** TGA graph of pristine CNF and PANI modified CNF. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
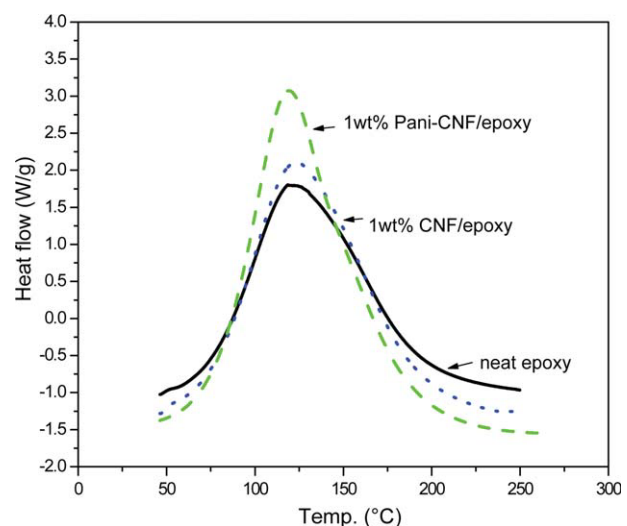


**Figure 3** Non-isothermal DSC curves of different epoxy systems at a heating rate of 10°C/min. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

**TABLE I**
**Total Reaction Heat ($\Delta H_{total}$) and Maximum Exothermic Heat Flow Temperature ($T_E$) of Different Epoxy Resin Systems**

| Cure system | $\Delta H_{total}$ (J/g) | $T_E$ (°C) |
|---|---|---|
| Neat epoxy | 598 | 122.3 |
| Epoxy/CNF | 610 | 123.4 |
| Epoxy/PANI-CNF | 644 | 118.2 |

pre-exponential factor. Equation (5) also can be transformed as follows:

$$\ln k_i = -E_{a,i}/RT + \ln A_i \qquad (6)$$

By plotting $\ln k_i$ versus $1/T$, we can determine the activation energy values to determine the specific effect of CNFs on the activation energy of the reaction.

## RESULTS AND DISCUSSION

Figure 1 shows the SEM micrographs of CNFs with and without the PANI surface modification. The nanograss on the CNF consists of PANI nanofibres with an average diameter of 10–40 nm and average length of 70–400 nm. The approximate percentage of PANI in the PANI modified CNF was found by means of TGA. This is seen in the TGA graph in Figure 2. After scanning from 25 to 900°C at a rate of 10°C/min, there was a degradation of about 1.34 g in the pristine CNFs, whereas there was a degradation of 2.66 g in the PANI modified CNFs. If we take into account the moisture content present in the PANI modified CNFs, the calculated PANI percentage is ∼ 25 wt % of the PANI modified CNFs.

Figure 3 shows the non-isothermal DSC curves of epoxy RIM 135/H 137 cured at a heating rate of 10°C/min for three different cases: (1) neat epoxy resin/curing agent; (2) epoxy with 1 wt % CNF; and
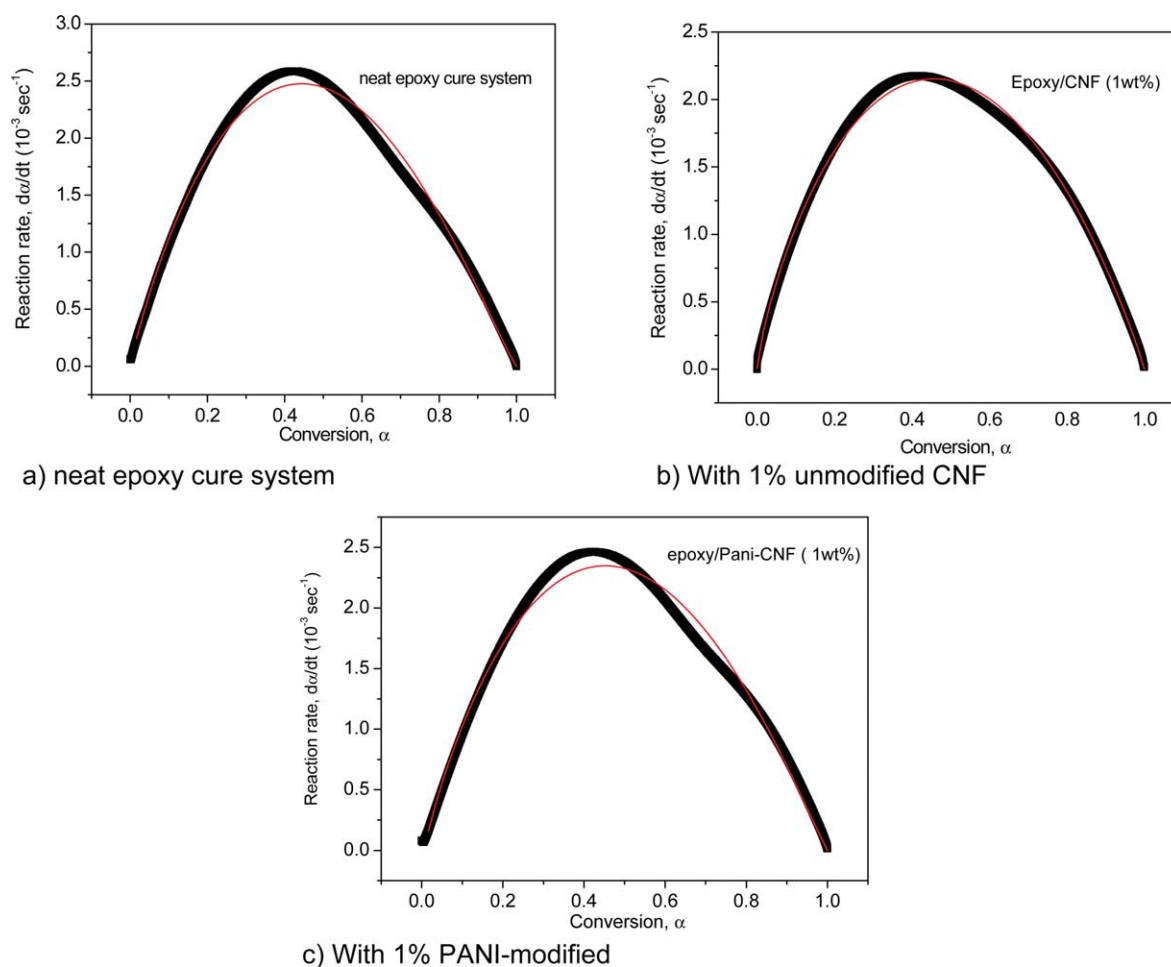


a) neat epoxy cure system



b) With 1% unmodified CNF



c) With 1% PANI-modified

**Figure 4** The experimental and fitting curves of $d\alpha/dt$ versus $\alpha$ for epoxy-diamine cure systems with or without CNF by non-isothermal DSC with the heating rate of 10°C/min. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

**TABLE II**
**Reaction Rate Constants and the Corresponding Reaction Orders Obtained by Fitting Non-Isothermal DSC Data (Scan Rate of 10°C/min)**

| Cure system | $k_1$ ($\times 10^{-6}$/sec) | $k_2$ ($\times 10^{-3}$/sec) | $m$ | $n$ |
|---|---|---|---|---|
| Neat epoxy | 3.89 | 2.24 | 0.78 | 1.12 |
| Epoxy/CNF | 1.28 | 2.78 | 0.83 | 0.93 |
| Epoxy/PANI-CNF | 3.07 | 3.83 | 0.86 | 1.07 |

(3) epoxy with 1 wt % PANI modified CNF. It can be seen that both unmodified and PANI modified CNF can accelerate the cure reaction of epoxy with diamine. The accelerating effect is typically observed by increasing the heat flow peak and the slope of heat flow-time curves. PANI-CNF accelerates the reaction rate much more than unmodified CNF.

Table I summarizes the values of $\Delta H_{total}$ and $T_E$ of different epoxy cure systems. From Table I, it can be learnt that CNF has a negligible effect (<2%) on the values of $\Delta H_{total}$ and $T_E$ of epoxy cure system.

It can be seen that PANI modified CNFs not only accelerate the cure reaction but also have a significant effect on the values of $\Delta H_{total}$ and $T_E$. This may be explained as follows. Epoxy reacts with primary and secondary amine groups and can be catalyzed by tertiary amine group as a Lewis base promoter according to the ring-open mechanism.[17] The epoxy-secondary amine reaction is the "fast" reaction, whereas epoxy-primary amine reaction is the "slow" reaction. Combined with secondary amine groups in PANI, the value of $T_E$ decreases significantly and the cure reaction of epoxy cure system is accelerated by PANI-CNF. Although the amount of PANI is very small (about 0.16% per unit weight of epoxy cure system, calculated by the PANI-CNF loading and the PANI percentage of PANI-CNF), a significant increase of $\Delta H_{total}$ of epoxy cure system is seen in the presence of PANI modified CNF. This is consistent with previous epoxy/PANI cure kinetic study.[18] PANI can react with epoxy as the curing agent and the reaction heat is dependent on the ratio of epoxy to PANI. In previous literature,[18] the reaction heat, $\Delta H$, of epoxy/PANI was measured as



**Figure 5** The experimental and fitting curves of $d\alpha/dt$ versus $\alpha$ for epoxy-diamine cure systems with or without CNF by means of isothermal cure at 45°C. [Color figure can be viewed in the online issue, which is available at www.interscience. wiley.com.]
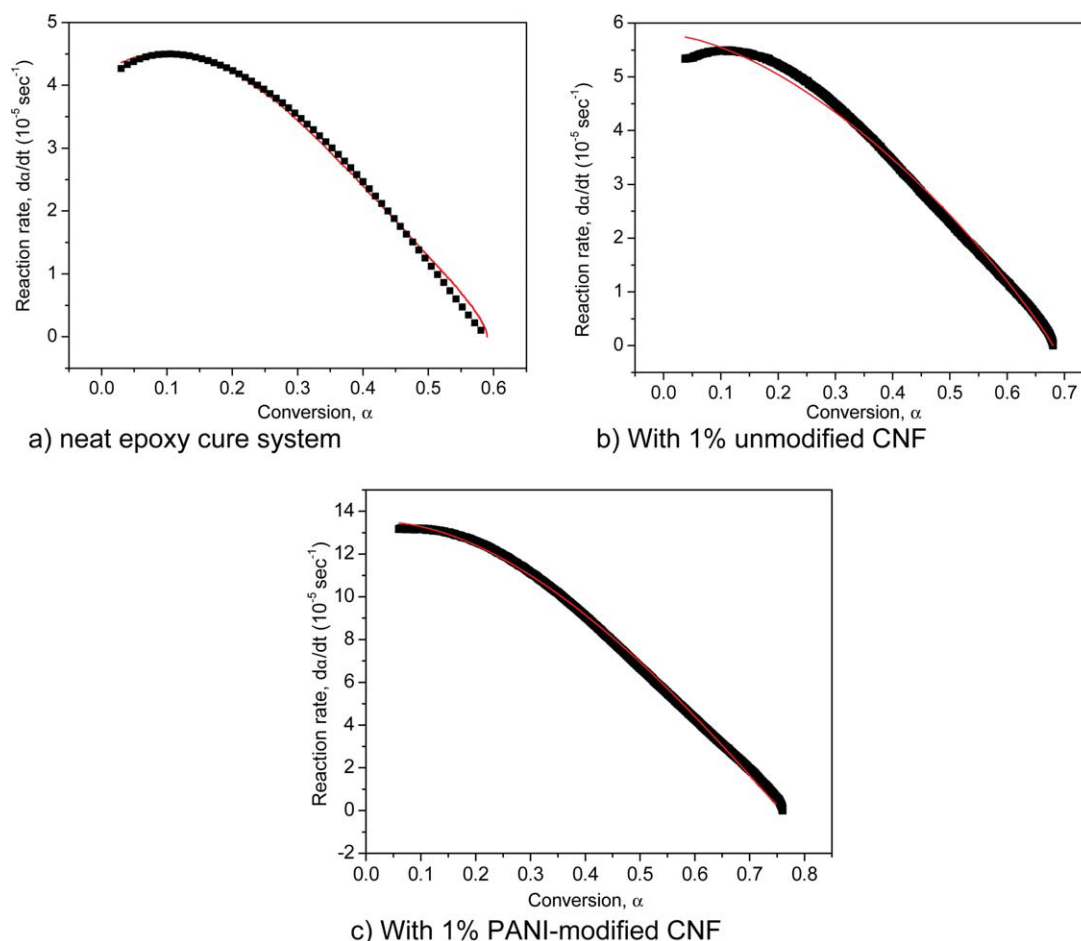
**Figure 6** The experimental and fitting curves of $d\alpha/dt$ versus $\alpha$ for epoxy-diamine cure systems with or without CNF by means of isothermal cure at 60°C. [Color figure can be viewed in the online issue, which is available at www.interscience. wiley.com.]
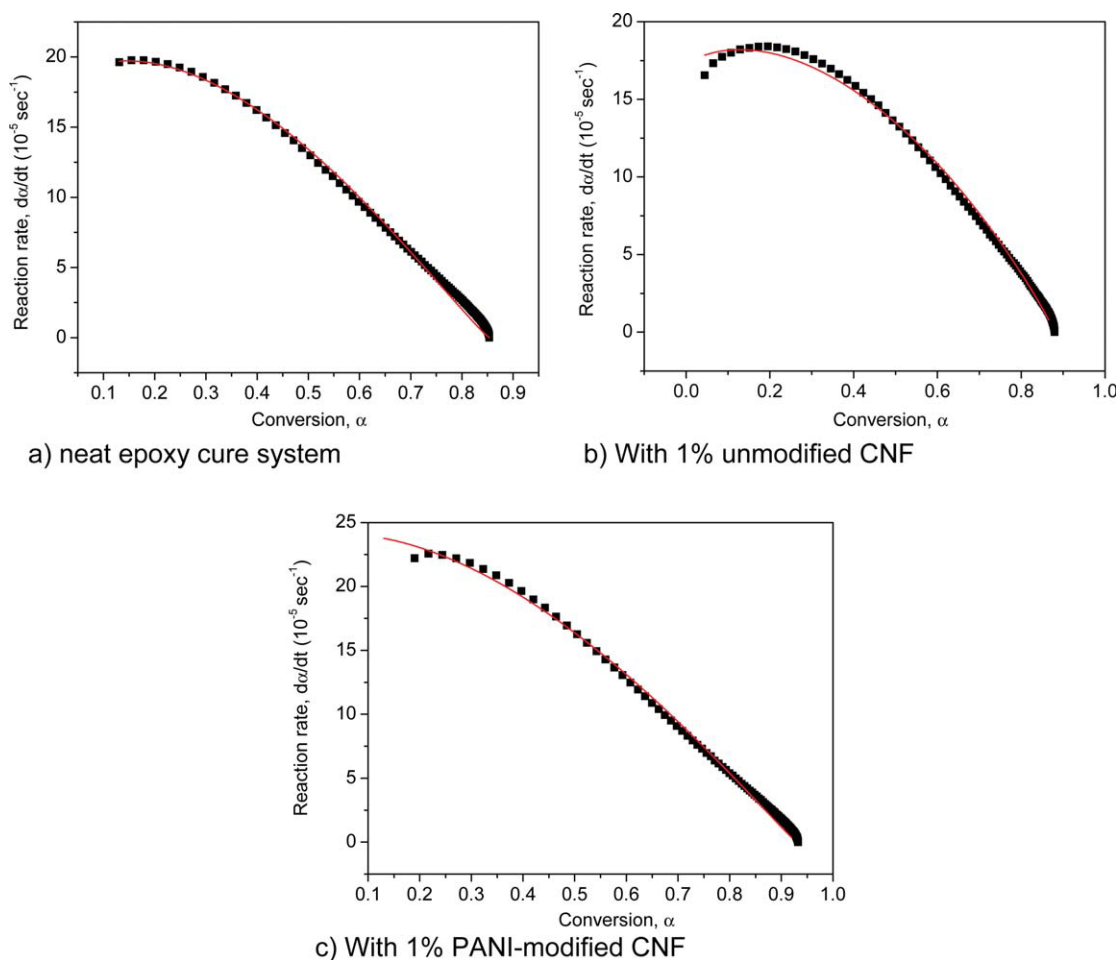
240 J/g when the weight ratio of epoxy to PANI was 25 (PANI's percentage equals about 3.85%), whereas ΔH was 420 J/g when the weight ratio was 15 (PANI's percentage equals about 6.25%). Hence, it can be deduced that small amounts of PANI can affect the reaction heat significantly during the reaction of epoxy with PANI.

The autocatalytic model was used to fit the experimental data. Figure 4 shows the experimental and fit curves of the reaction rate, $d\alpha/dt$, versus conversion, $\alpha$, for epoxy-diamine cure systems with or without CNF by means of non-isothermal DSC scan at a heating rate of 10°C/min. The thin line represents the fit data and the thick line represents the experimental data. Table II summarizes the fitting parameters.

The reaction rate constant is dependent on the reaction temperature, $T$, whereas the reaction mechanism is independent on $T$. So the reaction order values $m$ and $n$ obtained from the non-isothermal DSC data should be able to predict the isothermal DSC data. Figures 5–7 show the experimental and the fit-

ting curves of the reaction rate, $d\alpha/dt$, versus conversion $\alpha$ for epoxy-diamine cure systems with or without CNFs for isothermal cures at 45°C, 60°C, and 75°C, respectively.

Table III summarizes the reaction parameters of isothermal cure at different temperatures. From Table III, it can be seen that the initial and final conversions have similar trends in different epoxy cure systems. In all three cases, we found no residual heat was observed after isothermal cure at 75°C for 10 h.

According to eq. (6) and Table III, two activation energies, $E_{a1}$ and $E_{a2}$, were obtained by plotting ln $k_1$ and ln $k_2$ against $1/T$. The activation energy values are presented in Table IV. $k_1$ is the $n$th-order reaction rate constant and $k_2$ is the autocatalytic reaction rate constant. $k_1$ governs the early-stage reaction, whereas $k_2$ affects the autocatalytic reaction after the initial stage.[17,18] From Table IV, it can be seen that adding CNFs can lower both reaction activation energies. This is agreeable with the non-isothermal DSC cure with different epoxy systems, as shown in Figure 2. In both the nanocomposites (unmodified
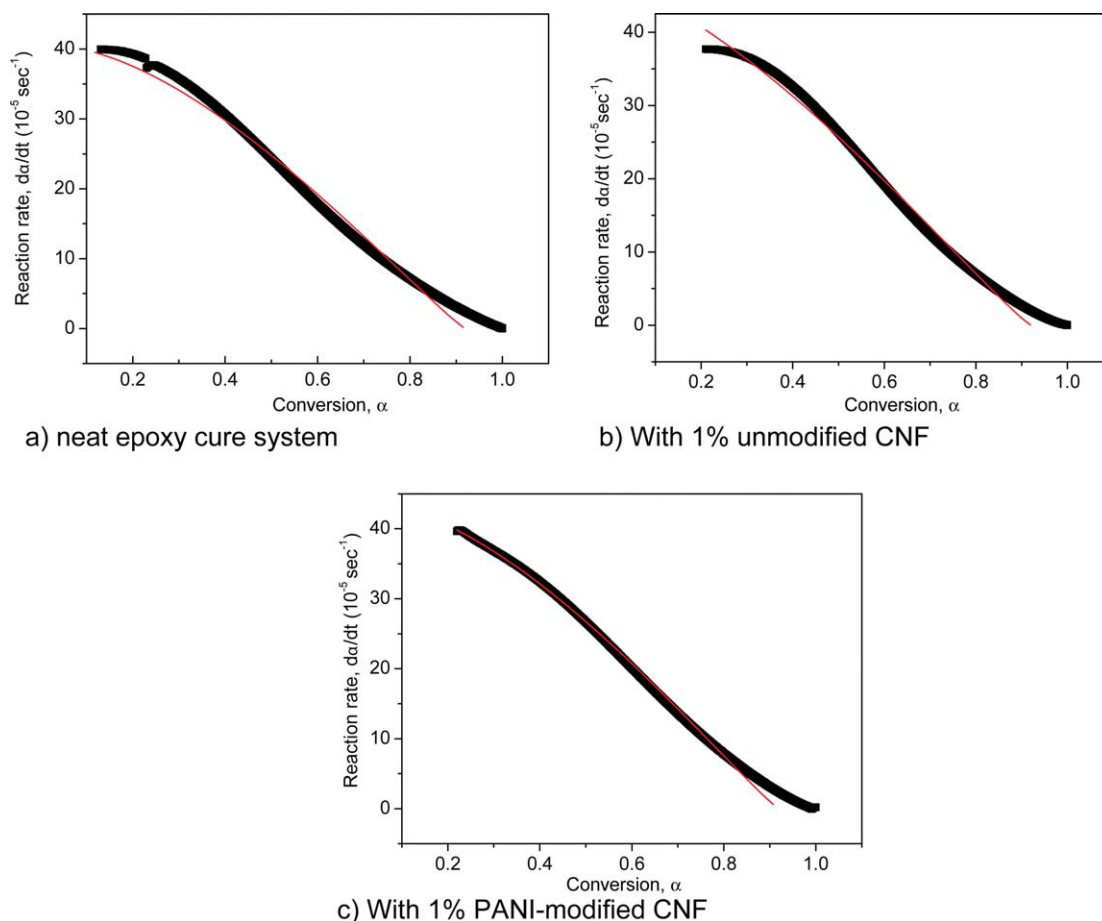
a) neat epoxy cure system



b) With 1% unmodified CNF



c) With 1% PANI-modified CNF

**Figure 7** The experimental and fitting curves of $d\alpha/dt$ versus $\alpha$ for epoxy-diamine cure systems with or without CNF by means of isothermal cure at 75°C. [Color figure can be viewed in the online issue, which is available at www.interscience. wiley.com.]

CNFs/epoxy and PANI modified CNFs/epoxy), $E_{a1}$ of epoxy cure reaction decreases dramatically, whereas $E_{a2}$ decreases only slightly. This suggests that the rate increase might be due to an accelerated process at the initial stage of the reaction. In this stage, hydroxyl groups of unmodified CNFs tend to

react with the epoxide group and open the rings of epoxide. Then, the etherification of opened epoxide rings with diamine can occur more easily than the reaction of epoxide with diamine directly. In the case of PANI-CNF, most hydrogen groups of CNF have been consumed by intermolecular interaction with amine groups of PANI. However, the PANI modification provides many secondary and tertiary amine groups which react with the epoxide ring. So both unmodified and PANI modified CNFs affect the reaction rate mostly in the early-stage initial stage. In the latter stage, the curing reaction is mainly between the opened epoxide ring and secondary amine obtained from the primary diamine curing agent. Xie et al.[19] obtained similar results in studying the effects of carbon nanotubes (CNT) on

**TABLE III**
**Reaction Rate Constants and the Corresponding Reaction Orders Obtained by Fitting Data from Isothermal Cure at Different Temperatures**

| Cure system | $k_1$ ($\times 10^{-3}$/sec) | $k_2$ ($\times 10^{-3}$/sec) | $\alpha_0$ | $\alpha_f$ |
|---|---|---|---|---|
| Neat epoxy | | | | |
| 45°C | 0.07 | 0.18 | 0.03 | 0.59 |
| 60°C | 0.20 | 0.39 | 0.10 | 0.85 |
| 75°C | 0.63 | 0.76 | 0.13 | 1.0 |
| Epoxy/CNF | | | | |
| 45°C | 0.08 | 0.07 | 0.03 | 0.68 |
| 60°C | 0.19 | 0.25 | 0.04 | 0.88 |
| 75°C | 0.35 | 0.56 | 0.15 | 1.0 |
| Epoxy/PANI-CNF | | | | |
| 45°C | 0.18 | 0.11 | 0.06 | 0.76 |
| 60°C | 0.25 | 0.27 | 0.19 | 0.93 |
| 75°C | 0.46 | 0.63 | 0.22 | 1.0 |

**TABLE IV**
**Activation Energies of Different Epoxy Cure Systems**

| Cure system | $E_{a1}$ (kJ/mol) | $E_{a2}$ (kJ/mol) |
|---|---|---|
| Neat epoxy | 65.98 | 67.38 |
| Epoxy/CNF | 45.41 | 64.02 |
| Epoxy/PANI-CNF | 28.66 | 53.58 |

cure kinetics of a phenolic-epoxy reaction. They found that $E_{a1}$ of the epoxy cure reaction decreased about 20 kJ mol$^{-1}$ and $E_{a2}$ remained almost same by adding 1 wt % CNT. From Table IV, it can also be seen that both activation energies of epoxy cure reaction with PANI-CNF decrease much more than those with unmodified CNF.

## CONCLUSIONS

In this work, the low temperature cure reaction of epoxy EPIKOTE$^{TM}$ RIM 135 and L 137 with unmodified and PANI modified CNFs was investigated by non-isothermal and isothermal DSC. To investigate the effect of CNFs on the epoxy cure reaction, an autocatalytic cure kinetic model was proposed and analyzed.

It was observed that both unmodified and PANI modified CNFs can accelerate the cure reaction of epoxy with diamine. By means of an autocatalytic cure kinetic model, the activation energies of epoxy cure reaction were obtained and compared. It was studied that both the activation energies of epoxy cure systems were decreased in the presence of unmodified and PANI modified CNFs. The PANI modified CNFs accelerated the epoxy curing reaction much more than the unmodified CNFs.

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