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Effect of Non-Woven Carbon Nanofiber Mat Presence on Cure Kinetics of Epoxy Nanocomposites

Darunee Aussawasathien,[*1] *Erol Sancaktar*[2]

Summary: An investigation was carried out into the cure kinetics of carbon nanofiber (CNF) mat-epoxy nanocomposites, composed of bisphenol-A based epoxy resin and diethylene triamine as a curing agent. It was observed that the rate of cure reaction for CNF mat-epoxy nanocomposites was higher than that for neat epoxy resin at low curing temperatures and the presence of the CNF mat produced the maximum influence at a certain curing temperature and time. At high curing temperature and long curing times, the effect of CNF mat on the cure rate was insignificant. The CNF mat-epoxy composite exhibited somewhat lower value of activation energy than that of the neat epoxy system at the beginning of the curing stage. The weight fraction of CNF mat also affected the cure reaction of epoxy nanocomposites at the same curing temperature. As the amount of CNF mat increased, the cure rate was higher at the same cure time. However, at high CNF mat loading, the cure reaction was retarded since the amount of epoxy and hardener decreased dramatically at high CNF contents together with the hindering effect of the CNF mat on the diffusion of epoxy resin and the curing agent, leading to lower crosslinking efficiency. Although the curing efficiency of epoxy nanocomposites dropped at high CNF mat content, the glass transition temperature (T_g) was still high due to the ultra-high strength of the CNF mat. The cure kinetics of CNF mat-epoxy nanocomposites was in good agreement with Kamal's model.

Keywords: calorimetry; carbon nanofiber mat; curing of polymer; epoxy; nanocomposites

Introduction

Carbon nanofibers are classified as a novel super-strong material and suitable to be used as reinforcement in composite materials. At present, CNFs are generally produced by the vapor-grown carbon method, based on the catalytic decomposition of hydrocarbons in the vapor phase. However, vapor-grown CNFs (VGCNFs) cannot be made in continuous fiber form, thus having limited ranges of properties and applications. Recently, CNFs based on electrospun polymer (i.e. polyacrylonitrile (PAN)) nanofibers manufactured using the electrospinning technique have been extensively studied. The electrospinning technique can generate CNFs with extraordinary properties such as high surface area, high aspect ratio, and high interconnecting network.[1–3]

There have been a number of experimental studies, using differential scanning calorimetry (DSC), to determine the effect of reinforcing fillers such as glass fibers, VGCNFs, and carbon nanotubes on the cure reaction of the epoxy and its composites.[4–7] It was found that carbon nanotubes have significant effects on the cure reaction of epoxy system consisting of tetraglycidyl-4,4′-diaminodiphenylmethane (TGDDM) and 4,4′-diaminodiphenylsulfone (DDS) as curing agents, whereas the presence

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[1] National Metal and Materials Technology Center, 114 Thailand Science Park Paholyothin Rd., Klong 1, Klong Luang, Pathumthani 12120, Thailand
Fax: (+66) 256 46338;
E-mail: daruneea@mtec.or.th

[2] Department of Polymer Engineering, University of Akron, OH 44325-0301, USA

of VGCNFs had only a negligible effect on the cure kinetics of this epoxy system.[8,9] Attempts to reinforce composites by adding VGCNFs have often been unsuccessful.[4] The curing mechanism deteriorated by the presence of VGCNFs. Cures at equivalent catalyst concentrations in the vinyl ester resin proceeded more slowly in the presence of VGCNFs and this became more pronounced as the amount of VGCNFs was increased. The addition of more catalyst was shown to compensate for this loss of activity. The precise deactivation route is not known. Perhaps catalyst adsorption or deactivation occurred on the fiber surfaces as the fiber loading increased, thus ultimately deteriorating physical properties.

Due to its unique electrospun nanofibers properties mentioned above combined with high thermal conductivity of CNFs (8–70 W/m.K versus 0.15–0.17 W/m.K for epoxy resin), we expect non-woven CNF mats to influence the cure reaction of its composites with epoxy resins. In this work, the DSC was utilized as a tool to determine the cure kinetics of epoxy resin reinforced by electrospun PAN fibers based CNFs non-woven mat. For this purpose, we assumed that the heat evolution monitored and recorded by DSC is proportional to the extent of consumption of the epoxide group in the epoxy resin or the amine group in the curing agent. The data were generated from both isothermal and dynamic DSC measurements during curing.

Experimental Part

A DSC (Thermal Advantage 2920) was used for the dynamic and isothermal curing experiments and data analysis under N_2 flow. The heating rate of 10 °C/min was applied to the sample for the dynamic-cure study and the sample was scanned over the temperature range of 25 °C to 300 °C. After first thermal scanning, the sample was quenched to −10 °C using liquid nitrogen and immediately the second thermal scan was started with the same temperature range as of the first scan. Glass transition temperature (T_g) was estimated at the onset point of an endothermic shift from the second scan, while the curing temperature was estimated from the extrapolated mid-point of the exothermic peak from the first scan.

The isothermal curing experiments were conducted at four temperatures (40, 50, 60, and 70 °C). The reaction was considered complete when the signal leveled off to the baseline. The total area under the exothermic 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 using liquid nitrogen to −10 °C and then reheated at 10 °C/min to 300 °C to determine the residual heat of reaction, ΔH_r (J/g). An aluminum hermetic pans was filled with 80 %wt by EPON 815C, from Shell Chemicals, which was added with 20 %wt by diethylenetriamine (DETA, Epikure 3290 from Resolution Performance Products), and subsequently, by CNF mat.[10] The weight fractions of CNF mat in the epoxy system were varied, approximately, as 0, 1.43, 2.86, and 5.41 %wt.

The gel fraction of the cured epoxy resin and its composites was measured using the solvent extraction method (ASTM D 2765-84).[11]

Results and Discussion

The effect of CNF mat on the cure reaction of epoxy nanocomposits was studied at different temperatures as seen in Figure 1. Figure 1 demonstrates that the residual heat of reaction from subsequent dynamic scan for each isothermal cure decreases as the curing temperature was increased for both neat resin and its CNF mat composites and then go to approximately zero when the complete cure occurred at about 70 °C for 1 h isothermal cure. The epoxy nanocomposites containing CNF mat yielded lower residual heat of reaction when compared to that of the neat epoxy resin for the curing temperature lower than 70 °C. The large

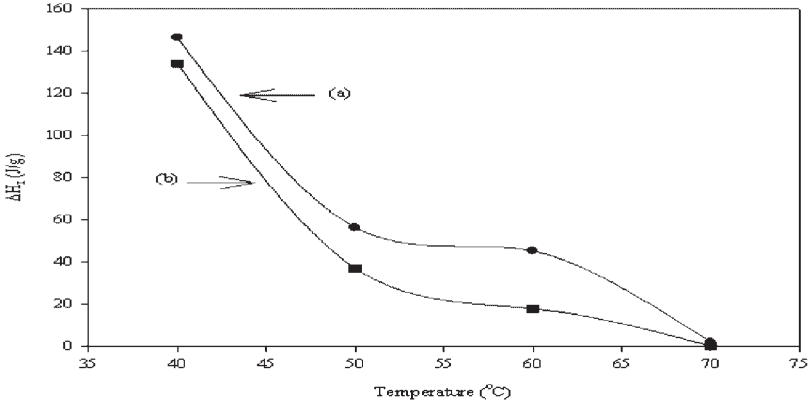

Figure 1.
Residual heat of reaction (ΔH_r) versus curing temperature for: (a) neat epoxy resin, and (b) 2.86 %wt CNF mat-epoxy nanocomposites after isothermal cure for 1 h at various curing temperatures (40, 50, 60, and 70 °C).

extent of residual heat difference between the neat epoxy resin and its composites was obtained for 1 h isothermal cure at 60 °C, which was about 60% difference.

This result implies that the curing reaction can be completed at shorter time for the CNF mat-epoxy nanocomposites compared with the neat resin at the same curing temperature as obviously seen in Figure 2. At the same curing temperature and curing time, the CNF mat-epoxy composite exhibited lower residual heat of reaction than the neat epoxy sample. Especially in the middle of the reaction, the vast extent of difference was obtained. For example, the large amount of residual heat difference was clearly evident at about 120 min for isothermal cure at 50 °C.

Figure 3 represents the effect of CNF mat contents on the curing reaction. It can be obviously observed that as the amount of CNF mat increases the residual heat decreases and then levels off at a certain amount of CNF mat for the studied conditions. However, it could be possible that the curing reaction would be decelerated at high CNF mat loading. There are two competitive effects derived from CNF mat: a) catalytic effect due to high thermal conductivity of CNF mat, and b) chemical absorption effect which might be dominant at high CNF mat content. When the extent

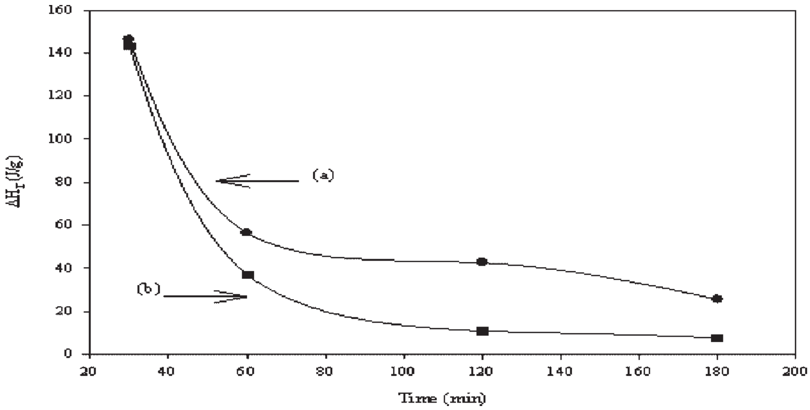

Figure 2.
Residual heat of reaction versus curing time for: (a) neat epoxy resin, and (b) 2.86 %wt CNF mat-epoxy nanocomposites after isothermal cure at 50 °C for various curing times (30, 60, 120, and 180 min).

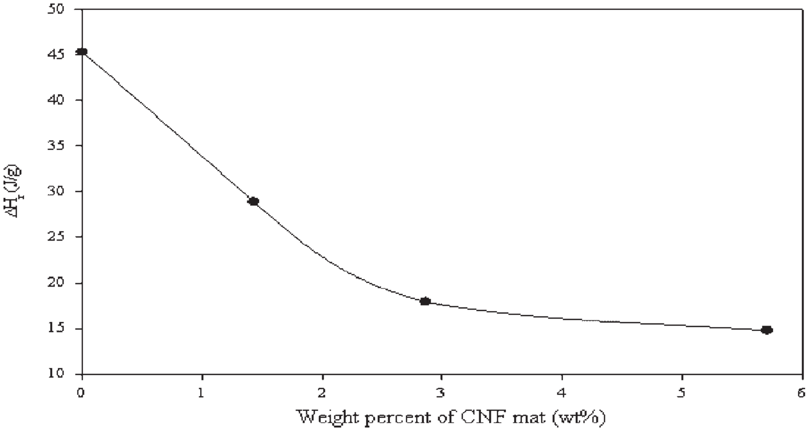

Figure 3.
Residual heat of reaction versus CNF mat contents (0, 1.43, 2.86, and 5.41 %wt) after isothermal cure at 60 °C for 1 h.

of CNF mat went up, CNF mat largely hindered the diffusion of reactants, consequently retarding the curing reaction.

It is demonstrated in Figure 4 that the gel content slightly increased about 1.0% as the amount of CNF mat increased up to 6.0 %wt for the cure conditions at 100 °C for 1 h. This may result from high thermal conductivity and surface area of CNF mat, which can induce faster heat transfer rate, accelerating the curing reaction. However, when the CNF mat loading was increased to 10 %wt, the gel content dropped rapidly since the amount of epoxy and hardener decreased dramatically at high CNFs contents together with the hinder effect of CNF mat to the diffusion of epoxy resin and curing agent, leading to low crosslinking efficiency.

The average values of total heat of reaction, ΔH_T, and T_g from 2^{nd} temperature scan after rapid cooling (no residual heat of reaction identified by the absence of exothermic peak) obtained for each CNF mat content in the composites and neat epoxy system are presented in Table 1. Total heat of reaction decreased as the CNF mat contents increased, which is the evident for the assumption that CNF mat impeded the cure reaction at some degrees. However, the presence of the CNF mat had the positive effect on the T_g of nanocomposites,

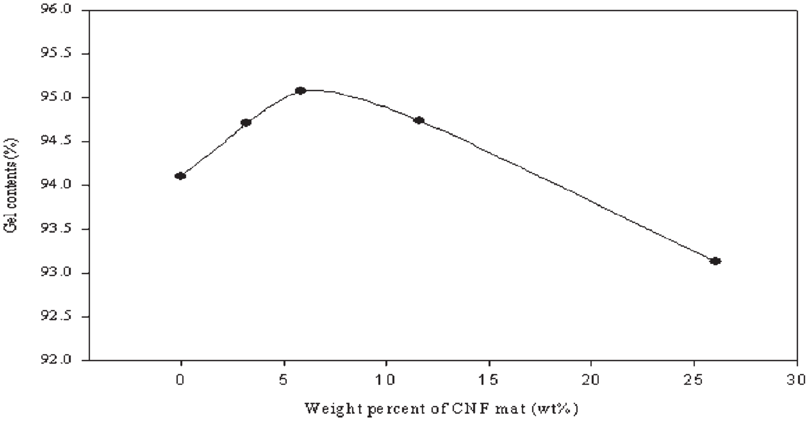

Figure 4.
Gel contents of Epon815C-Epicure3290 and its composites with CNFs at different loadings, cured at 100 °C for 1 h.

Table 1.
Total heat of reaction (ΔH_T) and glass transition temperature (T_g) of Epon815C-Epicure 3290 system at different CNF mat contents.

CNF mat content (%wt)	ΔH_T (W/g)	T_g (°C)
0	435.2	67.9
2.86	392.1	70.5
5.41	380.5	76.0

showing higher T_g value compared with neat epoxy system at high amount of CNF mat content. This can be contributed to the ultra-high strength of CNF mat in nature.

Figure 5 demonstrates typical isothermal DSC curves for epoxy resin and its composite filled with non-woven CNF mat at 50 °C. Initially, the CNF mat-epoxy composite yielded higher heat reaction and then decay to roughly the same level compared with the neat resin. Figure 6 shows typical plots of reaction rate ($d\alpha/dt$) versus time at 50 °C for the neat epoxy resin and its nanocomposite. The reaction rate is tended to increase with time and passed through a maximum while the reaction rate peak became higher and shifted to lesser times with the presence of CNF mat. The

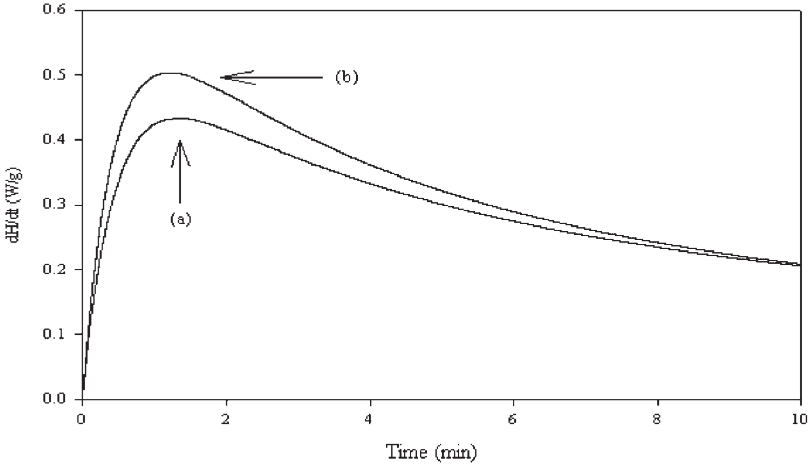

Figure 5.
Isothermal DSC curves for: (a) neat epoxy resin, and (b) 2.86 %wt CNF mat-epoxy nanocomposite at 50 °C.

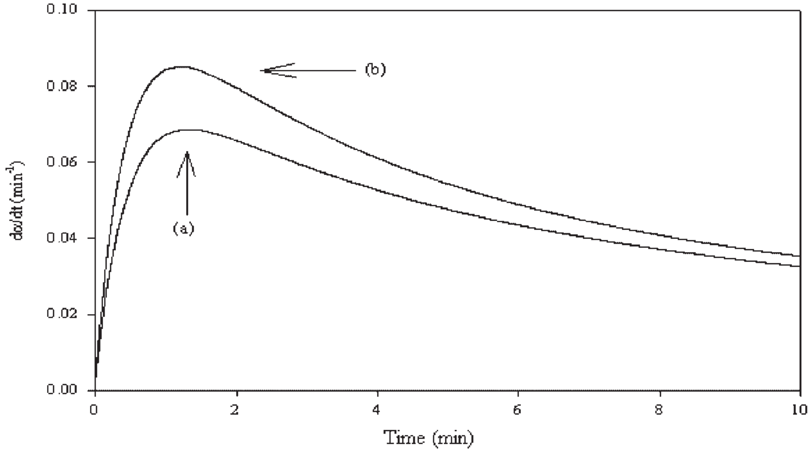

Figure 6.
Reaction rate versus time curves for: (a) neat epoxy, and (b) 2.86 %wt CNF mat-epoxy nanocomposites at 50 °C.

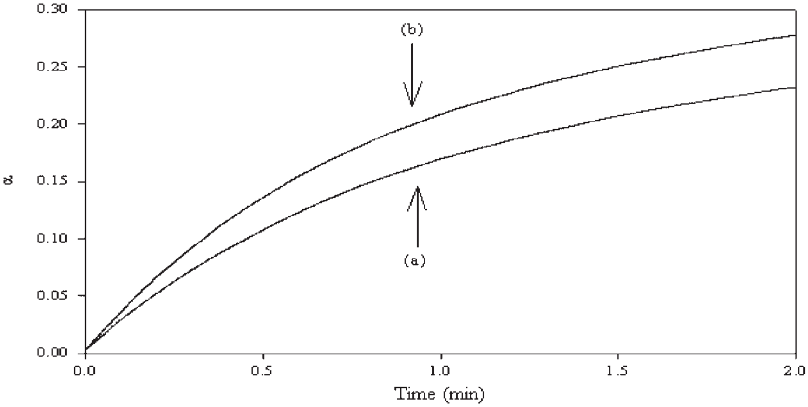

Figure 7.
Conversion versus time curves for: (a) neat epoxy, and (b) 2.86 %wt CNF mat-epoxy nanocomposite at 50 °C.

same behavior was also applied to the plot of conversion versus time at 50 °C for the neat epoxy resin and its composite (Figure 7).

Figure 8 shows DSC data on the pristine epoxy-amine system and its composites with CNF mat as a reinforced-filler plotted as dα/dt versus α at 50 °C. It is obviously

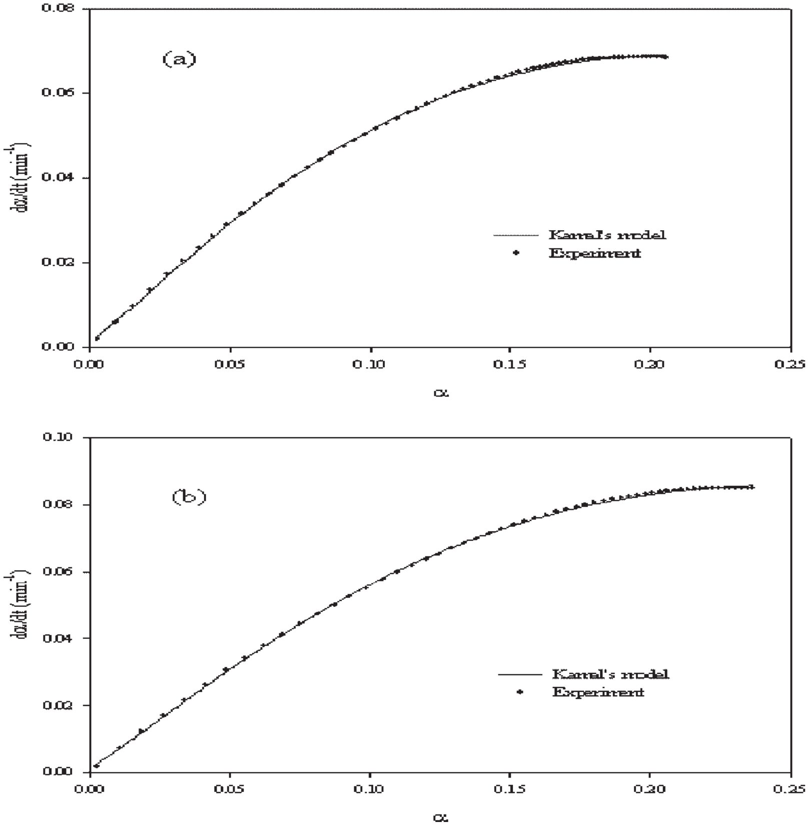

Figure 8.
Reaction rate versus conversion curves with model predictions at 50 °C for: (a) neat epoxy, and (b) 2.86 %wt CNF-epoxy composite.

seen that the maximum rate was observed at conversion around 20–25%, as expected for autocatalytic reaction (20–40%). The kinetics of autocatalyzed reactions are described by the following equation,[12] Kamal's model:

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

where m and n are reaction orders and $m + n$ is the overall order, k_1 and k_2 are the rate constants. The cure fitting of the reaction rate and the conversion prediction for isothermal experiments in this study using Kamal's model was precisely obtained.

The rate constant is temperature dependent through an Arrhenius relationship given by:

$$k = A\ \exp(-E/RT) \qquad (2)$$

where A is the preexponential factor, E is the activation energy, R is the gas constant, and T is the absolute temperature.

The activation energy could be obtained from the slope of the plot between ln(k) and 1/T (Figure 9). The values of the activation energies for neat epoxy and its composite are listed in Table 2. Compared with the neat epoxy, the CNF mat-epoxy nanocomposites exhibited slightly lower activation energy for k_1, which governs the early stage autocatalytic reaction. In this study, the cure reaction for short period at quite low temperature was carried out, which could not get complete cure, therefore the activation energy after the initial autocatalytic stage, which is derived from k_2 could not be observed.

Table 2.
Activation energies and preexponential factors for neat epoxy resin and 2.86 %wt CNF mat-epoxy composite.

CNF (%wt)	E_1 (kJ/mol)	ln (A_1)
0	51.48	12.9
2.86	46.44	11.0

Conclusion

The rate of cure reaction of CNF mat-epoxy nanocomposites was higher than neat epoxy resin at low curing temperature and exhibited the maximum influence at the certain curing temperature and time. The content of CNF mat also affected the cure reaction of the epoxy nanocomposite at the same curing temperature. The presence of non-woven CNF mat in the composites enhanced the cure reaction in terms of residual heat, heat flow rate, reaction rate, and conversion at the initial stage of the cure course at the same cure temperature and time, compared with the neat epoxy resin. The CNF mat-epoxy

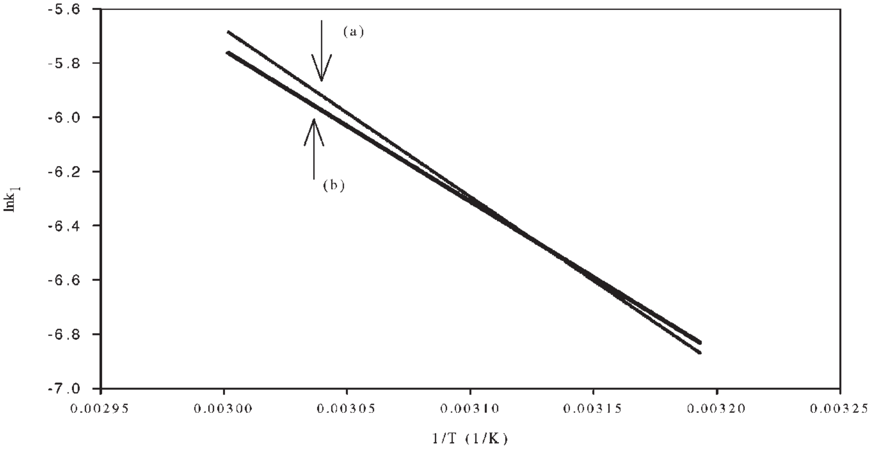

Figure 9.
Curves of ln (k_1) versus 1/T for: (a) neat epoxy resin, and (b) 2.86 %wt CNF-epoxy composite.

composite exhibited somewhat the lower value of activation energy than that of the neat epoxy system at the beginning of curing stage. At high CNF mat loading, the cure reaction was retarded since the amount of epoxy and hardener decreased dramatically at high CNFs contents together with the hinder effect of CNF mat to the diffusion of epoxy resin and curing agent, leading to low crosslinking efficiency. Although, the curing efficiency of epoxy nanocomposites dropped at high CNF mat content but the T_g was still high due to the ultra-high strength of CNF mat in nature.

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[1] Y. Wang, S. Serrano, J. J. Santiago-Avilés, *Synth. Met.* **2003**, *138*, 423.
[2] Y. Wang, J. J. Santiago-Avilés, *Carbon* **2003**, *41*, 2653.
[3] C. Kim, S.-H. Park, J.-I. Cho, D.-Y. Lee, T.-J. Park, W.-J. Lee, K.-S. Yang, *J. Raman Spect.* **2004**, *35*, 928.
[4] J. Mijovic, *J. Appl. Polym. Sci.* **1986**, *31*, 1177.
[5] M. F. Grenier-Loustalot, P. Grenier, *Polymer* **1992**, *33*, 1187.
[6] J. Mijovic, H. T. Wang, *J. Appl. Polym. Sci.* **1989**, *37*, 2661.
[7] M. Opalicki, J. M. Kenny, L. Nicolais, *J. Appl. Polym. Sci.* **1996**, *61*, 1025.
[8] H. F. Xie, B. H. Liu, Z. R. Yuan, J. Y. Shen, R. S. Cheng, *J. Polym. Sci. Part B: Polym. Phys.* **2004**, *42*, 3701.
[9] O. S. Carneiro, J. A. Covas, C. A. Bernardo, G. Caldeira, F. W. J. Hattum, J. M. Ting, R. L. Alig, M. L. Lake, *Comp Sci Tech.* **1998**, *58*, 401.
[10] D. Aussawasathien, E. Sancaktar, ASME International Mechanical Engineering Congress and Exposition, Orlando, FL, **2005**.
[11] ASTM Standard D 2765-84.
[12] H. Xie, B. Liu, Q. Sun, Z. Yuan, J. Shen, R. Cheng, *J. Appl. Polym. Sci.* **2005**, *96*, 329.