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Cure kinetics behavior of a functionalized graphitic nanofiber modified epoxy resin

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ABSTRACT

Understanding curing behavior of nano-modified thermoset resin is critical for many applications. An appropriate incorporation of nanoparticles can stimulate improvements to many properties of epoxy resins when used as matrices in fiber reinforced composites. In this study, the curing behavior of an epoxy resin modified by a type of reactive graphitic nanofibers (r-GNFs), that were previously developed, was characterized using a dynamic differential scanning calorimetry (DSC) method. The activation energy of pure epoxy resin and the r-GNF modified epoxy resin during the cure reaction was determined based on a model-free method. The results from DSC kinetic analysis indicated that the addition of the r-GNFs offered a catalytic action for cure reaction of epoxy resin at high temperature range so that a larger extent of cure was obtained over pure epoxy. The faster curing behaviors of the r-GNF modified epoxy system will be essential for enabling future energy efficient infusion processing for manufacturing high quality and high performance structural composite applications.

1. Introduction

Epoxy resin, as the most widely used matrix material for structural fiber-reinforced polymer (FRP) composites, due to its excellent processability and properties [1–3], is an appropriate candidate material for making further improvements through new technology involving nano-scale additives. In manufacturing an FRP, the curing reaction first occurs such as to form optimal adhesion between the matrix and fibers and is very important in determining the mechanical properties of the end composite products. Therefore, cure kinetics of the matrix material is a key parameter for manufacturing high-performance FRP composites.

In order to meet the ever higher structural performance requirements for new FRP composite applications, the performance of epoxy resin needs to be further promoted to match the advanced performance of the fiber reinforcements. For many applications, including those in the demanding aerospace industry, the rapid development of nanoscience and technology offers the possibility to produce materials with properties that would be unattainable by traditional means. The use of carbon nanotubes (CNTs) or graphitic carbon nanofibers (CNFs or GNFs) as polymer reinforcements is a particularly attractive option to enhance the properties of the polymer matrices. The addition of nano-fillers can influence the interaction of the polymer matrix with fiber reinforcements and the curing process of the resin matrix itself can be changed. The processing behavior of matrix materials with nanofillers is significantly different from those of a neat polymer matrix, and so an understanding of curing performance of the nano-modified epoxy matrix can hence contribute to an improved design and manufacturing for the resulting composite parts.

In past decades extensive studies concerning mechanisms and kinetics of epoxy resin cure have been presented in the literature. Kinetic analyses of pure epoxy resin cures from differential scanning calorimetry (DSC) data have reported a wide range of activation energy values (28–158 kJ/mol) [4,5]. Although variation in activation energy for pure epoxy resin appears to be common, some reports gave approximately constant activation energy values during the cure reaction [6,7]. On the other hand, with rapid development of nanocomposites, recent studies have also been dedicated to understanding the effects of carbon nanofillers on the cure kinetics of epoxy resins [8–12]. To date, several researchers have studied the curing kinetics of epoxy systems with CNF concentration levels about 1–5 wt% [8,12]. In these investigations, there have been a number of inconsistent conclusions and conflicting explanations proposed for the reaction mechanisms of an epoxy resin system with nanofillers. In summary, the effects of carbon nanofillers on the cure behavior of epoxy resins are still not conclusive.

Despite the considerable current research efforts in the field of epoxy resin based composites, numerous issues have yet to be addressed. For example, most reported experimental studies on epoxy-based nanocomposites have focused on mechanical property evaluations of the composites using higher than 2 wt% CNTs.

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A kind of nano-epoxy reinforced with a type of reactive graphitic nanofibers (r-GNFs) was previously developed in our group [13,14]. Our previous research also showed that epoxy matrix with 0.3 wt% r-GNF loading (called nano-epoxy) possessed greatly enhanced comprehensive performance with broad ranges of improvement [13–19], in particular, this nano-modified epoxy resin has been shown to have great potential for the application in FRP as matrix through an energy efficient resin infusion technology [20,21]. Therefore, it is a fertile field to carry out studies on the curing kinetics for the nano-epoxy resin. To our knowledge, whether and how a small amount (<1 wt%) of carbon nanofibers with functional groups impact the curing characteristics of the epoxy resins has not been reported except for our previously published paper [22]. In our previous study, a constant activation energy method was assumed and finally led to a conclusion that addition of r-GNFs slightly increased activation energy of epoxy system during the curing process [22]. However, extensive studies on curing kinetics of epoxy resins indicated that activation energy during the curing process of epoxy resin was not necessarily a constant [4,5,8–11,23]. Attaining a clear understanding of the curing processes of the nano-epoxy will be important for its practical application in making FRP.

In this study, we investigated the effect of the r-GNFs with low loading levels on cure kinetics of epoxy resin system. Further, a model-free method without assumption of constant activation energy during curing process was used to investigate how GNFs with low loading levels influenced the cure kinetics of epoxy system. By comparing with that predicted by the constant activation energy method, the experimental findings provided the detailed information for understanding curing mechanisms of the r-GNFs modified epoxy system and hence were of practical importance.

2. Experimental

2.1. Materials

The epoxy (EPON 828), a type of liquid diglycidyl ether of bisphenol A (DGEBA) epoxy resin, was first mixed with the curing agent (EPIKURE W), an aromatic diamine curing agent, at the stoichiometric ratio (24 parts amine to 100 parts epoxy by weight) as control samples. The corresponding chemical structures of epoxy resin and curing agent were shown in Fig. 1. Graphene plate edges exposed on the GNFs surface provide potential reactive sites for introducing other functional groups. With the attachment of 3,4′-oxydianiline (ODA) linker molecules on their surface, the functionalized graphitic nanofibers (GNF-ODA) were prepared by Vanderbilt University [19,24]. Its basic structure is shown in Fig. 2.

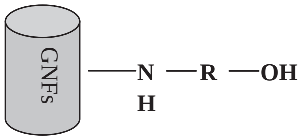


Fig. 2. Reactive graphitic nanofibers in the liquid nano-reinforcement (LNR).

The prepared r-GNF solutions (also called liquid nanoreinforcement, or LNR) were further mixed with one control sample to form the r-GNF modified epoxy samples with 0.3 wt% fiber loadings. To uniformly disperse the r-GNFs in the samples, a glass rod was first used to stir the mixture at room temperature until the samples turned black and then degassed in a vacuum oven to remove the air include during the mixing process, and finally followed by sonication for 1 h. Ice cubes were added every 10 min to prevent the pre-cure reaction during the sonication process.

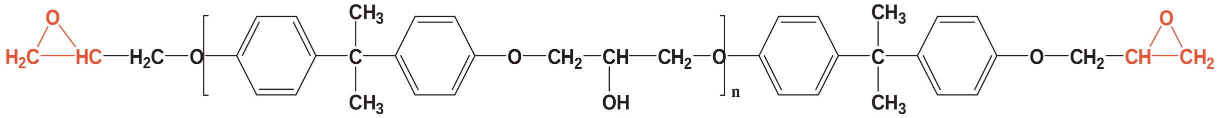
2.2. Measurements

About 8–10 mg of the r-GNFs modified epoxy and pure epoxy samples were weighed and loaded onto the aluminum crucibles. The lid was sealed onto the crucible and then the sample was immediately placed in the DSC furnace. For every curing experiment, a fresh mixture of curing agent and epoxy samples with the r-GNF solutions was used. To establish thermal equilibrium of the DSC, prior to starting the DSC measurements a settling time of about 30 s was set. All DSC curing experiments were taken with a dry nitrogen gas flow of 80 mL/min. Thermal analysis was performed using a TA instruments (TA 2920 Differential Scanning Calorimeter). Dynamic scans of the sample were made at the rates of 2, 5, 8, and 10 °C/min, respectively, over a temperature ranging from 25 °C to 320 °C. Runs were taken using an empty cell as a reference. DSC analysis for each sample was repeated three times. The corresponding reaction was assumed to end when the rate curve leveled off to the baseline. The heat flow data, which is a function of temperature and time, were achieved by integrating the area under the peak of the exotherm. These data were further processed to extract the fractional conversion and the rate of reaction.

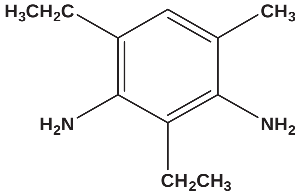
3. Cure kinetic studies of nano-epoxy versus pure epoxy

3.1. Kinetic models

In DSC a basic assumption for cure kinetics is that heat flow (dH/dt) relative to the instrumental baseline is proportional to the



(1)



(2)

Fig. 1. Chemical structures of (1) EPON 828 ($n = 0.2$) and (2) EPICURE W.

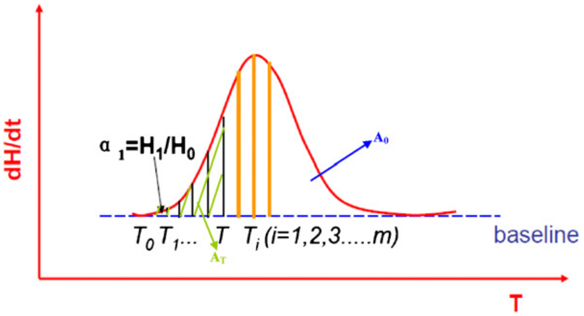


Fig. 3. A typical DSC curve for an exothermic cure reaction.

cure reaction rate ($d\alpha/dt$). In the temperature scanning experiments the heat capacity of the sample contributes to the heat flow, and this is compensated by the use of an appropriate baseline under the exothermic or endothermic peak produced by the reaction. A typical DSC scan for an exothermic cure reaction is shown schematically in Fig. 3.

In order to determine the evolution of the epoxy cure for modeling, the degree of cure at a given temperature (α) can be expressed as Eq. (1):

$$\alpha = \frac{A_T}{A_0} = \frac{H_T}{H_0} \tag{1}$$

where A_0 is the total area between the exothermal cure and the baseline, A_T is the area between the exothermal cure and the baseline at a given temperature (T), H_0 is the total heat of the reaction during the whole cure reaction, H_T is the heat of the reaction of partially cured samples at a given temperature (T).

The rate of conversion $d\alpha/dt$ at a given temperature T can be given as Eq. (2):

$$\frac{d\alpha}{dt} = \frac{dH/dt}{H_0} \tag{2}$$

Without knowing the exact reaction mechanism, it is reasonable to assume that the reaction rate at a given time is only a function of the conversion fraction (α) and temperature (T) [25]. A general expression often used in the analysis of DSC kinetic data [26] is

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \tag{3}$$

where at a given time and temperature $f(\alpha)$ is some function of the fractional conversion (α). The apparent rate constant (k) is dependent on temperature and usually assumed to be of the Arrhenius form:

$$k(T) = A\exp\left(-\frac{E}{RT}\right) \tag{4}$$

where A is a constant, R is the gas constant (8.31 J/mol K), E is the apparent activation energy, and T is the absolute temperature.

For nonisothermal DSC tests of thermosetting resin cure, the kinetic parameters can be determined from multiple heating rate scans. By the proper transformation, the above equation becomes

$$\frac{d\alpha}{dT} = \frac{A}{\beta}\exp\left(-\frac{E}{RT}\right)f(\alpha) \tag{5}$$

where $\beta = dT/dt$ is a constant heating rate.

From Eq. (5), it is seen that this equation has no exact analytical solution. Therefore, some necessary mathematical methods have been developed to deal with it so that the corresponding kinetic behaviors of cure reaction can be described. Two kinetic methods widely used to study dynamic kinetics of thermosetting polymers are model-fitting and model-free methods [27–31].

In the model fitting methods the nth order and the autocatalytic models are commonly used for simple reactions, i.e. $f(\alpha) = (1-\alpha)^n$ and $f(\alpha) = \alpha^m(1-\alpha)^n$. From a single DSC dynamic scan, the values of α and $d\alpha/dt$ and corresponding temperature T are used to solve the kinetic parameters by multiple linear regression. A disadvantage of this method is that the particular kinetic models have to be first assumed, however, for an unknown system, this assumed prerequisite is problematic.

The model-free method for the analysis of data from temperature scans is based on integral form of Eq. (5):

$$\int_0^\alpha \frac{d\alpha}{f(\alpha)} = \left(\frac{A}{\beta}\right)\int_{T_0}^{T} \exp\left(-\frac{E}{RT}\right)dT \tag{6}$$

which may be still written as

$$g(\alpha) = \left(\frac{A}{\beta}\right)\int_0^{T} \exp\left(-\frac{E}{RT}\right)dT = \frac{A}{\beta}G(T) \tag{7}$$

The right-hand side of Eq. (7) can be reduced to an exponential integral by substituting $x = E/RT$ to give

$$G(T) = \frac{E}{R}p(x) \tag{8}$$

where

$$p(x) = -\int_{x_0}^{x} \left(\frac{e^{-x}}{x^2}\right)dx \tag{9}$$

Various approximations of the exponential integral $p(x)$ have been developed for the application of Eqs. (7)–(9) to DSC data. The widely accepted examples are the methods of Doyle and Ozawa [28]. By taking Doyle's approximation for $p(x)$ in Eq. (9), Ozawa obtained the approximate relationship

$$\ln(\beta_i) = \ln\frac{A_\alpha E_\alpha}{R} - \ln g(\alpha) - 5.331 - 1.052\frac{E_\alpha}{RT_{\alpha,i}} \tag{10}$$

where E_α is a constant for a given conversion α. This is the commonly used Flynn–Wall–Ozawa method. Thus, for a given constant α, the plot of ($\ln\beta$) versus ($1/T$) obtained from DSC curves using multiple heating rates (β_i) gives a straight line where the slope can be used to determine the apparent activation energy.

If a peak exotherm temperature is used in Eq. (10), activation energy of the systems can also be estimated. This is called Ozawa's method.

$$\frac{d(\ln\beta)}{d(1/T_p)} = -1.052\frac{E_c}{R} \tag{11}$$

According to Eq. (11), the activation energies (E_c) of the systems can be determined from the slope in a plot of $\ln\beta$ versus $1/T_p$.

The apparent activation energy determined from the Flynn–Wall–Ozawa method was reported to be more reliable than that from the other methods. Furthermore, the Flynn–Wall–Ozawa method also was less sensitive to instrumental noise due to its integral character [32].

3.2. *Cure kinetic studies of nano-epoxy versus pure epoxy*

The dynamic thermograms obtained on pure epoxy system and the r-GNFs modified epoxy systems were reported in Fig. 4. A single exothermic peak was observed for the cure of pure epoxy system as well as for the r-GNFs modified epoxy system, and the total area under the respective thermograms was assumed to be the total heat of the reaction for the respective reaction systems.

Table 1 represents the onset temperature (T_i), peak temperature (T_p), final cure temperature (T_f), and heat of curing (ΔH) in the r-GNFs modified epoxy and pure epoxy systems. It can be observed that the onset, peak, and final cure temperature increased with increasing heating rates for two systems because the lower heating rate offered longer time for chemical groups of the systems

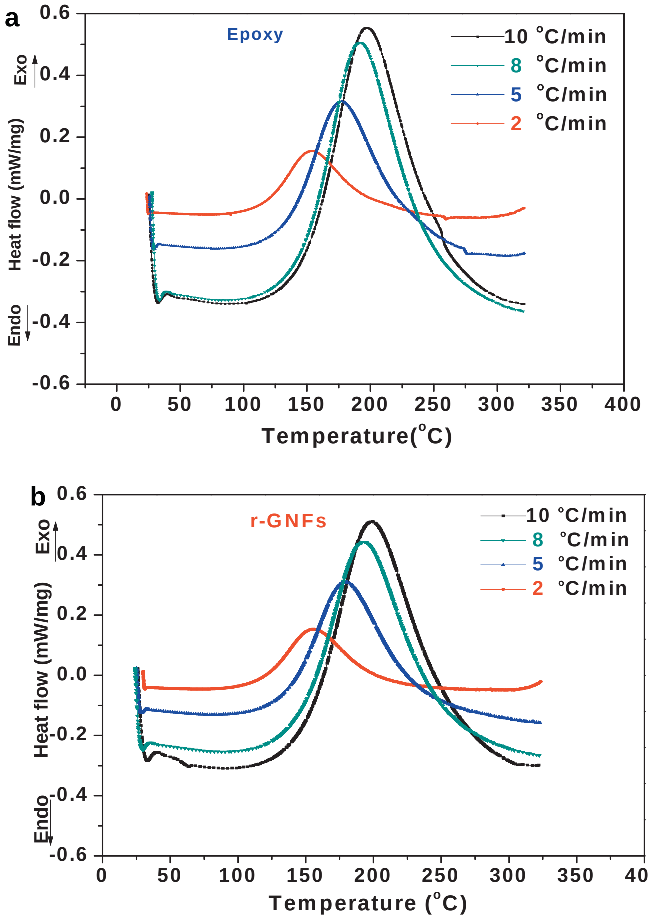


Fig. 4. Non-isothermal DSC curves from curing of the r-GNFs modified epoxy and pure epoxy resins (a) pure epoxy; and (b) r-GNFs modified epoxy.

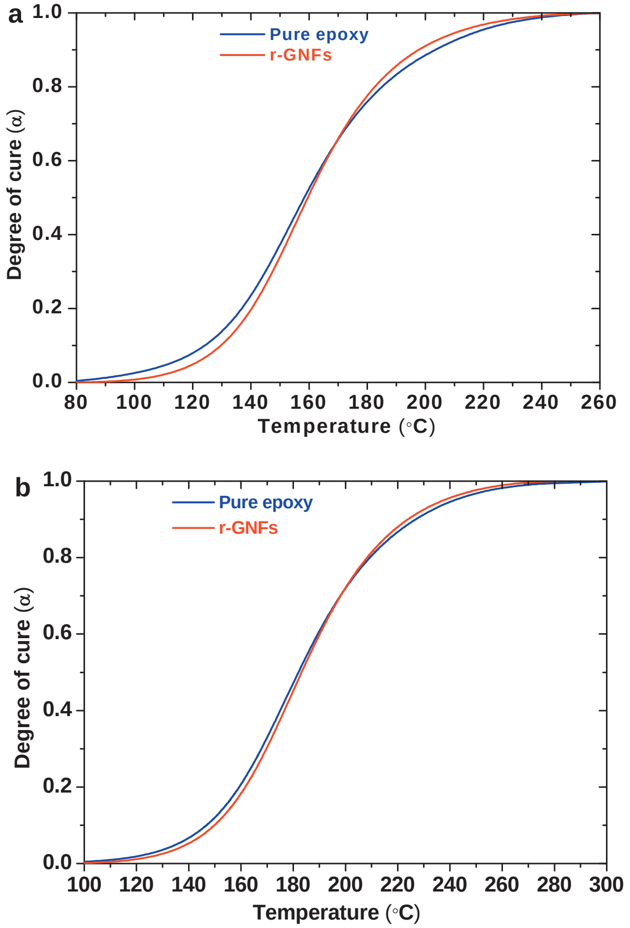


Fig. 5. The fractional extent of conversion with temperature of r-GNFs modified epoxy and pure epoxy systems (a) 2 °C/min, and (b) 5 °C/min.

to react, however, at faster heating rates there is less time for the reaction of the systems and therefore the DSC curves shift to a higher temperature to compensate for the reduced time. The results also indicated that the addition of r-GNFs retarded the cure reaction in the initial stage of cure reaction so that relatively higher temperature was needed to initiate the cure reaction compared to pure epoxy because of the steric hindrance from the r-GNFs [33]. This delayed initial cure reaction behavior was further verified as shown in Fig. 5. At low temperature range the steric hindrance of nanofillers interfered with the mobility of the reacting species, disrupted the reaction stoichiometry on the local scale, and resulted in decelerating the propagation reaction. In order to overcome the steric hindrance of the nanofillers and activate the initial cure reaction, more heat energy input and so higher temperature were needed at the very beginning of the reaction.

Table 1
Initial curing temperature, peak temperature, final cure temperature, and heat of curing in the r-GNFs modified epoxy and pure epoxy systems.

Heating rate (°C/min)		2	5	8	10
Pure epoxy	T_i (°C)	67.6	76.6	84.7	82.1
	T_p (°C)	154.1	177	191.2	198.1
	T_f (°C)	282.9	295.9	307.5	317.3
	ΔH (J/g)	356.8	374.1	354	357.5
r-GNFs	T_i (°C)	76.9	78.5	93	93.3
	T_p (°C)	156.2	177.6	191.9	199.1
	T_f (°C)	284.7	297.3	311.7	329.2
	ΔH (J/g)	391.2	407.7	369.6	394.4

However, it was not the case at higher temperature range. We speculate that the higher temperature prompted the mobility of the reacting species, increased the local density of the reacting species, and promoted the cure reaction. On the other hand, the high thermal conductivity of the r-GNFs further weakened the retarding effect of the steric hindrance from the addition of nanofillers [33]. Furthermore, according to the amine–epoxide polymerization reaction, the reactive hydroxyl groups on the surface of r-GNFs also participated in an opening of the epoxide rings like an amino curing agent, reacted with epoxy to form the ester bond, and facilitated the primary amine–epoxide reaction. Thus, the r-GNFs played a catalytic role in the curing reaction evolution. Higher reaction heat of curing from the r-GNFs modified epoxy samples over that of pure epoxy also implied that the extent of cure for the r-GNFs modified epoxy samples was larger than that of pure epoxy samples.

The catalytic effects of the r-GNFs on the curing reaction rate can be clearly observed in Fig. 6. Starting early in the reaction, the r-GNF modified epoxy system exhibited faster reaction rate, with the result that less time was needed to reach complete conversion than for the pure epoxy system. This observation was consistent with the previous analysis. This behavior became more apparent in Fig. 7. At the early stage of the cure reaction the reaction rate of conversion was slow for both systems. As the cure reaction progressed, the maximum rate of conversion appeared at about $\alpha = 0.47$ for the r-GNFs modified epoxy system and at about $\alpha = 0.42$ for the pure epoxy system. The acceleration of cure imparted by r-GNFs can has a positive effect on the processing of composites by reducing the time needed for cure and from saving energy. This observation was

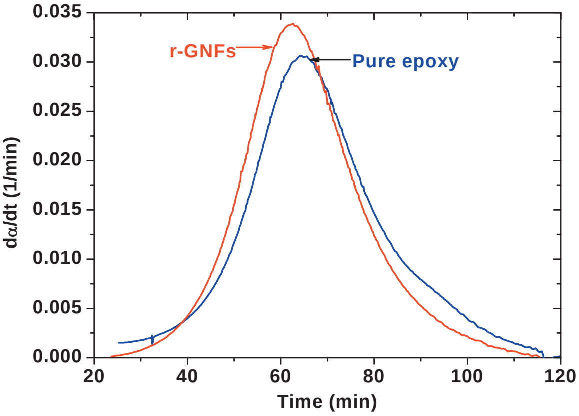


Fig. 6. The curing reaction rates of the r-GNFs modified epoxy and pure epoxy systems at 2 °C/min.

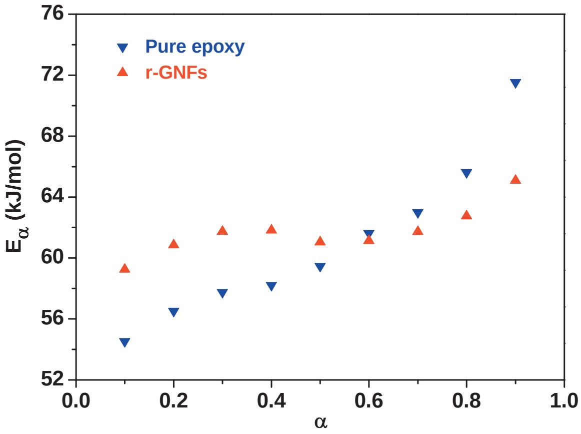


Fig. 8. Dependence of activation energy (E_α) on the degree of conversion (α).

consistent with the results of Kenny et al. [33]. However, the studies by Tao et al. found that nanofillers without surface treatment initiated curing at a lower temperature relative to the neat resin, while the overall degree of cure was lower [34]. Xie et al. also showed that with an increase of the CNFs or CNTs content the activation energy decreased in the early stage of the cure reaction. It was indicated that the CNTs or CNFs offered an acceleration effect on the early stage of the cure reaction, but in the later stage of the cure reaction CNTs or CNFs had an insignificant to negative effect on the curing reaction of epoxy resin [9,10]. Furthermore, a retardation effect of CNTs on the cure reaction of epoxy resin has been reported [11,12]. Therefore, we can speculate that during epoxy cure, the pure resin begins to cure first, as shown by its lower temperature and shorter onset time in DSC experiments. As the reaction proceeded, the enthalpy of reaction increased and larger extent of cure was finally achieved for the r-GNFs modified epoxy system.

It is known that the reaction activation energy E_α represents the potential barrier and the evolution of the cure reaction. Some researchers have reported that the reaction activation energy of epoxy resins is not constant during the cure reaction but the function of conversion [23]. As described above, the Ozawa method and the Flynn–Wall–Ozawa method can be used to determine activation energy of the systems. The main advantage of two methods is that the reaction activation energy can be directly derived without the assumption of the kinetic model of the curing reaction. Therefore, the effects of the r-GNFs on kinetic parameter of curing reaction of the epoxy were further studied according to the Ozawa and Flynn–Wall–Ozawa methods.

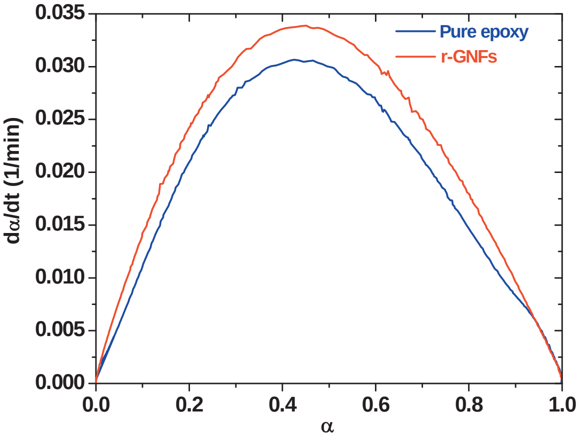


Fig. 7. The curing reaction rates vs. the degree of conversion of the r-GNFs modified epoxy and pure epoxy systems at 2 °C/min.

To obtain the change of reaction activation energy during the cure reaction, a set of α was chosen from the full range of experimental data at the multiple heating rates, i.e. $\alpha = 0.10, 0.2, \ldots, 0.90$, and 1.0. Based on Eq. (10) through linear fitting of $\ln(\beta)$ versus $1/T$, the values of E_α were obtained for a particular α. Fig. 8 represented the plot of E_α versus α for the pure epoxy and the r-GNFs modified epoxy, respectively. From the figure, it can be observed that the values of E_α were apparently different for different α and exhibited a significantly changing characteristic during the cure reaction for two epoxy systems. As shown in Fig. 8, at the very beginning of the cure reaction the value of E_α for the r-GNFs modified epoxy system was significantly larger than those for pure epoxy system, i.e. the values of activation energies for the r-GNFs modified epoxy system at $\alpha = 0.1$ and 0.2 gave big difference but not at $\alpha = 0.4$ and 0.5, however, at the last stage of cure reaction activation energies for the r-GNFs modified system became smaller than those for the pure epoxy system. We speculate that the retarding and catalytic effects of the r-GNFs on the cure reaction of epoxy systems in the different stages contributed to the competition of the steric hindrance and the participation of the reactive functional group in the reaction from the r-GNFs. Our previous work revealed that a kind of reactive group –OH* with the functionalized nanofibers, GNF-ODA, as shown in Fig. 2 could open epoxide rings of epoxy molecules and react with epoxy to form crosslinking structure of epoxy as an amino curing agent behaves though the amino groups in the structure of the nano-fibers did not tend to react with epoxy molecules [19]. Additionally, higher temperature accelerated this catalytic effect of reactive group containing r-GNFs and finally surpassed the steric hindrance from the structure. Therefore, during the last stage of cure reaction (higher temperature stage) smaller activation energies were obtained for the r-GNFs modified epoxy system, however, at the initial stage of cure reaction (lower temperature stage) the steric hindrance of the structure played a major role in the competition of the steric hindrance from the structure and the catalytic effect of the reactive functional group. That is to say, at the beginning stages r-GNFs had a retarding effect on the cure reaction and at the last half of the reaction it was overcome by the catalytic influence from reactive groups containing r-GNFs. So, the obtained values of the activation energy during the cure reaction reflected this behavior of the r-GNFs.

A comparison was made between the E_α-conversion data provide by the Flynn–Wall–Ozawa method with a method that yields a single activation energy that is assumed to be constant over the entire reaction. Constant activation energy method depends on only a specific temperature of the curing DSC curves, i.e. peak tem-

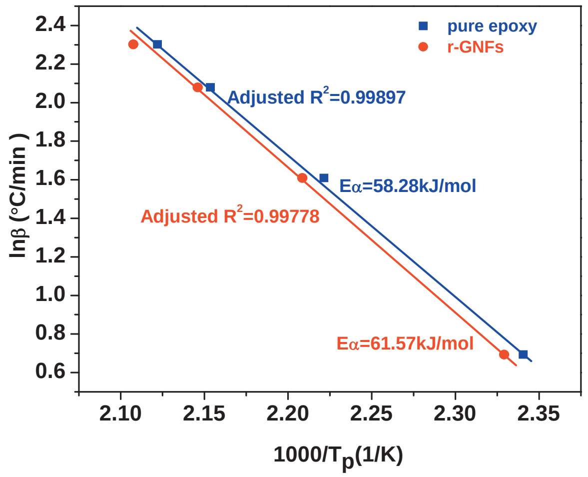


Fig. 9. Linear plots of ln(β) vs. $1/T_p$ based on Ozawa's method of pure epoxy and r-GNFs modified epoxy.

perature, not a set of temperatures. The value of constant activation energy (E_c) can be determined from the slope of the plot of ln(β) versus $1/T_p$ as shown in Fig. 9. The obtained values of the activation energy were 58.28 and 61.57 kJ/mol for pure epoxy and the r-GNFs modified epoxy systems, respectively. These values of the activation energy were located in the range of the activation energy from the Flynn–Wall–Ozawa method for $\alpha = 0.4–0.5$ as shown in Fig. 8.

From the above analysis, it can be concluded that the activation energies from the variable E method reflected the evolution of curing reaction for both epoxy systems because the Flynn–Wall–Ozawa method fitted well with the experimental results. Therefore, we concluded that the variable E method was more pragmatic in studying the cure kinetics of r-GNFs modified epoxy resins compared to the constant E method.

4. Conclusions

In this study the effect of the r-GNFs on the cure behavior of the epoxy resin was examined using non-isothermal differential scanning calorimetry. The specially functionalized nanofillers, r-GNFs, have been shown to have a dramatic influence on enhancing the key processing characteristics which should be beneficial for producing successful FRP composites. The results of the kinetic analysis indicated that compared to pure epoxy; the r-GNF modified epoxy system exhibited an evident catalytic action at the later stages, while slightly retarding the cure reaction of epoxy resin in the early stages. Therefore, the catalytic curing behavior of the epoxy resin resulting from the addition of r-GNF has the potential for a more efficient cure cycle in terms of time and energy conserved.

Acknowledgement

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