

Cure Behavior and Thermal Stability Analysis of Multiwalled Carbon Nanotube/Epoxy Resin Nanocomposites

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ABSTRACT: As-received multiwalled carbon nanotubes (MWCNTs) were first treated by a 3 : 1 (v/v) mixture of concentrated $\text{H}_2\text{SO}_4/\text{HNO}_3$ and further functionalized by ethylenediamine/dicyclohexylcarbodiimide/tetrahydrofuran solution. MWCNT/epoxy nanocomposites were prepared. Their cure behaviors were investigated by dynamic differential scanning calorimetry. Quantitative analysis of the activation energy as a function of the degree of curing was carried out by the Flynn-Wall-Ozawa method. The fitted multiple regression equations for values of the activation energy of different systems were obtained. MWCNTs have the retardation effect on the cure reaction

of epoxy resin, while the functional groups on the surface of amine-modified MWCNTs could accelerate the cure reactions. Thermal stability was studied by thermogravimetric analysis. The filling of amine-modified MWCNTs is beneficial to lower the cure activation energy and improve thermal stability of the nanocomposite. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 2980–2988, 2008

Key words: multiwalled carbon nanotubes; curing; thermal properties; differential scanning calorimetry (DSC); thermogravimetric analysis (TGA)

INTRODUCTION

Since the landmark paper reported the discovery of carbon nanotubes (CNTs),¹ a great interest has been motivated for their potential applications in diverse fields.^{2,3} Owing to their remarkable properties including high strength, good electrical conductivity, and excellent thermal conductivity, CNTs are candidates for applications as fillers in composites materials to enhance mechanical properties, electrical, and thermal transport. Especially, polymer-based CNT composites have attracted a continuously increased interest. The studies on CNT/polymer nanocomposites have been reported for various kinds of organic polymers.^{4–6} In most of the cases, homogeneous dispersion of CNTs is hindered by “entangled” and “agglomerate” structures of CNTs. It has been suggested that oxidation or chemical functionalization of CNTs and covalent attachment of polymer chains to the CNTs make the dispersion better and strength of the interfacial bonding between the CNTs and the polymer matrices stronger,^{7–9} which is beneficial to the performance of CNT/polymer composites.

Among polymers, epoxy resins are especially interesting because of their high modulus, low

shrinkage in cure, high adhesion, good chemical, and corrosion resistance.⁸ Multiwalled CNTs (MWCNTs) present the large potential for efficient improvement of the performance of polymer composites.^{9,10} In an attempt to make an optimum use of MWCNT/epoxy resin nanocomposites, it is necessary to understand the nature of their curing process. The final properties of the nanocomposites depend significantly on the curing conditions. There are some investigations on the cure behavior of MWCNT/epoxy resin nanocomposites and the effect of the functional groups on the surface of MWCNTs on cure reaction.^{11–14} Most researches are related to the influence of MWCNTs on the apparent activation energy of the global reaction. Few studies are concerned with the interpretation of the dependence of activation energy on the extent of cure reaction. Moreover, quantitative analysis of the activation energy as a function of the fractional extent of conversion is also deficient. In the present studies, the cure behaviors of MWCNT/bisphenol-A glycidol ether epoxy resin (DGEBA)/2-ethyl-4-methylimidazole (EMI-2,4) nanocomposites were investigated by dynamic differential scanning calorimetry (DSC). With the increase of the extent of cure reaction, the momentarily changed activation energy was studied in detail. The effects of MWCNTs on the glass transition temperature and thermal stability of the epoxy-matrix nanocomposites were also discussed.

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EXPERIMENTAL

Materials

MWCNTs used in this work were provided by the Nanotech Port Company, Shenzhen, China. The as-received MWCNTs synthesized by the chemical vapor deposition (CVD) possessed the average diameter of 50 nm and the length of 1–2 μm . Epoxy resin utilized in this study was a nominally difunctional epoxy resin, Epon 828, supplied by Shanghai Resin. Epon 828 is, basically, DGEBA with the epoxy value of 0.48–0.52 mol/100 g. The curing agent, EMI-2,4, was offered by Beijing Chemical Reagent (Shanghai, China).

Preparation of samples

MWCNTs were treated using a mixture of H_2SO_4 and HNO_3 with a volume ratio of H_2SO_4 to HNO_3 of 3 : 1 by stirring at 40°C for 10 h. And then, MWCNTs were washed using deionized water, filtered, and subsequently dried in a vacuum oven at 100°C for 12 h. Dried acid-treated MWCNTs were further functionalized by ethylenediamine (EDA)/dicyclohexylcarbodiimide(DCC)/tetrahydrofuran(THF) (weight ratio of EDA to DCC to MWCNTs is 20 : 20 : 1) solution, reacted at room temperature and stirred for 48 h to produce amine-modified MWCNTs.¹⁵ As-received MWCNTs or amine-modified MWCNTs were first suspended in ethanol solution in an ultrasonic bath at room temperature for 0.5 h. The epoxy/ethanol solution was poured into the dilute suspension of MWCNTs. Subsequently, the mixture was again sonicated at room temperature for 1 h to break down the agglomerations of MWCNTs. The solvent in the mixture was filtered, and then the mixture was degassed in a vacuum oven at 80°C for 4 h to remove bubbles before adding the curing agent. An appropriate amount of the curing agent was then added to the epoxy resin as its temperature was lowered to 40–50°C. After degasification, the mixture was quickly poured into a preheated steel mold coated with the mold release agent. The mold was placed in an oven. The MWCNT/epoxy resin systems were procured at 70°C for 1 h, cured at 110°C for 1.5 h, and postcured at 140°C for 1.5 h.

Instrumental analysis

The surface and fractured surface morphologies of MWCNT/epoxy resin nanocomposite and dispersion state of amine-modified MWCNTs in epoxy resin were examined using a field emission scanning electron microscope (FESEM) (FEI SIRION 200, USA). The Fourier transform infrared spectroscopy (FTIR) spectra of neat epoxy resin (DGEBA) and MWCNT/

TABLE I
Compositions of the Specimens (by weight)

Systems	DGEBA	EMI-2,4	MWCNTs
C ₀	100	6	0
C ₁	100	6	0.5 (as-received MWCNTs)
C ₂	100	6	0.5 (amine-modified MWCNTs)

epoxy resin nanocomposite were recorded between 400 and 4000 cm^{-1} using a Bruker EQUINOX 55 FTIR spectrometer. The reactants DGEBA, EMI-2,4, and as-received MWCNTs or amine-modified MWCNTs were mixed in appropriate weight ratios, then the mixtures were dispersed by sonication for 1 h to break down the agglomerations of MWCNTs. The obtained specimens were numbered (see Table I). The cure behaviors of the specimens were studied by nonisothermal DSC using a Perkin-Elmer DSC-7 system. The specimens were scanned at four different heating rates of 5, 10, 15, and 20 K/min under a constant flow of nitrogen at 50 mL/min. The thermal stability of unfilled cured epoxy resin and MWCNT/epoxy resin nanocomposites were investigated by thermogravimetric analysis (TGA) with a Perkin-Elmer TGA7 instrument. The experiments were performed under 40 mL/min nitrogen gas flow. The weight loss was recorded from 20 to 800°C at a heating rate of 20°C/min. Glass transition temperatures (T_g s) were measured by DSC (Perkin-Elmer DSC-7 system). Test data were measured from 25 to 300°C at a heating rate of 10°C/min.

RESULTS AND DISCUSSION

Characterization of MWCNT/epoxy resin nanocomposite

Figure 1 shows the surface and fractured surface morphologies of MWCNT/epoxy resin nanocomposite (C₂). It can be observed that amine-modified MWCNTs were effectively dispersed in epoxy resin matrix. Chemical functionalization could decrease the Van der Waals force between nanotubes, which is beneficial to obtain the good dispersion state of MWCNTs in the epoxy resin.

Cure behavior analysis

The FTIR spectra of neat epoxy resin (DGEBA) and MWCNT/epoxy resin nanocomposite (C₂) are presented in Figure 2. We can analyze the cure by FTIR technique. In this study, degree of curing of MWCNT/epoxy nanocomposite (C₂) was calculated. It is known that epoxy group has three characteristic peaks in the fingerprint region: 830, 1250, and 913 cm^{-1} . The band at 830 cm^{-1} would be overlapped by the bending vibration of two adjacent hydrogen atoms of benzene ring with para

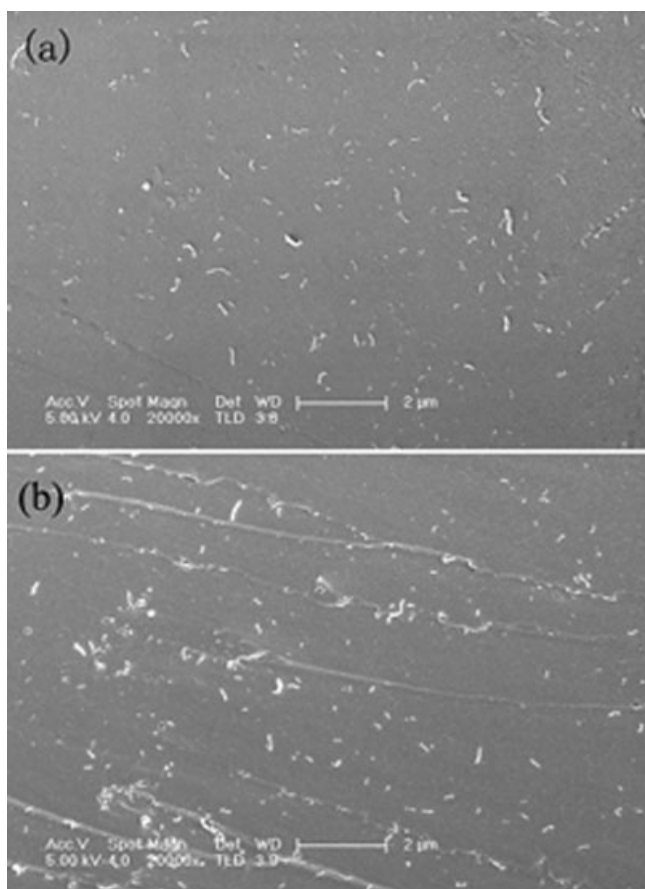


Figure 1 FESEM photographs of MWCNT/epoxy resin nanocomposite (C_2). (a) Surface morphology; (b) fractured surface morphology.

orientation. However, the feature at wavenumber 913 cm^{-1} would be little interfered; namely, it shows good anti-interference ability.¹⁶ The intensity of the band at 913 cm^{-1} decreases with increasing degree of curing, which means that the band at 913 cm^{-1} can sensitively reflect the change of epoxy group and better obey Beer-Lambert Law. According to

Beer-Lambert Law, the absorption peak at 1610 cm^{-1} of benzene ring can be regarded as the internal standard, so degree of curing (α) can be determined as usual:

$$\alpha = 1 - \frac{A'_{913}/A'_{1610}}{A_{913}/A_{1610}} \quad (1)$$

where A is original absorbance of net epoxy without cure; A' is the absorbance of cured epoxy nanocomposite.

The bands at 913 and 1610 cm^{-1} are remarkable in the spectrum of DGEBA [exhibited in Fig. 2(a)]. However, the band at 913 cm^{-1} is nearly absent from the spectrum of MWCNT/DGEBA/EMI-2,4 nanocomposite [shown in Fig. 2(b)]. In terms of eq. (1), degree of curing of MWCNT/epoxy resin nanocomposite (C_2) is $\sim 98\%$, which indicates that the cure reaction is basically completed.

The curing mechanism of DGEBA/EMI-2,4 system includes two stages consisting of the adduct and etherification reactions.¹⁷ The adduct reactions were regarded as the catalyst that initiated the etherification reactions which crosslink the epoxy resins and determine their final performance. Previous work showed that the adduct formation was necessary before the etherification reactions. Accordingly, low EMI-2,4 concentrations can be used to analyze the etherification reactions by suppressing the adduct formation.¹⁷ To objectively meet this specification, the molar heat of the reaction ΔH should approach a constant. When the concentration of EMI-2,4 is between 3 and 10 wt % (gram mass of EMI-2,4 per 100 g mass of DGEBA), the variation amplitude of ΔH is small. However, the cure reaction will be incomplete if the content of EMI-2,4 is below 3 wt %. In the present studies, the concentration of EMI-2,4 is 6 wt % which is in the range of 3–10 wt %. The DSC curing curves with different heating rates

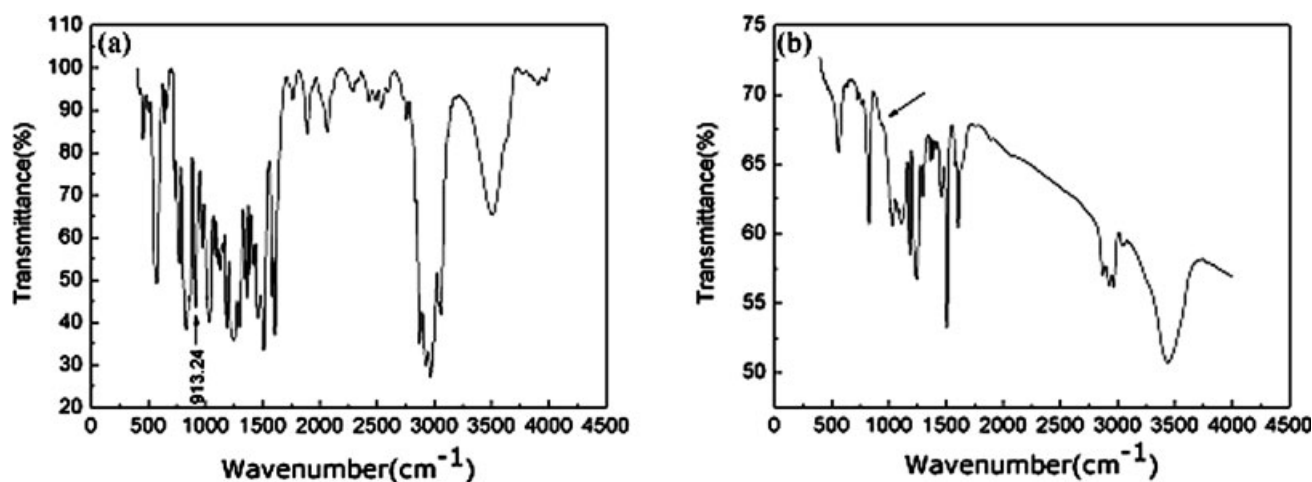


Figure 2 FTIR spectra of (a) DGEBA and (b) MWCNT/DGEBA/EMI-2,4 nanocomposite (C_2).

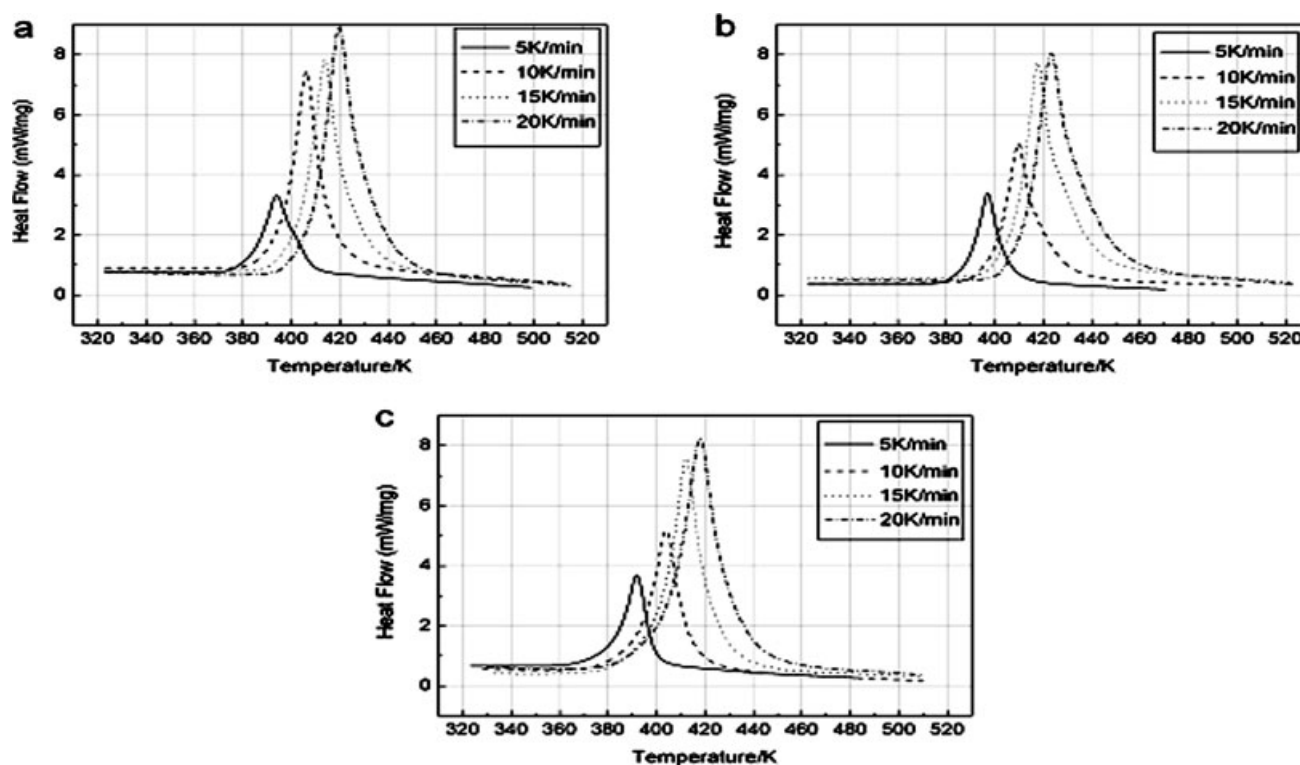


Figure 3 DSC curing curves with different heating rates of the systems: (a) C_0 ; (b) C_1 ; (c) C_2 .

of C_0 , C_1 , and C_2 are displayed in Figure 3(a–c), respectively. It can be seen that only a main exothermic peak of the etherification reaction appears. So the heat of reaction for the etherification reaction peak is approximately the total heat of the curing reaction. In addition, the functional groups on the chemically modified MWCNT surface can act as curing agents to react with the epoxy resin. However, the released heat is much smaller than the heat of the curing reaction, which denotes that it can be negligible. Consequently, ΔH can be regarded as a constant over the whole cure reaction. From a dynamic DSC run, the total area A of the exothermal peak (the region between the exotherm and the baseline) is in direct proportion to the molar heat of the reaction ΔH released during the whole cure reaction. The fraction extent of conversion α at any temperature T can be expressed as:

$$\alpha = \Delta H_T / \Delta H = A_T / A \quad (0 \leq \alpha \leq 1) \quad (2)$$

where ΔH_T is the heat of reaction of partially cured samples heated up to the temperature T .

Figure 4 reveals a comparison of the curing kinetics, at the heating rate of 20 K/min, among C_0 , C_1 , and C_2 systems. All curves present a sigmoidal form, which indicates that MWCNT/epoxy resin systems have an autocatalytic kinetics. It is known that DGEBA/EMI-2,4 system has autocatalytic kinetics. Namely, the filling of as-received MWCNTs

or amine-modified MWCNTs does not change the cure mechanism of epoxy resin. Additionally, it can be observed from Figure 4 that C_1 system shows the characteristic of delayed cure reaction, which denotes that MWCNTs have the retarding effect on the cure reaction of epoxy resin because of their steric hindrance.¹² The possible mechanism for MWCNTs to inhibit the cure reaction of epoxy resin system may be the decrease of the propagation reaction speed. With respect to MWCNT/epoxy resin system, the contents of DGEBA and EMI-2,4 are

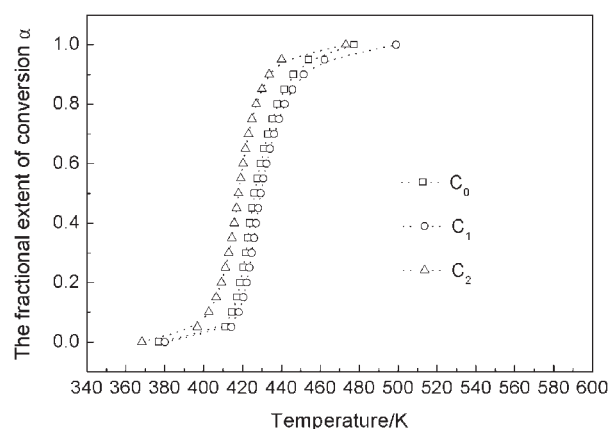


Figure 4 Advancement of the cure reactions for nonisothermal cure at 20 K/min heating rate of C_0 , C_1 , and C_2 systems. Dotted lines are given only for showing the tendency.

lower than those in the corresponding unfilled epoxy resin and viscosity may increase,¹⁸ which results in decelerating the propagation reaction and extends the gel time of epoxy resin. Compared with C₀ system, C₂ system displays the feature of accelerated cure reaction, which may be directly due to the role of functional groups on the surface of amine-modified MWCNTs as negative ionic catalysts of curing reaction of epoxy resin. According to the curing mechanism for the DGEBA/EMI-2,4 system,¹⁷ amine groups on the MWCNT surface could play the role of curing agents and facilitate the primary amine-epoxide reaction. Therefore, these amine groups weaken the retardation effect on the cure reaction caused by MWCNTs.

It is known that the activation energy E_α represents the potential barrier and the mechanism of the cure reaction. Consequently, the study on the activation energy contributes to better understanding of the cure behaviors of MWCNT/epoxy resin systems. The isoconversional method assumes that the activation energy is the function of the degree of curing. Two different isoconversional methods can be used: the Friedman method (differential isoconversional method) and the Flynn-Wall-Ozawa method (integral isoconversional method). The attraction of the two isoconversional methods stems from the possibility of being able to determine the activation energy for certain prerequisites, without knowing the kinetic model of the reaction mechanism. Opfermann and Kaisersberger¹⁹ simultaneously discussed the reliability of the Flynn-Wall-Ozawa analysis and the Friedman analysis by two simulated examples possessing a two-step reaction. He reported that the values for the activation energy are more reliable in the Flynn-Wall-Ozawa analysis than in the Friedman analysis; moreover, the Flynn-Wall-Ozawa analysis reacts with less sensitivity to noise, owing to its integrating character, than the Friedman analysis; however, the latter provides a better visual separation of more reaction steps. Jubsilp et al.²⁰ had the same conclusion on the Flynn-Wall-Ozawa analysis and the Friedman analysis. In addition, in the epoxy/amine system, the overall reaction order is known as 2.²¹ Therefore, the Flynn-Wall-Ozawa method is more suitable for the study on the activation energy. In this article, we use the Flynn-Wall-Ozawa method to calculate the activation energy of the cure reactions of C₀, C₁, and C₂ systems. This method is based on eqs. (3) and (4).

$$\ln \beta = \ln \left(\frac{AE_\alpha}{R} \right) - \ln g(\alpha) - 5.331 - 1.052 \left(\frac{E_\alpha}{RT} \right) \quad (3)$$

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} \quad (4)$$

where $g(\alpha)$ is the integral conversion function.

As a result, the plot of $\ln \beta$ versus $1/T_\alpha$ at the same α from a series of dynamic DSC thermograms at different heating rates would render a straight line where the slope allows the determination of the activation energy. Figure 5(a–c) present Flynn-Wall-Ozawa plots of C₀, C₁, and C₂ systems for various values of α ($\alpha = 0.05, 0.10, 0.15, 0.20, \dots, 0.90, 0.95$). A good linear relationship can be observed from Flynn-Wall-Ozawa plots. Values of E_α of C₀, C₁, and C₂ systems obtained for each value of α are displayed in Figure 6. The dependence of the activation energy of C₀, C₁, and C₂ systems as a function of degree of curing can be seen from Figure 6. Trying various multiple regression equations to fit the values of E_α , we found that cubic polynomial can have enough goodness of fit, namely, if high-order moments are applied to fit the values of E_α , the coefficient of the items whose numbers of order are greater than or equal to 4 in the polynomial expressions will be smaller than 10^{-5} . Accordingly, cubic polynomial is good enough to fit the values of E_α . The fitted multiple regression equations for values of E_α of C₀, C₁, and C₂ systems are expressed in eqs. (5), (7), and (9), respectively.

C₀ system:

$$E(\alpha) = 72.10884 - 50.89411\alpha + 117.38249\alpha^2 - 100.52538\alpha^3 \quad \alpha \in (0, 1) \quad (5)$$

$$dE/d\alpha = -50.89411 + 234.76498\alpha - 301.57614\alpha^2 < 0 \quad (6)$$

C₁ system:

$$E(\alpha) = 70.7959 - 20.39616\alpha + 58.39689\alpha^2 - 56.15943\alpha^3 \quad \alpha \in (0, 1) \quad (7)$$

$$dE/d\alpha = -20.39616 + 116.79378\alpha - 168.4789\alpha^2 < 0 \quad (8)$$

C₂ system:

$$E(\alpha) = 72.68158 - 48.09871\alpha + 88.92645\alpha^2 - 80.45939\alpha^3 \quad \alpha \in (0, 1) \quad (9)$$

$$dE/d\alpha = -48.09871 + 177.8529\alpha - 241.37817\alpha^2 < 0 \quad (10)$$

It can be observed from Figure 6 that the values of E_α of C₀, C₁, and C₂ systems decrease with the increase of α , which can be further proved by the fact that with respect to C₀, C₁, and C₂ systems, the differential equation of $E(\alpha)$, that is, $dE/d\alpha$, is smaller than zero, which denotes that $E(\alpha)$ is a decreasing function. The corresponding expressions

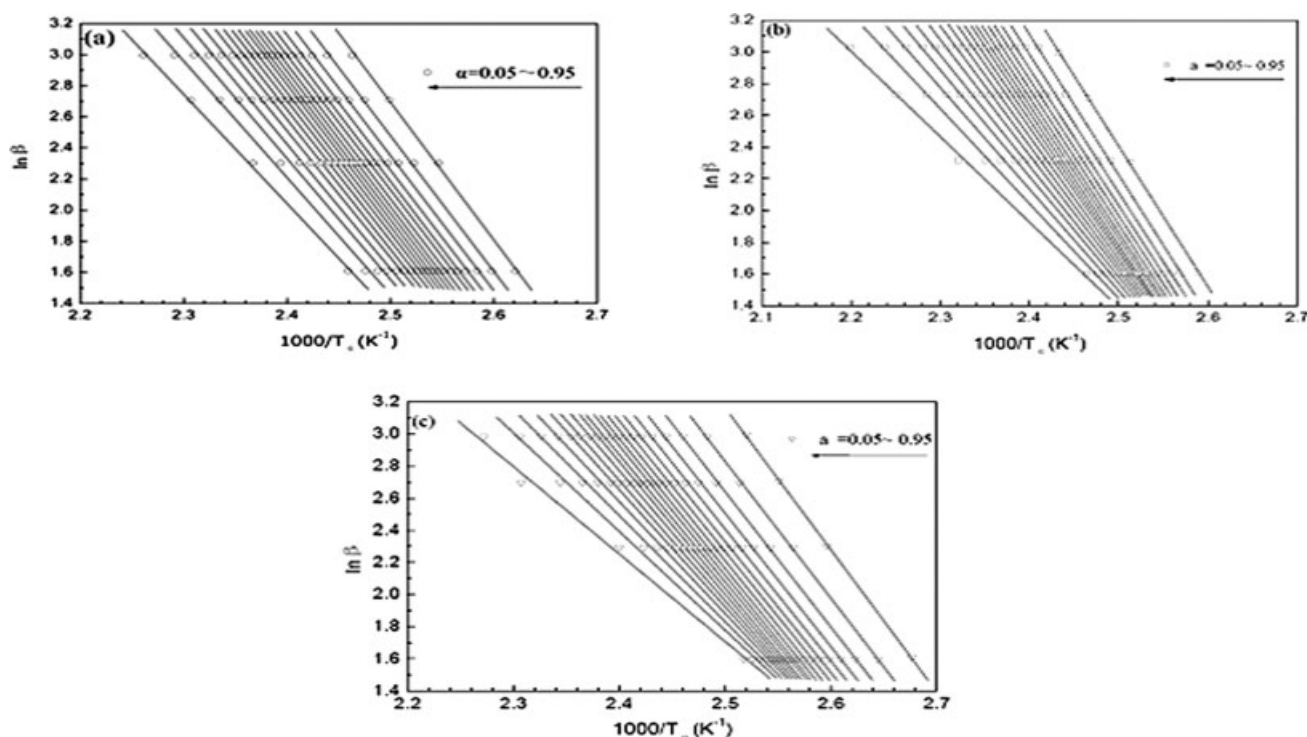


Figure 5 Flynn-Wall-Ozawa plots at various degrees of curing of C_0 , C_1 , and C_2 systems. (a) C_0 ; (b) C_1 ; (c) C_2 .

of $dE/d\alpha$ are revealed in eqs. (6), (8), and (10). In terms of the above discussion, the filling of as-received MWCNTs or amine-modified MWCNTs does not change the cure reaction mechanism of epoxy resin, namely, the process of cure is still autocatalytic. The first step in the cure reaction of DGEBA/EMI-2,4 system is the formation of both 1 : 1 and 2 : 1 adducts.¹⁷ The 2 : 1 adduct, which contains the nucleophilic alkoxide ion, was considered to be the catalyst that activated the etherification reaction. Moreover, the number of the 2 : 1 adduct does not reduce because the alkoxide ion is continuously regenerated during the etherification reaction. Based upon the fact that the heat of cure is mainly generated from the etherification reaction, it is reasonable to expect a decrease in E_α of MWCNT/DGEBA/EMI-2,4 systems. Additionally, the reason for E_α following the sequence $C_1 > C_0$ may be due to the inhibition effect caused by MWCNTs on the cure reactions of epoxy resin. This type of the retarding effect enhances potential barrier of the cure reaction, so the activation energy is increased. Furthermore, the phenomena for E_α following the sequence $C_2 < C_0$ may be attributed to the role of amine groups on the amine-modified MWCNT surface. These amine groups accelerate the primary amine-epoxide reaction and efficiently weaken the retardation effect caused by MWCNTs on the cure reaction, which is conducive to lower potential barrier of cure and decrease the cure activation energy.

According to the above analysis, the Flynn-Wall-Ozawa method fits well with the experimental results. Furthermore, we also check whether the obtained kinetic parameters could describe the cure isothermally made at different temperatures. As the curing process had a finite reaction rate at time zero, a rate equation proposed by Sourour and Kamal was used for the treatment of isothermal experiments:²²

$$\frac{d\alpha}{dt} = (k_1 + k_2\alpha^m)(1 - \alpha)^n \quad (11)$$

where k_1 and k_2 are the kinetic rate constants, and m and n are kinetic exponents. This equation has been used for the auto-catalyzed reaction.

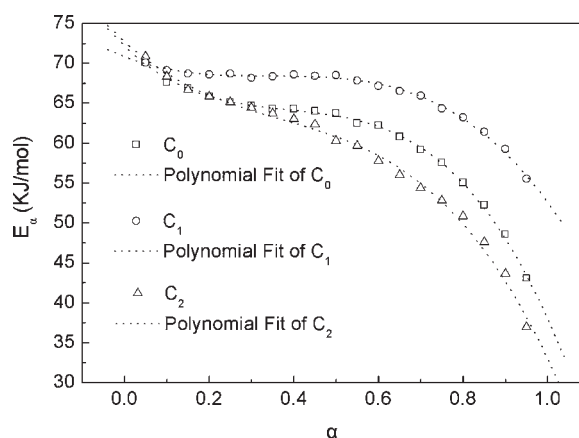


Figure 6 Values of the activation energy of C_0 , C_1 , and C_2 systems obtained from Flynn-Wall-Ozawa plots at different α .

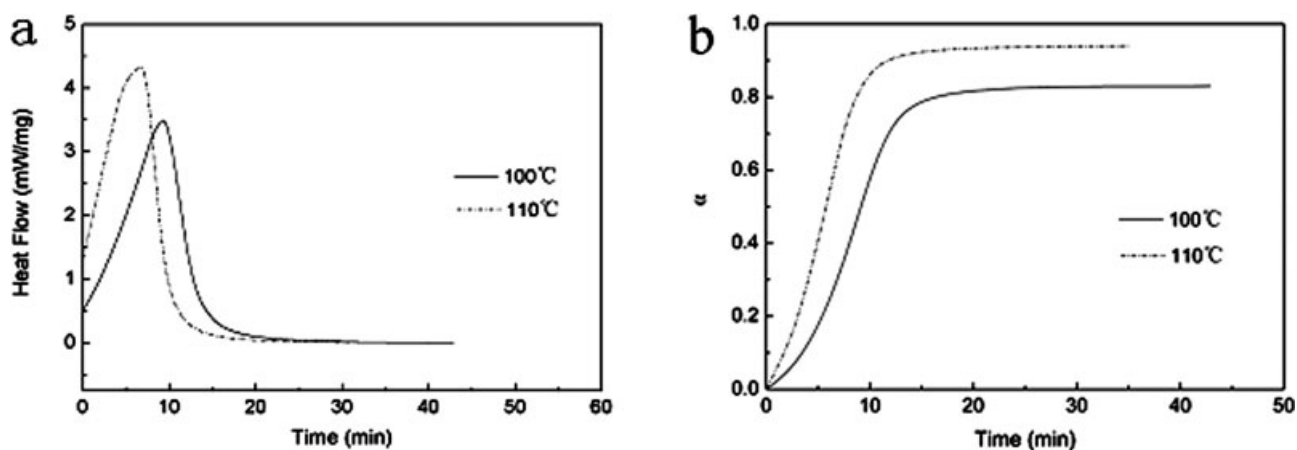


Figure 7 (a) Isothermal DSC curves for C_2 system at $T_{\text{iso}} = 100, 110^\circ\text{C}$; (b) degree of curing α versus time at different isothermal temperatures for C_2 system.

Both reaction constants depend on temperature following the classic Arrhenius equation:

$$k(T) = A \exp\left(-\frac{E}{RT}\right) \quad (12)$$

Isothermal DSC thermogram of C_2 system is shown in Figure 7(a) and conversion versus time for C_2 system is presented in Figure 7(b). The complete heat of cure for C_2 system is 425.9 J/g. By the Flynn-Wall-Ozawa method and eqs. (11) and (12), the parameters m , n , k_1 , and k_2 can be obtained (when T is 100°C , $m = 0.504$, $n = 1.482$, $k_1 = 0.01181$, $k_2 = 0.3431$; when $T = 110^\circ\text{C}$, $m = 0.584$, $n = 1.407$, $k_1 = 0.03061$, $k_2 = 0.4759$). Figure 8 shows a comparison of C_2 system experimental data and the model-fitted results of Kamal model [eq. (11)]. It can be seen that the results agreed well with the reaction, which indicates that the obtained kinetic parameters could also describe the isothermal cure of C_2 system.

Thermal stability analysis

Figure 9 shows the weight loss curves and the corresponding differential curves (DTG) for unfilled cured epoxy resin and MWCNT/epoxy resin nanocomposites. It can be observed that all systems undergo the decomposition mainly as a two-stage process. In the first stage process, the onset decomposition temperatures (T_{onset1}) of C_0 , C_1 , and C_2 are 394.2, 391.9, and 396.4°C, respectively. In the second stage process, the onset decomposition temperatures (T_{onset2}) of C_0 , C_1 , and C_2 are separately 602.1, 561.1, and 605.8°C. When as-received MWCNTs were added, T_{onset1} was observed to decrease slightly and T_{onset2} to descend remarkably. So the filling of as-received MWCNTs has a negative effect on thermal stability of the nanocomposite. This is due to the poor affinity between as-received MWCNTs and epoxy resin matrix, which increases vacancies or voids in the nanocomposite. However, the addition of

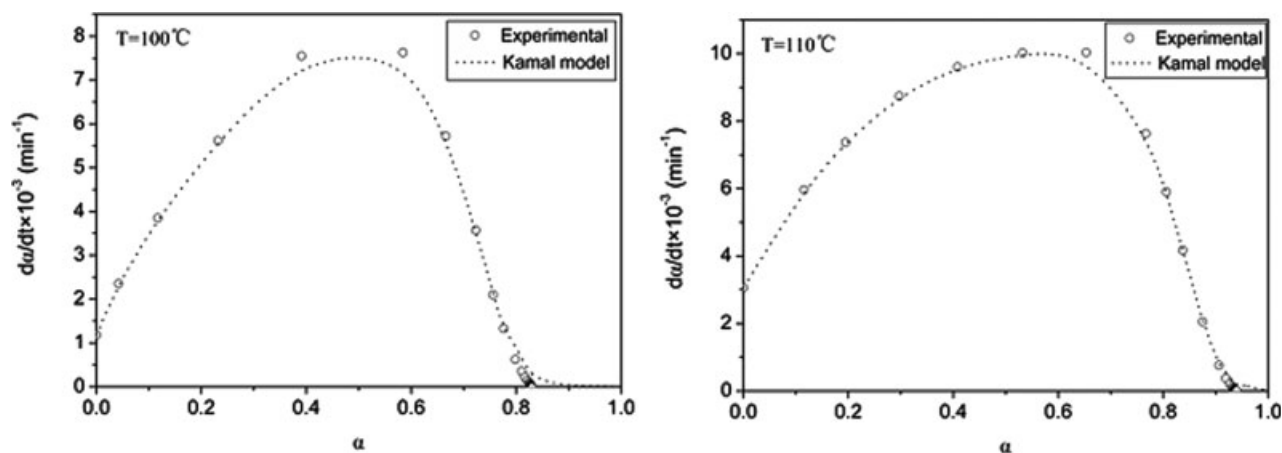


Figure 8 Curves of reaction rates versus conversion with model predictions. The dotted lines represent the autocatalytic model (DGEBA/EMI-2,4).

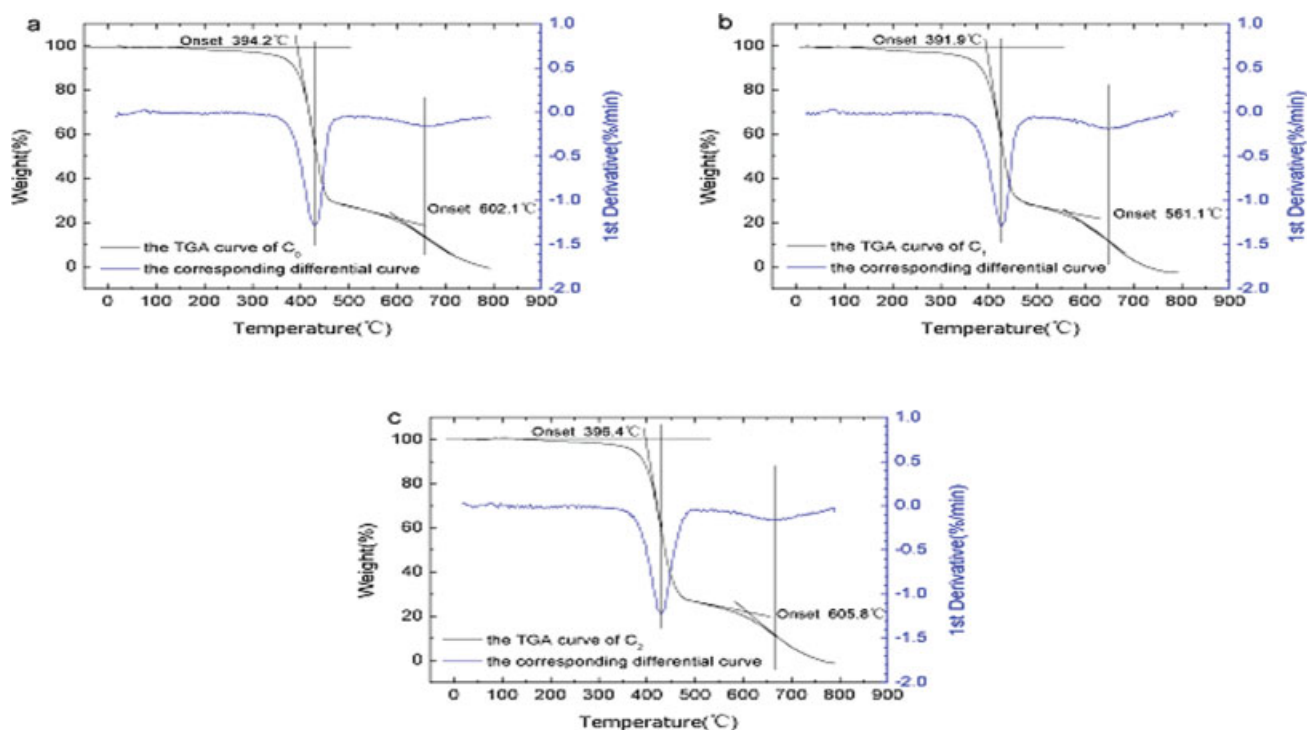


Figure 9 TGA and DTG curves of the different systems: (a) C_0 ; (b) C_1 ; (c) C_2 . [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

amine-modified MWCNTs enhances the values of $T_{\text{onset}1}$ and $T_{\text{onset}2}$, which indicates the thermal stability improvement of the nanocomposite. The reason may be attributed to the fact that amine-modified MWCNTs have a better affinity for the polymer matrix than as-received MWCNTs (that is, unmodified MWCNTs). To further prove the active influence of the functional groups on the surface of amine-modified MWCNTs on thermal properties of epoxy matrix, we studied the glass transition of amine-modified MWCNT/epoxy resin nanocomposite by DSC. Figure 10 exhibits DSC glass transition curves of C_0 and C_2 systems. The glass transition temperatures (T_g s) of the polymer matrix depend on the free volume of the polymer, which is correlated with the affinity between the filler and the polymer matrix. Molecular motion in the bulk state depends on the presence of holes, or places where there are vacancies or voids. With regard to the motion of polymer chains, cooperative motions are required. Thus for a polymeric segment to move from its present position to an adjacent site, a critical void volume must first exist before the segment can jump. The important point is that molecular motion cannot take place without the presence of holes. These holes, collectively, are called free volume. Additionally, the glass transition of polymer does not take place at a definite temperature, but completes in a certain temperature range. In this work, we define the temperature at which the glass transition reaches to $\Delta c_p/2$ (c_p is

the specific heat capacity) as T_g . It can be seen from Figure 10 that T_g s of unfilled cured epoxy resin (C_0) and MWCNT/epoxy resin nanocomposite (C_2) are 181.686 and 244.631°C, respectively. Obviously, the incorporation of amine-modified MWCNTs leads to the increase of the T_g value of MWCNT/epoxy resin nanocomposite. The covalent bonding of amine groups to the epoxy matrix is strong, which could decrease the free volume of the nanocomposite and thus T_g ascends.

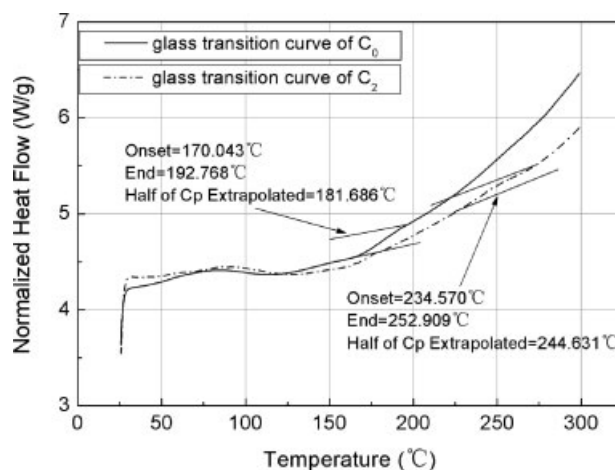


Figure 10 DSC glass transition curves of unfilled cured epoxy resin (C_0) and MWCNT/epoxy resin nanocomposite (C_2).

CONCLUSIONS

MWCNT/DGEBA/EMI-2,4 nanocomposites were prepared. Their cure behaviors were studied by nonisothermal DSC. FESEM microphotographs showed that amine-modified MWCNTs were dispersed uniformly in the epoxy resin matrix. The filling of as-received MWCNTs or amine-modified MWCNTs does not change the cure reaction mechanism of epoxy resin. MWCNTs have the retarding effect on the cure reaction of epoxy resin owing to their steric hindrance, while functional groups on the surface of amine-modified MWCNTs could play the role of curing agents and promote the primary amine-epoxide reaction. The Flynn-Wall-Ozawa method was applied to calculate the activation energy of the cure reactions of different systems. $E(\alpha)$ is a decreasing function, which denotes that the values of the activation energy decrease with increasing the degree of curing. Moreover, amine groups on the surface of MWCNTs contribute to lowering potential barrier of cure and decreasing the cure activation energy. The addition of amine-modified MWCNTs enhances thermal stability of the nanocomposite.

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