

Kinetics Studies on the Accelerated Curing of Liquid Crystalline Epoxy Resin/Multiwalled Carbon Nanotube Nanocomposites

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ABSTRACT: A new class of nanocomposite has been fabricated from liquid crystalline (LC) epoxy resin of 4,4'-bis(2,3-epoxypropoxy) biphenyl (BP), 4,4'-diamino-diphenyl sulfone (DDS), and multiwalled carbon nanotubes (CNTs). The surface of the CNTs was functionalized by LC epoxy resin (ef-CNT). The ef-CNT can be blended well with the BP that is further cured with an equivalent of DDS to form nanocomposite. We have studied the curing kinetics of this nanocomposite using isothermal and nonisothermal differential scanning calorimetry (DSC). The dependence of the conversion on time can fit into the autocatalytic model before the vitrification, and then it becomes diffusion control process. The reaction rate increases and the activation energy decreases with increasing concentration of the ef-CNT. At 10 wt % of ef-CNT, the activation energy of nanocomposite curing is lowered by about 20% when com-

pared with the neat BP/DDS resin. If the ef-CNT was replaced by thermal-insulating TiO₂ nanorods on the same weight basis, the decrease of activation energy was not observed. The result indicates the accelerating effect on the nanocomposite was raised from the high-thermal conductivity of CNT and aligned LC epoxy resin. However, at ef-CNT concentration higher than 2 wt %, the accelerating effect of ef-CNTs also antedates the vitrification and turns the reaction to diffusion control driven. As the molecular motions are limited, the degree of cure is lowered. © 2010 Wiley Periodicals, Inc. *J Polym Sci Part B: Polym Phys* 49: 301–309, 2011

KEYWORDS: carbon nanotubes; curing kinetics; differential scanning calorimetry (DSC); liquid crystalline epoxy resin; nanocomposites; thermal conductivity

INTRODUCTION Epoxy resins are widely used as adhesives, coatings, paints, composites, and dental therapy, because they have good adhesion, little dimensional changes, remarkable chemical resistance, and mechanical properties.^{1–7} Epoxy resin having a rigid rod segment may form high crystallinity domains under certain conditions. With mesogenic groups along the main chain and crosslinking capability between chains, liquid crystalline (LC) epoxy resin should be a good candidate for self-reinforcing composite materials.^{8–13} Epoxy resins can be further reinforced with a second phase, such as carbon nanotubes (CNTs), to fabricate a polymer composite possessing high modulus, high strength and toughness, good thermal stability, thermal, and electrical conductivity.^{14,15}

Carbon nanotubes (CNT) have been found to have unique atomic structure, high aspect ratio and excellent mechanical, thermal, and electrical properties, making them ideal reinforcing components in nanocomposite materials.^{16,17} Also, CNTs have remarkable advantages over conventional carbon fibers in composite processing due to their high flexibility,¹⁸ and thus, a great interest has been stimulated for their many potential applications including polymer enhancement. The

incorporation of CNTs into epoxy resin bulk material not only improves the thermal and mechanical properties of epoxy resins but also modify their processing behaviors.¹⁹

The addition of CNT influences the curing process. The study of the effect of CNT on the curing process is essential for designing, analyzing, and optimizing CNT-reinforced epoxy resins.²⁰ Wu and Chung added different types of carbon fillers in epoxy resin and found that carbon fillers increased the total heat of the curing reaction and accelerated the curing reaction.¹⁴ Tao et al. studied three different grades of CNTs and found that all CNTs initiated curing at lower temperature but decreased the overall degree of cure.²⁰ Xie et al. discovered CNTs have an acceleration effect on the curing reaction of tetraglycidyl-4,4'-diaminodiphenylmethane (TGDDM)/CNTs nanocomposite.¹⁵ Most of the researches suggested the curing kinetics of epoxy resins was influenced due to the steric hindrance and the increased surface area introduced by carbon fillers. However, we would like to discuss this issue from another aspect. In addition to their superior electrical and mechanical properties, CNTs are also extremely thermally conductive. They are primary conductive

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along the tube and insulating across. The thermal conductivity of a CNT at room temperature has an average value of 650–830 W/mK and had been measured to be greater than 3000 W/mK, exceeding the thermal conductivity of diamond and graphite (2000 W/mK). For SWNT, the conductivity can even reach 6000 W/mK at room temperature theoretically. On the other hand, cured LC polymers of a certain molecular orientation arranged by magnetic field or shear force have shown better thermal conductivity.^{21,22} The thermal conductivity of both epoxy CNTs and aligned LC epoxy resin can have impact on the curing kinetics of the epoxy resins.

The surface ligands grafted on CNTs surface via delicate modifications also affect the curing kinetics of CNTs/epoxy resin nanocomposite. Abdalla et al.²³ reported the activation energy of epoxy resin Epon 828 containing carboxylated CNT curing with diethyltoluenediamine is higher than the neat resin (61.7 KJ/mol vs. 47.7 KJ/mol) due to the heterogeneous dispersion hindering the curing process. Wang et al.²⁴ have shown the epoxide-grafted single wall CNTs (SWCNTs) contributed to the slight decreasing of the activation energy of nanocomposite curing. However, the SWCNTs were cut to the length of 200 nm and coated by polymerized glycidyl methacrylate with benzoyl peroxide, which is used as the initiator.

In this article, we present a method to fabricate nanocomposite materials composed of LC epoxy resin, 4,4'-bis(2,3-epoxypropoxy) biphenyl (BP), and multiwalled CNTs. 4,4'-Diaminodiphenyl sulfone (DDS) was used as hardener for the curing reaction of the LC epoxy resin. Both isothermal and nonisothermal kinetic studies were performed using differential scanning calorimetry (DSC) to calculate the activation energy of the reaction and to understand the effect of CNTs on the curing mechanisms by applying different kinetic models. For the purpose of comparison, the nanocomposites composed of nonthermal conductive TiO₂ nanorods, and LC epoxy resin was prepared.

KINETIC MODELS

To study the curing kinetics of the nanocomposites, both dynamic and isothermal measurements were conducted using DSC. The dynamic kinetic studies are based on Kissinger model and Ozawa model.^{25,26} Isothermal studies were carried out according to autocatalytic model developed by Kamal.²⁷

Dynamic Kinetic Model

The information obtained from the dynamic scan of the curing reaction can be used to build a dynamic kinetic model to describe the curing behaviors. The Kissinger model and the Ozawa model are built on the *n*th-order model theory, and the basic reaction rate equation is shown below. The rate constant *k* is assumed to be of Arrhenius-type:

$$r = \frac{d\alpha}{dt} = k(1 - \alpha)^n = A \exp\left(-\frac{E_a}{RT}\right)(1 - \alpha)^n \quad (1)$$

The reaction rate *r* is defined as the change of the reaction α (curing degree in this case) per unit time *t* and *n* is the reac-

tion order. *A* is the pre-exponential factor, *E_a* is the activation energy required for the reaction, *R* is the gas constant, and *T* is the reaction temperature. When taking *q* as the heating rate, and assuming the fastest reaction rate happens at $dr/dt = 0$, the heating rate can then be related to the activation energy as described in eq 2.

$$q \frac{E_a}{RT_p^2} = An(1 - \alpha_p)^{n-1} \exp\left(\frac{-E_a}{RT_p}\right) \quad (2)$$

T_p and α_p are the exothermic peak temperature and the corresponding curing degree, respectively. The activation energy can be obtained from the peak temperature in dynamic scan as described in the following relationship and calculated from the slope of the plot:

$$E_a = -R \frac{d[\ln(q/T_p^2)]}{d(1/T_p)} \quad (3)$$

Ozawa developed an alternative method to describe the relationship between activation energy, heating rate, and exothermic peak temperature under the assumption that the extent of reaction at the exothermic peak is constant and independent on the heating rate. The equation is given as:

$$\log q = (1/2.303) \ln q = -0.4567(E_a/RT_p) + [\log(AE_a/R) - \log f(\alpha) - 2.315] - \frac{R}{1.052E_a} = \frac{d(1/T_p)}{d(\ln q)} \quad (4)$$

Again, the activation energy can be obtained from the slope of the plot of $(\ln q)$ against $(1/T_p)$. As activation energy is the extent of a reaction energy barrier, it can be used to describe the kinetic effect of a cure reaction. The activation energy does not give any information about the reaction mechanism but the rate of the reaction. Nevertheless, when the activation energy of the reaction and the curing rates at various temperatures are known, we are able to model the cure kinetics for industrial process control purpose to optimize the product performance.

Isothermal Kinetic Model

The two dynamic models are formulated based on *n*th-order theory, assuming the reaction rate remains the same throughout the reaction process, and this does not describe the curing behaviors of epoxy/amine system accurately. The curing reaction between epoxy and amine is an autocatalytic reaction, in which the product also functions as a catalyst, resulting in the rate of reaction to change with time. The reaction rate usually increases with time from its initial value and decreases later as the reaction proceeds. This can be observed from an isothermal thermograph where the maximum reaction rate occurs at some point of the reaction other than at the beginning. Hence, we performed an isothermal DSC experiments and use Kamal's isothermal kinetic model to more precisely describe the autocatalytic reactions

of the LC epoxy/DDS/CNT nanocomposite systems in our study.

In DSC analysis, the distribution of the heat of reaction $H(t)$ for curing is given by

$$H(t) = \int_0^1 \Phi(t) dt \quad (5)$$

where $\Phi(t)$ is the heat flow measured by the DSC experiment.

A basic assumption underlying the application of DSC to a thermoset curing is that the heat evolution recorded in DSC experiments is proportional to the extent of the reaction, which, in our research, is the epoxide group consumption in the epoxy resin or the reactive group consumption in the curing agent. That means that the heat of reaction $H(t)$ is proportional to the degree of conversion $\alpha(t)$. The degree of conversion is defined as the ratio of the amount of heat generated at time t to the overall reaction heat:

$$\alpha(t) = \frac{H(t)}{H_{\text{Tot}}} \quad (6)$$

where H_{Tot} is the total heat developed in the process at full conversion and the curing conversion rate ($d\alpha/dt$) is thus:

$$\frac{d\alpha}{dt} = \left(\frac{dH}{dt} \right) \frac{1}{H_{\text{Tot}}} \quad (7)$$

If we apply the simplest model corresponding to an n th-order kinetic expression:

$$\frac{d\alpha}{dt} = k(1 - \alpha)^n \quad (8)$$

where n is the reaction order; and k is the rate constant given by Arrhenius temperature dependence:

$$k = A \exp\left(\frac{-E_a}{RT}\right) \quad (9)$$

A in the equation is the pre-exponential constant; E_a , the activation energy; R , the gas constant; and T , the absolute temperature.

For the autocatalytic systems such as the curing of epoxy resins, Kamal and Sourour developed a mathematic model to predict the rate of conversion and the extent of reaction based on calculating the changing reaction rate.²⁷ The rate of conversion and the extent of reaction are related to one another with two kinetic constants (k_1 , k_2) and two reaction orders (m , n) as follows:

$$\frac{d\alpha}{dt} = (k_1 + k_2\alpha^m)(1 - \alpha)^n \quad (10)$$

where α is the conversion of epoxy groups at time t . k_1 describes the rate constant of the reaction of order n catalyzed by an accelerator; k_2 is the rate constant of the autocatalytic reaction of order m . Vyazovkin and Sbirrazzuoli²⁸ have applied this model to predict the curing reaction of isophorone diamine cured epoxy novolac resin.

EXPERIMENTAL

Materials

The LC epoxy resin, BP, was synthesized according to the previous study.⁸ The BP has an epoxy equivalent weight (EEW) of 180. The multiwalled CNTs were purchased from DESUN Nano Company (Taiwan) with average diameter ~ 20 – 30 nm, length ~ 15 μm . The curing agent DDS was purchased from Acros.

Carbon Nanotubes Functionalization

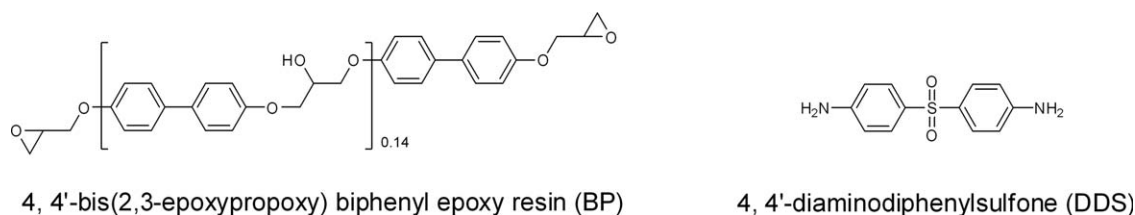
CNTs (4 g) were added into a 400 mL mixture of HNO_3 : H_2SO_4 (volume ratio = 1:3). The mixture was refluxed at 80 $^\circ\text{C}$ for 6 h and cooled to room temperature before it was diluted with distilled water 1:5 by volume. The solution was then filtered using a PTFE filter (0.2 μm pore size). The filtered CNTs were washed with excess water until no residual acid was present and then dried at 105 $^\circ\text{C}$ for 24 h in a vacuum oven. Further functionalization was carried out through esterification between the acid-washed CNTs (a-CNT) and the epoxy resin. a-CNT (2 g) was dissolved in 200 mL THF and ultrasoned in a 100 W bath sonicator for 1 h. BP (3 g) was also dissolved in 300 mL THF and ultrasoned for 1 h. The two solutions were then mixed together and sonicated for another hour. KOH (2 wt %) was added into the solution as catalyst before the solution was refluxed at 70 $^\circ\text{C}$ for 6 h. The epoxy-functionalized CNTs (ef-CNT) were collected, filtered, and dried as black powder. Pristine CNTs (p-CNT), a-CNT, and ef-CNT were characterized by Fourier transform infrared spectroscopy (FTIR; JAS CO FT/IR-480 Plus). The transmission electron microscopic (TEM) investigation was carried out by using a Joel JEM 1230 electron microscope to observe the surface of ef-CNT.

Preparation of ef-CNT/BP Mixture

1.50 g BP and required amount of ef-CNT (0.50, 1, 2, 4, and 10 wt %, respectively) was dissolved in 20 mL THF. Different sizes of zirconium oxide milling balls were used to ball mill the mixture for homogenous mixing. Solvent was removed later using a rotary evaporator, and the gray powder product was vacuum dried overnight.

Preparation of TiO_2 /BP Mixture

TiO_2 nanorods were synthesized according to previous study.²⁹ A Joel JEM 1230 electron microscope was used to study the morphology of TiO_2 nanorods and the high-resolution transmission electron microscopic (HR-TEM) images were obtained by using a Joel JEM 2000 FX transmission electron microscope operated at an accelerating voltage of 200 kV. The TiO_2 nanorods were first dried in a vacuum oven overnight and then mixed with epoxy resin in 0.50, 4, and 10 wt %, respectively. The mixture was carefully ground in an agate mortar and dissolved in THF for ball mill process similar to the preparation of ef-CNT/BP/DDS nanocomposite. The mixture thickened after ball milling. Solvents were



SCHEME 1 Chemical structures of BP and DDS.

removed using a rotary evaporator to obtain the white powder product.

Polarized Optical Microscopy Evaluation

A Zeiss Axiophot microscope equipped with cross polarizers, a digital camera (Canon PowerShot A640), and a Mettler FP82HF optical hot-stage connected to a Mettler FP90 controller was used to image the LC phase of nanocomposite samples during the curing process. Samples were pressed between glass slides, and the experiment was performed in a nitrogen environment. The samples were heated at a rate of 2 °C/min until the temperature that was able to melt the samples at 157 °C. The temperature was held until the samples completely melted (about 30 min), and then the samples were cooled down to the room temperature at a rate of 0.5 °C/min. As the birefringence appeared at 137 °C, the temperature was held for observation.

Dynamic DSC Measurement

The above mixture was mixed with curing agent (DDS) according to predetermined EEW ratio in solvent and rapidly removed the solvent to avoid curing reaction occurring.³⁰ The mixture was ground to fine powder and weighed 3–5 mg in aluminum pan. The dynamic measurements were carried out in a TA thermal series DSC (TA-Q200). The samples were heated at the heating rate of 5, 10, 15, 20, and 25 °C/min from room temperature to 290 °C in N₂, respectively.

Isothermal DSC Measurement

For the isothermal scan, the samples were rapidly heated in DSC (TA Q-200) from room temperature to desired temperature (160, 180, 200, 220, and 240 °C) and held for 50–70 min in N₂.

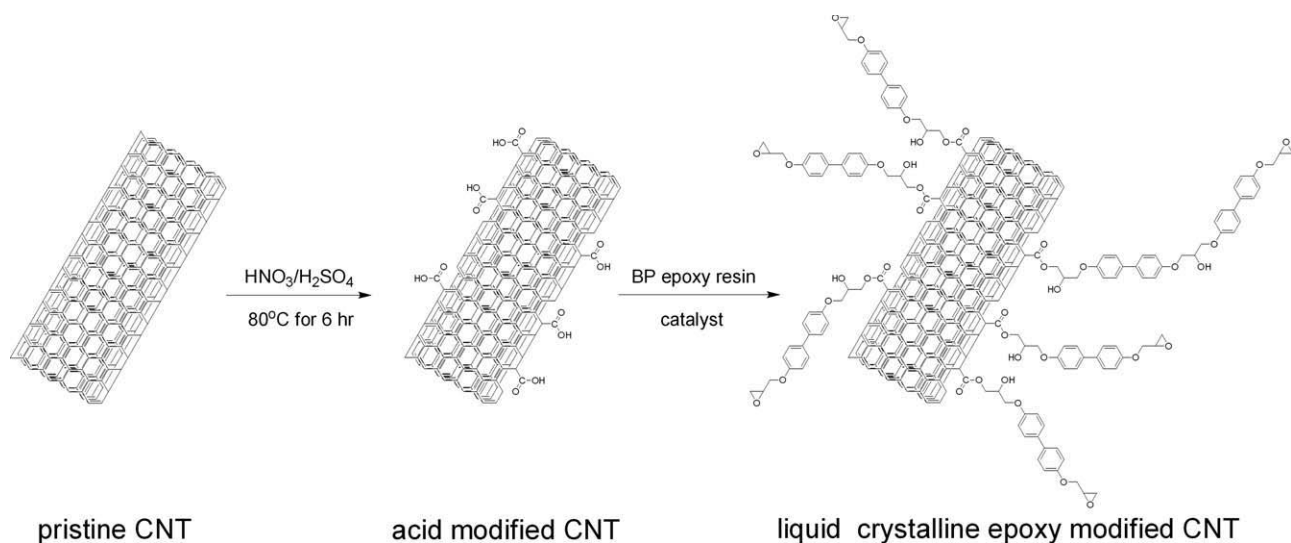
RESULTS AND DISCUSSION

Matrix of the Nanocomposite

The matrix of the nanocomposite was made by blending equivalent amount of LC epoxy resin of 4,4'-bis(2,3-epoxypropoxy) biphenyl and curing agent of 4,4'-diaminodiphenyl sulfone. Scheme 1 shows the chemical structure of each component in the matrix.

CNT Functionalization

The synthetic route to obtain LC-functionalized CNT (ef-CNT) is shown in Scheme 2. After the oxidation of p-CNT surface by HNO₃/H₂SO₄ mixture, carboxylic acid groups form on the surface of the CNT, which is a-CNT. Then, BP epoxy resin reacts with the carboxylic acid on a-CNT surface to obtain ef-CNT by using KOH as catalyst. The variation of the surface ligands of p-CNT, a-CNT, and ef-CNT are detected and characterized by using FTIR, respectively. The FTIR spectra of the p-CNT, a-CNT, and ef-CNT are shown in Figure 1. The 1579 cm⁻¹ absorption peak is the C=C stretching vibration of the benzene rings on the nanotubes and is found in both a-CNT



SCHEME 2 Synthesis of liquid crystalline epoxy-modified CNT.

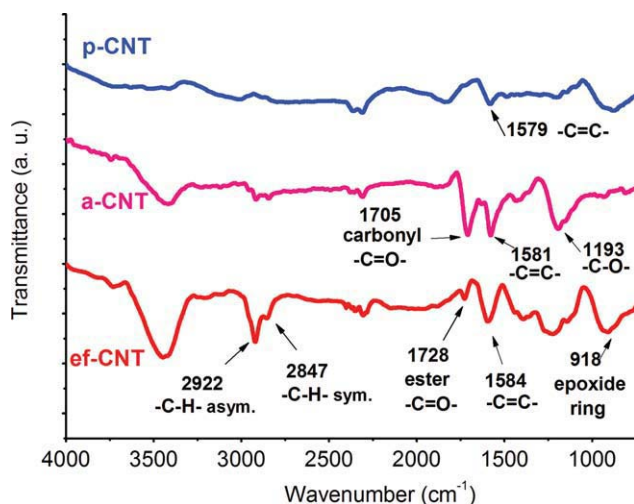


FIGURE 1 FTIR spectra of pristine CNT, a-CNT, and ef-CNT.

(1581 cm^{-1}) and ef-CNT (1584 cm^{-1}). After acid wash, the a-CNT spectrum shows C=O stretching at 1705 cm^{-1} and O—H at 3418 cm^{-1} . The 1193 cm^{-1} is C—O stretching vibration. The carbonyl can also be observed in the ef-CNT IR spectrum at 1728 cm^{-1} . The C=O peak of ef-CNT is shifted when compared with a-CNT indicating the formation of ester. The epoxide attached to the CNTs gives a ring vibration signals at 918 cm^{-1} . These peaks are similar to those reported in literature.^{31,32} The presence of the epoxide ring peak implies that not all the epoxy rings are opened and reacted, leaving the possibilities for further reaction.

ef-CNT/BP/DDS Nanocomposite

Compared with the common epoxy resin, LC epoxy resin has the ability to form crystalline. The LC structure of BP/DDS resin has been observed as shown in Figure 2(a). To be able to flow and rearrange, LC epoxy resin has molecules with rigid rod segment and is less bulky than the common epoxy resin. From the research conducted earlier,³⁰ we have found that LC epoxy resin requires less energy to cure when we compared a commercial epoxy resin, tetramethyl biphenyl epoxy resin (TMBP), with the BP LC epoxy resin using DDS curing agent. TMBP curing has higher activation energy (96.8 kJ/mol) than that of BP (79.1 kJ/mol) due to its greater steric hindrance and results in a lower reaction rate. Moreover, LC epoxy resin exhibits better thermal stability through denser crosslinking, higher θ_g (TMA), better strength, and higher modulus.

The DDS cured BP LC epoxy resin can be further strengthened by CNTs inclusion. Figure 2(b) shows, under the polarized light, the crystalline size of BP/DDS resin has been greatly increased as 2 wt % ef-CNT incorporated into the resin. The detailed synthesis, morphology, and physical properties of this nanocomposite will be present in a separate publication. To understand how the CNTs affect the curing reaction of nanocomposites, the kinetics of BP/DDS with different ef-CNT contents are carefully studied and discussed below.

Dynamic Study

From the dynamic scan thermographs (in the Supporting Information), we can observe the exothermic peaks shift to the right as the heating rate increases and more energy is acquired for the reaction to occur. According to the Kissinger model and Ozawa model, the heating rate is directly related to the inverse of the peak temperature and the activation energy can then be calculated using the method described earlier. The calculated activation energies from both models are summarized in Table 1. The values obtained from both models are very similar but slightly higher for the Ozawa model due to different equation derivation, which is consistent with the reported data.³³

From Table 1, we discover that the curing activation energy decreases with the increasing CNT concentrations in a non-linear manner for the ef-CNT/BP/DDS system, indicating the effect is not merely caused by the change in the ratio of resin/reinforcing components. A decrease in activation energy implies that less energy of the reacting resin components is required and indicating an accelerating effect. This implies that the addition of CNTs into epoxy resin encourages the curing reaction happening. Samples with higher ef-CNT content react much faster when the same amount of

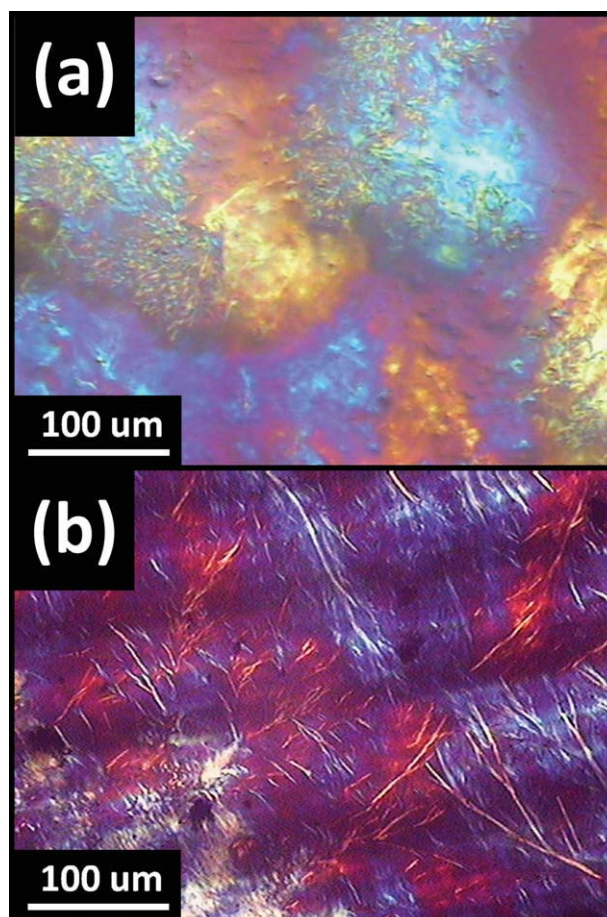


FIGURE 2 POM image of (a) cured BP/DDS resin system and (b) cured 2 wt % ef-CNT/BP/DDS nanocomposite.

TABLE 1 The Activation Energy for the ef-CNT/BP/DDS Nanocomposites Curing Calculated from the Kissinger and the Ozawa Model for Different CNT Compositions

Sample name	E_a by Kissinger Model (kJ/mol)	E_a by Ozawa Model (kJ/mol)
0.00 wt % ef-CNT/BP/DDS	70.88	75.21
0.50 wt % ef-CNT/BP/DDS	68.82	73.29
1.00 wt % ef-CNT/BP/DDS	67.27	71.79
2.00 wt % ef-CNT/BP/DDS	64.89	69.51
4.00 wt % ef-CNT/BP/DDS	61.37	66.12
10.00 wt % ef-CNT/BP/DDS	56.08	61.03

energy is applied. The faster curing phenomenon is indeed observed during the bulk sample fabrication process.

Isothermal Study

To consider the autocatalytic effect, the isothermal DSC study was carried out for the ef-CNT/BP/DDS nanocomposites holding at different reaction temperatures until the heat flow stopped changing. From the thermographs (in the Supporting Information), the maximum reaction rate does not occur at the time zero, suggesting the epoxy resin/amine curing reaction is an autocatalytic system. In the study, we assume that as the curve reaches zero, the curing reaction completes. It can be seen that the reaction completes within a shorter time period at higher isothermal temperatures as more heat energy is provided for the molecules to react.

To apply Kamal's isothermal model, the four parameters, k_1 , k_2 , m , n , in the reaction rate equation must be computed. They are calculated and summarized in the Supporting Information. The main assumption here is that the cure mechanism is the same over all the temperature range studied. The m values increased with increasing curing temperatures, whereas the n values showed an opposite trend and both increase with the ef-CNT additions in general. Both the reaction rate constants k_1 and k_2 values increase with increasing cure temperature and the ef-CNT concentrations. Jang et al.³⁴ mentioned in their study that they considered the reaction order m was related to the maximum cure rate and n to the postcure reaction. As a result, at high curing temperature, the reaction rate increases (m increases) and less postcure reaction is required (n decreases). The data show that the m and n values generally agree with the finding of Jang et al.

The effect of the ef-CNT additions can be further recognized by comparing the values obtained among different ef-CNT contents. The m values grow with the ef-CNT content and drop back at high ef-CNT contents. The reason for it is because ef-CNTs encourage cure reaction and increases the maximum cure rate as more ef-CNTs are added. However, at high ef-CNT content, although the heat transfer rate is further speeding up, the curing of the sample is impeded by the rapid vitrification of epoxy resin and the physical presence of large amount of ef-CNTs, leading to a drop in the maximum reaction rate. The decrease in n values is more obvious at low ef-CNT concentrations for the curing proceeds more

quickly with ef-CNT additions. As more ef-CNT is incorporated, the postcure becomes more difficult due to the fast molecular network forming and an increase in n values is found. The average value for $n + m$ reported is between 2 and 3. Most of the values fall into the trend except at the lower temperatures. The reason for the deviation of the reaction orders is that the heat energy is not enough and the conversion rate is too low at those temperatures.

Both the reaction rate constants k_1 and k_2 values increase with the cure temperatures and ef-CNT concentrations. From the assumption, k_1 and k_2 are functions of temperatures and follow the Arrhenius relationship, their respective activation energies can then be calculated from the plot of $\ln k_1 (T)$ and $\ln k_2 (T)$ as function of $1/T$ and the values are summarized in Table 2.

The activation energy from isothermal kinetic study shows the same decreasing trend with the increase of ef-CNT content, as what has been found in the dynamic study. The values calculated in isothermal are smaller than those in dynamic kinetic study as reported in the literature.³⁵ The E_1 and E_2 are similar with E_1 to be slightly greater because E_2 describes the later part of the reaction. From the dynamic DSC measurements, the activation energy of nanocomposites curing is found to decrease with the increasing of ef-CNT content. Similar results are observed in isothermal study.

Although many researchers have reported an observation on CNTs' accelerating effect on epoxy resin curing, few discuss the mechanisms behind.²⁴ We speculate the accelerating effect of CNTs is related to the high thermal conductivity of CNTs. Because epoxy resin is a thermal insulator (thermal conductivity = 0.2–0.5 W/mK), it takes relatively a longer time for the heat to transfer from the outside environment to the center. Multiwalled CNTs, on the other hand, have a generally high thermal conductivity value of 650–830 W/mK (theoretical value can be as high as 6000 W/mK). However, the thermal conductivity of CNT/polymer composite may be low³⁶ and is strongly influenced by the interface and the adhesion between the CNTs and polymer matrix.³⁷ With a strong interfacial interaction, the CNTs are homogeneously dispersed in the polymer matrix through functionalization and form a "thermal pathway" within the matrix. The heat energy from the outer environment can be transferred into

TABLE 2 The Activation Energy and Pre-Exponential Constants Calculated for the Curing of ef-CNT/BP/DDS Nanocomposites with Different CNT Composition

Sample Name	E_1 (KJ/mol)	E_2 (KJ/mol)
0.00 wt % ef-CNT/BP/DDS	66.69	58.11
0.50 wt % ef-CNT/BP/DDS	63.90	56.60
1.00 wt % ef-CNT/BP/DDS	62.93	55.16
2.00 wt % ef-CNT/BP/DDS	61.37	53.60
4.00 wt % ef-CNT/BP/DDS	59.34	52.94
10.00 wt % ef-CNT/BP/DDS	58.35	51.31

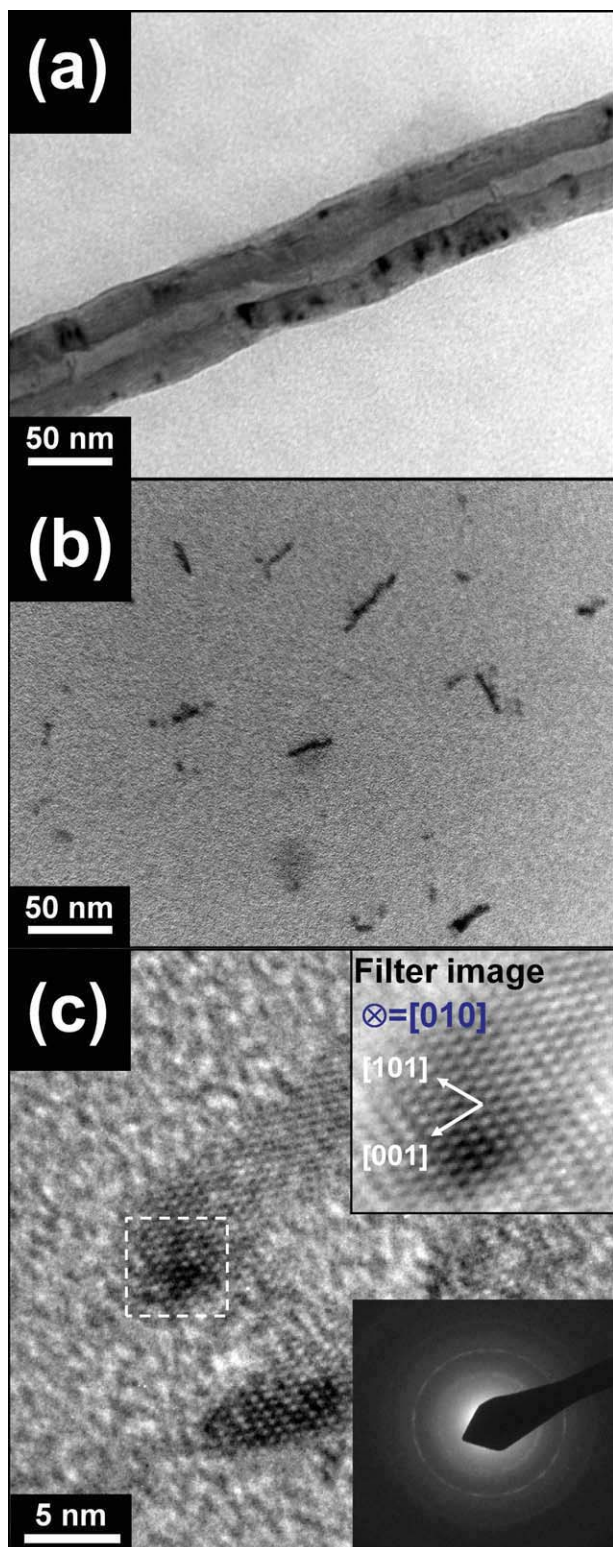


FIGURE 3 TEM images of (a) ef-CNT and (b) TiO₂ nanorod. (c) The HR-TEM image of TiO₂ nanorod with the insets of lattice image and diffraction pattern.

the epoxy resin and distributed within the matrix much more quickly and more effectively to stimulate the curing reaction happening. As a result, the activation energy is lowered. The high thermal conductivity of the CNTs is considered to be the origin for the decrease in activation energy. To testify our hypothesis, we have chosen a thermal insulating nanofiller, TiO₂ nanorods, to be added into the BP/DDS epoxy resin system and performed the same kinetic studies.

TiO₂/BP/DDS Nanorod Nanocomposite

In 2002, Jang et al. found in their studies that in the dynamic DSC experiment, the heat of cure was independent of the heating rate at a given composition for hybrid materials but dependent on the kind of fillers.³⁴ To give evidence for the relationship between thermal conductivity of fillers and the reaction activation energy, we introduced a thermal insulating filler, TiO₂ nanorods, and conducted the dynamic DSC experiments on TiO₂/BP/DDS nanocomposite.

The TiO₂ nanorods are synthesized in our laboratory.^{29,38} Figure 3(a,b) shows the difference on morphology between ef-CNT and TiO₂ nanorods. The HR-TEM image of TiO₂ nanorods [Fig. 3(c)] reveals that the dimensions of the TiO₂ nanorods are 20–30 nm in length and 4–5 nm in diameter. The upper right inset image shows the crystallinity of TiO₂ nanorods, and the corresponding selected-area diffraction pattern of the TiO₂ nanorods is shown in the lower right inset of Figure 3(c). The calculated activation energy is summarized in Table 3.

TiO₂ is nonthermal conducting and has thermal conductivity of 10.3–11.7 W/mK. The values may be higher than the epoxy resin matrix (thermal conductivity = 0.2–0.5 W/mK), but they are quite low if compared to the thermal conductivity of multiwalled CNTs (650–830 W/mK). From the calculations, we can see that the activation energy of curing for this system does not change much with the nanocomposite made from TiO₂ nanorods. This implies that the incorporation of TiO₂ nanorods does not have an accelerating effect on the epoxy curing reaction because it does not help on the heat transferring process. Undoubtedly, thermal conductivity of fillers has great impact on the curing behaviors of epoxy resins. The effect of filler type on the activation energy of nanocomposite curing with different amount of filler as illustrated in Figure 4. We can observe that the CNTs can promote the curing reaction of epoxy resins and speed up the reaction rate due to their high thermal conductivity. On the other hand, TiO₂ nanorods have low thermal conductivity and show no effect on the epoxy resin curing kinetics.

Modeling the Curing Behaviors

The parameters of the reaction rate equation obtained from the isothermal study can be used to formulate the reaction rate constants and further predict the curing behaviors of the reacting system. Curing of nanocomposite materials in practical applications are much more complex, because it involves in more factors and interactions among the ingredients to be considered. Keenan pointed out that the true chemical reaction kinetics can hardly be described for a resin system of practical use, yet kinetic models can be a useful

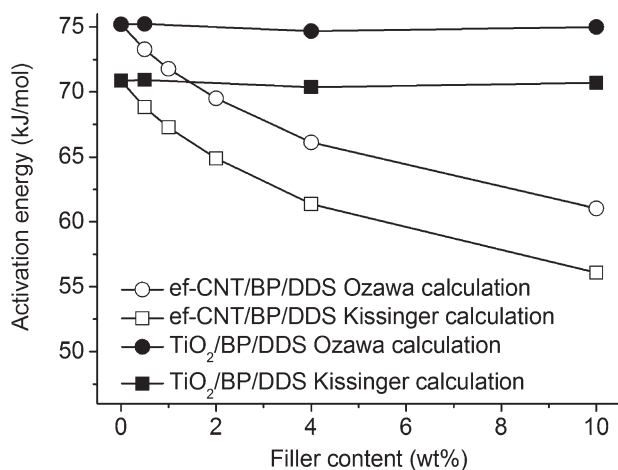
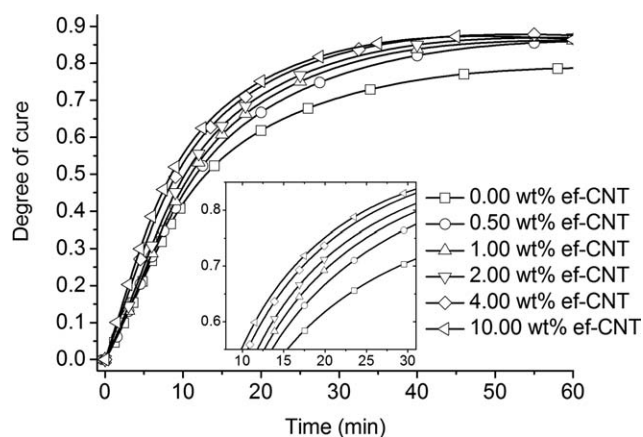
TABLE 3 The Activation Energy for the TiO₂/BP/DDS Nanocomposites Curing Calculated from the Kissinger and the Ozawa Model for Different TiO₂ Compositions

Sample Name	E_a by Kissinger Model (kJ/mol)	E_a by Ozawa Model (kJ/mol)
0.00 wt % TiO ₂ /BP/DDS	70.88	75.21
0.50 wt % TiO ₂ /BP/DDS	70.92	75.24
4.00 wt % TiO ₂ /BP/DDS	70.38	74.69
10.00 wt % TiO ₂ /BP/DDS	70.71	75.01

tool in providing empirical parameters for modeling and controlling the curing process.³⁹

From the isothermal kinetic study, we are able to derive the relationship between the curing degree and the time at various temperatures for the ef-CNT/BP/DDS nanocomposites. The predetermined BP/DDS is cured at 180 °C for 6 h and postcured for 220 °C for 4 h, 250 °C for 3 h based on Huang's research.³⁰ The change in cure degree with time of different ef-CNT concentrations at 180 °C is compared and shown in Figure 5. The bulk samples with different CNTs compositions are then cured under same temperature and time as the neat epoxy resin for comparison purpose. There is a good agreement between the model predictions and the experimental data. This provides an evaluation of the great predicting ability and the effectiveness of the model representing the cure behaviors of ef-CNT/BP/DDS nanocomposites.

The curing reaction of the epoxy/amine system has two stages. At the early stage, before vitrification, the curing reaction is chemical control and can happen rapidly. Thus, the curing rate is high, and the cure degree increases rapidly. Higher nanotube concentration speeds up the reaction and allows samples to reach the same curing degree in a much shorter period of time; for example, it would take 30 min for the epoxy resin to reach 70% cure but the 10 wt % sample only requires only half of the time (Fig. 5 inset). The steeper

**FIGURE 4** Effect of filler type on the activation energy of nano-composite curing with different amount of filler.**FIGURE 5** Modeling the degree of cure and curing time relationship of different ef-CNT compositions cured at 180 °C.

slopes in the figure represent faster curing rate. It is predicted that the curing degree increases with the ef-CNT concentrations.

However, from the model we can see that the rate of cure slows down and causes the lines to converge in the figure. Although the reaction continues to later stage, that is, the system reaches its gel point, the movements of polymer molecules are restricted because of a 3D network structure formed. The reaction then shifts to diffusion driven and the reaction rate slows down hastily due to vitrification. If the amount of heat is not enough to overcome the kinetic energy of the reaction required, and the molecules do not have enough energy to move around but crosslink locally instead, the diffusion control stage is forced to be antedated and occurs earlier. Uncured resins are trapped inside the network and results in incomplete curing. This can lead to deviations between model prediction and the experimental results. In high ef-CNT concentration samples, the vitrification stage is reached earlier than the neat epoxy resin with the faster reaction rate. As a result, at the end of the designated curing cycle, it is predicted that the highest degree of cure happens for the samples with 2 wt % ef-CNT loading comparatively. Further posture process would be required to further increase the degree of cure for high ef-CNT concentration samples.

CONCLUSIONS

The curing kinetics of ef-CNT/BP/DDS nanocomposite can fit into the autocatalytic model before the vitrification, and then it becomes diffusion control process. The curing activation energy/curing rate is strongly influenced by the thermal conductivity of the reinforcing materials for composites, because the activation energy decreases with increasing compositions of ef-CNT, which are excellent thermal conductors but remains unchanged with the addition of TiO₂ nanorods, which are thermal insulators. On the other hand, as the content of ef-CNT increasing, the alignment of BP/DDS resin might get better that would enhance the thermal conductivity of ef-CNT/BP/DDS nanocomposite. Although the curing

rate is increased by more ef-CNT additions, the curing degree shows an inverse trend. This is because when the curing reaction is accelerated, the vitrification stage of the epoxy resin is antedated and so does the diffusion control stage. Although the CNTs help decrease the curing reaction barrier, the cross-linked network structures restrict the polymeric molecule movement and results in relatively lower degree of cure.

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REFERENCES AND NOTES

- Schmidt, R. G.; Bell, J. P. *Adv. Polym. Sci.* **1986**, *75*, 33–71.
- Kinjo, N.; Ogata, M.; Nishi, K.; Kaneda, A. *Adv. Polym. Sci.* **1989**, *88*, 1–48.
- Gaschke, M.; Dreher, B. *J. Coat. Technol.* **1976**, *48*, 46–51.
- Schadler, L. S.; Giannaris, S. C.; Ajayan, P. M. *Appl. Phys. Lett.* **1998**, *73*, 3842–3844.
- Baley, C.; Davies, P.; Grohens, Y.; Dolto, G. *Appl. Compos. Mater.* **2004**, *11*, 99–126.
- Chen, M. H.; Chen, C. R.; Hsu, S. H.; Sun, S. P.; Su, W. F. *Dent. Mater.* **2006**, *22*, 138–145.
- Fujihara, K.; Teo, K.; Gopal, R.; Loh, P. L.; Ganesh, V. K.; Ramakrishna, S.; Foong, K. W. C.; Chew, C. L. *Compos. Sci. Technol.* **2004**, *64*, 775–788.
- Su, W. F. A. *J. Polym. Sci. Part A: Polym. Chem.* **1993**, *31*, 3251–3256.
- Su, W. F. A.; Schoch, K. F.; Smith, J. D. B. *J. Appl. Polym. Sci.* **1998**, *70*, 2163–2167.
- Harada, M.; Akamatsu, N.; Ochi, M.; Tobita, M. *J. Polym. Sci. Part B: Polym. Phys.* **2006**, *44*, 1406–1412.
- Harada, M.; Sumitomo, K.; Nishimoto, Y.; Ochi, M. *J. Polym. Sci. Part B: Polym. Phys.* **2009**, *47*, 156–165.
- Harada, M.; Ochi, M.; Tobita, M.; Kimura, T.; Ishigaki, T.; Shimoyama, N.; Aoki, H. *J. Polym. Sci. Part B: Polym. Phys.* **2004**, *42*, 758–765.
- Ochi, M.; Hori, D.; Watanabe, Y.; Takashima, H.; Harada, M. *J. Appl. Polym. Sci.* **2004**, *92*, 3721–3729.
- Wu, J. H.; Chung, D. D. L. *Carbon* **2004**, *42*, 3039–3042.
- Xie, H. F.; Liu, B. H.; Yuan, Z. R.; Shen, J. Y.; Cheng, R. S. *J. Polym. Sci. Part B: Polym. Phys.* **2004**, *42*, 3701–3712.
- Chen, E. C.; Wu, T. M. *J. Polym. Sci. Part B: Polym. Phys.* **2008**, *46*, 158–169.
- Ajayan, P. M.; Suhr, J.; Koratkar, N. *J. Mater. Sci.* **2006**, *41*, 7824–7829.
- Ajayan, P. M. *Chem. Rev.* **1999**, *99*, 1787–1799.
- Koval'chuk, A. A.; Shchegolikhin, A. N.; Shevchenko, V. G.; Nedorezova, P. M.; Klyamkina, A. N.; Aladyshev, A. M. *Macromolecules* **2008**, *41*, 3149–3156.
- Tao, K.; Yang, S. Y.; Grunlan, J. C.; Kim, Y. S.; Dang, B. L.; Deng, Y. J.; Thomas, R. L.; Wilson, B. L.; Wei, X. *J. Appl. Polym. Sci.* **2006**, *102*, 5248–5254.
- Harada, M.; Ochi, M.; Tobita, M.; Kimura, T.; Ishigaki, T.; Shimoyama, N.; Aoki, H. *J. Polym. Sci. Part B: Polym. Phys.* **2003**, *41*, 1739–1743.
- Kato, T.; Nagahara, T.; Agari, Y.; Ochi, M. *J. Polym. Sci. Part B: Polym. Phys.* **2006**, *44*, 1419–1425.
- Abdalla, M.; Dean, D.; Robinson, P.; Nyairo, E. *Polymer* **2008**, *49*, 3310–3317.
- Qiu, J. J.; Wang, S. R. *Mater. Chem. Phys.* **2010**, *121*, 295–301.
- Kissinger, H. E. *Anal. Chem.* **1957**, *29*, 1702–1706.
- Ozawa, T. *Bull. Chem. Soc. Jpn.* **1965**, *38*, 1881–1886.
- Kamal, M. R.; Sourour, S. *Polym. Eng. Sci.* **1973**, *13*, 59–64.
- Vyazovkin, S.; Sbirrazzuoli, N. *Macromolecules* **1996**, *29*, 1867–1873.
- Zeng, T. W.; Lin, Y. Y.; Lo, H. H.; Chen, C. W.; Chen, C. H.; Liou, S. C.; Huang, H. Y.; Su, W. F. *Nanotechnology* **2006**, *17*, 5387–5392.
- Huang, J. R. In Institute of Polymer Science and Engineering; National Taiwan University: Taipei, **2007**.
- Zhu, J.; Peng, H. Q.; Rodriguez-Macias, F.; Margrave, J. L.; Khabashesku, V. N.; Imam, A. M.; Lozano, K.; Barrera, E. V. *Adv. Funct. Mater.* **2004**, *14*, 643–648.
- Wang, S.; Liang, R.; Wang, B.; Zhang, C. *Nanotechnology* **2008**, *19*, 085710.
- Duswalt, A. A. *Thermochim. Acta.* **1974**, *8*, 57–68.
- Bae, J.; Jang, J.; Yoon, S. H. *Macromol. Chem. Phys.* **2002**, *203*, 2196–2204.
- Prime, R. B. *Polym. Eng. Sci.* **1973**, *13*, 365–371.
- Moniruzzaman, M.; Winey, K. I. *Macromolecules* **2006**, *39*, 5194–5205.
- Yuen, S. M.; Ma, C. C. M.; Chiang, C. L.; Chang, J. A.; Huang, S. W.; Chen, S. C.; Chuang, C. Y.; Yang, C. C.; Wei, M. H. *Compos Part A: Appl. Sci. Manuf.* **2007**, *38*, 2527–2535.
- Lin, Y. Y.; Chen, C. W.; Chu, T. H.; Su, W. F.; Lin, C. C.; Ku, C. H.; Wu, J. J.; Chen, C. H. *J. Mater. Chem.* **2007**, *17*, 4571–4576.
- Keenan, M. R. *J. Appl. Polym. Sci.* **1987**, *33*, 1725–1734.