



# Thermal properties and non-isothermal curing kinetics of carbon nanotubes/ionic liquid/epoxy resin systems



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## ABSTRACT

Nanocomposites of multi-wall carbon nanotubes in diglycidyl ether of a bisphenol A epoxy matrix were prepared using ionic liquid [BMIM]PF<sub>6</sub> as a dispersion agent and diaminodiphenyl methane as a hardener. The non-isothermal curing kinetics of the neat EP, CNTs/EP and CNTs/ILs/EP were investigated, and the activation energy was calculated using the Kissinger equation. Two-parameter autocatalytic equations of Šesták–Berggren model were constructed to describe the curing reaction rate quantitatively. The reaction orders, pre-exponential factor  $A$  and kinetic model  $f(\alpha)$  were determined by curve fitting, and the calculated curves described the observed reaction rate well. TGA and DMA were used to measure the thermal properties of the composites. Adding ILs increased the storage modulus of composites, but decreased the thermal stability. Fracture surfaces of CNTs/EP and CNTs/ILs/EP composites were observed by SEM. CNTs showed better dispersion state in CNTs/ILs/EP composites.

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## 1. Introduction

Epoxy resins possess excellent mechanical properties, high adhesiveness to many substrates, and good heat and chemical resistances, so they are widely used in coatings, electronics, adhesives, and as matrices for composites [1]. However, the inherent brittleness of epoxy resins constrains their engineering applications. Many attempts have been made to improve their properties, such as adding liquid elastomers, thermoplastics, and inorganic particles [2–6]. Recently, epoxy composites containing carbon nanotubes (CNTs) have attracted interest [7–10]. Because of their remarkable mechanical, thermal and electrical properties, CNTs have attracted the interest of the science and engineering community to dedicate significant effort to their applications. One of the promising applications of CNTs is developing polymer-based nanocomposites. The high flexibility, low mass density and large aspect ratio (typically >1000) make CNTs excellent candidates to substitute the conventional fillers in the fabrication of high-performance and multifunctional polymer nanocomposites [11–14].

For CNTs/polymer composites, good dispersion of CNTs and strong interfacial bonding between the CNTs and the polymer matrix are important factors for obtaining property improvements. However, CNTs are inherently inert and easily agglomerate. To

achieve the advantages of CNTs and to enhance the properties of CNTs/polymer nanocomposites, various approaches are used, such as covalent functionalization and non-covalent functionalization of CNTs [15–17]. In recent years, the ability of ionic liquids (ILs) to disperse or modify CNTs has attracted more and more attention [18–22]. Using ILs as dispersant is an effective approach to improve the dispersion of CNTs in a polymer matrix. Theoretical and spectroscopic studies have suggested that cation- $\pi$  stacking or electrostatic shielding between CNTs by ILs are the reasons for the favorable interactions [23].

In this paper, diglycidyl ether of bisphenol A-based epoxy resin dispersed with multi-wall CNTs were prepared and alkyl imidazole ionic liquid [BMIM]PF<sub>6</sub> was used to improve the dispersion of MWCNTs in the epoxy matrix. Up to now, the literature related to CNTs/ILs/EP composites is centered on the final properties of the materials, and few of them are focused on curing processing [24–26]. In factor, the surface properties of CNTs and dispersion of CNTs in the matrix will influence the curing process of epoxy resin, and the final properties of the composite depend significantly on the curing conditions, so understanding the cure reaction is very important for the design and optimization of manufacturing nanocomposites [27]. The effect of different types of carbon nanotubes on the curing process of epoxy resin was shown in many articles, but the results are often conflicting due to the large number of variables that can influence the cure of this composite [28]. The curing kinetics of epoxy resins has been experimentally studied using many techniques. One of the most widely used

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techniques is thermal analysis by differential scanning calorimetry (DSC) in isothermal or dynamic modes followed by kinetic analysis using phenomenological models. Rou et al. studied the curing kinetics of diglycidyl ether of bisphenol A and diglycidyl ether of hydroquinone epoxy resin system and found that Šesták–Berggren equation is adequate to describe the cure kinetics of the selected epoxy resin system [29]. In this work, the curing kinetic of EP, CNTs/EP and CNTs/ILs/EP systems were investigated by differential scanning calorimetry (DSC) using non-isothermal experiments. Two-parameter autocatalytic equations of Šesták–Berggren model were estimated. The work presented in this article will evaluate the effect of ILs on the curing of EP modified by CNTs and the results can provide guidance to select an appropriate curing temperature for the production process.

## 2. Experimental

### 2.1. Materials

Diglycidyl ether of bisphenol A (DGEBA) with an epoxy equivalent weight of 184–190 g/eq was purchased from Beijing Tonglian Hengxing Technology Co. Ltd. MWCNTs were purchased from Shenzhen Namigang Co. Ltd. The average diameter was 20–40 nm, the length was 5–15  $\mu\text{m}$ , and the purity was higher than 97%. Curing agent 4,4'-methylenedianiline (DDM) was purchased from Sinopharm Chemical Reagent Co. The alkyl imidazole ionic liquid [BMIM]PF<sub>6</sub> was from Shanghai Cheng Jie Chemical Co. Ltd.

### 2.2. Sample preparation

The sample of CNTs/ILs/EP was prepared as followed. 0.2 g of [BMIM]PF<sub>6</sub> and 10 mL of acetone were mixed firstly to form solution. 0.025 g of CNTs was dispersed in the solution and ultrasonicated for 1 h, then mixed with 5 g of epoxy resin preheated to 60 °C. The mixture was ultra-sonicated for 0.5 h and then stirred for 1.5 h at 60 °C. After removal of acetone through reduced pressure distillation, the stoichiometric amount of curing agent DDM was added and stirred for few minutes to obtain a uniform mixture. For the preparation of CNTs/EP sample, only acetone was used to disperse the CNTs and the subsequent steps were the same as for the CNTs/ILs/EP. EP was also mixed with DDM to compare with the composites. The three systems, EP, CNTs/EP and CNTs/ILs/EP were used for dynamic DSC measurements.

EP, CNTs/EP, and CNTs/ILs/EP mixtures were cast into a mold and thermally cured at 110 °C for 1 h, 140 °C for 4 h and further post cure at 160 °C for 1 h to produce cured specimens. The samples were used to measure thermal properties and observe the morphology of fracture surfaces.

### 2.3. Dynamic DSC measurements

#### 2.3.1. Measurements

Dynamic DSC measurements were performed using a DSC-204F1 (NETZSCH, Germany) calibrated with an indium standard. Approximately, 10 mg of the mixture of each system was placed in an alumina pan and cured at different heating rates (2, 5, 10, and 20 °C/min) over a temperature range from 25 to 300 °C under nitrogen atmosphere. The reaction was considered to be complete when the DSC curve leveled off to a baseline. Four specimens for each system and each heating rate were performed.

#### 2.3.2. Theoretical fundamentals

In the kinetic analysis DSC technique, the measured reaction heat is assumed to be directly proportional to the reacted epoxy

groups. Therefore, the conversion of epoxy groups and the reaction rate can be expressed by Eqs. (1) and (2)

$$\alpha = \frac{\int_0^t Q dt}{\int_0^{t_f} Q dt} \quad (1)$$

$$\frac{d\alpha}{dt} = K(T)f(\alpha) \quad (2)$$

where  $\alpha$  is the curing conversion,  $t$  is the reaction time,  $t_f$  is the time to reaction completion,  $Q$  is the heat flow measured by DSC,  $d\alpha/dt$  is the rate of reaction,  $f(\alpha)$  is a kinetic model dependent function of  $\alpha$ , and  $k(T)$  is the reaction rate constant, which is dependent on the temperature and follows the Arrhenius law (Eq. (1)).

$$K(T) = A \exp(-x) \quad (3)$$

where  $A$  is the pre-exponential factor,  $x$  is equal to  $E_a/RT$ , in which  $E_a$  is the activation energy,  $R$  is the gas constant and  $T$  is the absolute temperature.

Several models can be used to describe the non-isothermal curing reaction kinetics. Málek proposed a method for judicious selection of reaction models and rational calculation of the involved model parameters for a thermally stimulated physical or chemical process under linear temperature programs [30]. According to the Málek method, the apparent activation energy  $E_a$  for a non-isothermal process must be known previously. The  $y(\alpha)$  function is proportional to the  $f(\alpha)$  function, representing characteristic of specified models. The mathematical properties of the  $y(\alpha)$  and  $z(\alpha)$  functions for the basic kinetic models include JMA( $n$ ), RO( $n$ ) and SB( $m, n$ ) models [31], the curvature of the  $y(\alpha)$  vs.  $\alpha$  curve and the maximum location of the  $y(\alpha)$  and  $z(\alpha)$  functions can be used to guide the choice of a kinetic model. So the two special functions  $y(\alpha)$  and  $z(\alpha)$  can be defined as the diagnostic signatures for the determination of the reaction models and calculation of the model parameters.

$$y(\alpha) = \left( \frac{d\alpha}{dt} \right) \exp(x) \quad (4)$$

$$z(\alpha) = \pi(x) \frac{d\alpha}{dt} T / \varphi \quad (5)$$

where  $\varphi$  is the heating rate,  $\pi(x)$  is an approximation of the temperature integral. There are many approximate expressions in literature; the 4th rational expression of Senum and Yang gives sufficiently accurate results [32].

$$\pi(x) = \frac{x^3 + 18x^2 + 88x + 96}{x^4 + 20x^3 + 120x^2 + 240x + 120} \quad (6)$$

By determining whether the peak conversions ( $\alpha_m, \alpha_p^\infty$ ) of the normalized  $y(\alpha)$  and  $z(\alpha)$  functions and conversion  $\alpha_p$  corresponding to the maximum experimental rates satisfy a set of specific conditions proposed by Málek [30,31], one can confirm an appropriate kinetic model and further obtain a method to calculate the model parameters.

The  $E_a$  can be calculated using various methods; in this paper, the Kissinger method [33,34] was selected.

$$\ln \left( \frac{\varphi}{T_p^2} \right) = \ln \frac{AR}{E_a} - \frac{E_a}{RT_p} \quad (7)$$

where  $T_p$  is the peak temperature of the DSC curve at a certain heating rate, and  $\varphi$  is the heating rate. The  $E_a$  is determined by the slope of  $\ln(\varphi/T_p^2)$  versus  $1/T_p$ .

### 2.4. Thermal properties measurement

Their thermal stability was evaluated using a Q600 SDT thermogravimetric analyzer (TA, USA) at the heating rate of 10 °C/min from

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