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Investigation of curing kinetics of sodium carboxymethyl cellulose/epoxy resin system by differential scanning calorimetry

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ABSTRACT

Sodium carboxymethyl cellulose (CMC) have been used to disperse carbon nanotubes (CNTs) and have potential applications to make the CNTs/epoxy or CNTs/epoxy/carbon fiber composites. In this paper, the curing kinetics of epoxy resins with and without CMC and cured with 4,4′-diamino diphenyl methane (DDM) hardener was studied by non-isothermal differential scanning calorimetry (DSC). A two-parameter (m, n) autocatalytic model was used to describe the cure kinetics of the epoxy resins. The kinetic parameters were calculated with the Málek method and least square regression (LSR) method, respectively. The curves by Málek method and LSR method both show a good agreement with the experimental data for Epoxy/DDM and CMC/epoxy/DDM systems. The results, based on the two methods, showed that the activation energy was no obvious difference with the addition of CMC, which indicated that the CMC have no effect on the curing reaction without changing the kinetic model.

1. Introduction

Epoxy resins are the most important thermosetting polymers [1]. It was widely used as adhesives in the aerospace industry, surface coatings and matrices in high performance composites [2] due to their superior characteristics such as good mechanical properties, thermal stability, chemical resistance and flame retardancy. Most of the commercially available epoxy resins are oligomers of diglycidyl ether of bisphenol A (DGEBA) [1]. When these oligomers react with the hardener, the epoxy resin will becomes a thermosetting polymer. These epoxy resin polymers have good thermal, electrical and mechanical properties, but they are brittle and have poor resistance to the crack propagation. These advantage and disadvantage of epoxy resins are predetermined by the chemical structure of the resin and hardener, as well as by the network achieved after curing. To alternate the epoxy resins weak point, almost all of epoxy resins are modified with various additives and fillers, such as low molecular weight polymers, reactive oligomeric compounds, plasticizers, nano-fillers, nano-particles and carbon nanotube [1,3]. The use of nano-particles in nano-particles/epoxy composites has attracted wide attention, such as carbon nanotubes/epoxy composites [2,4] and carbon nanofibers/epoxy composites [5]. However, fabrication of homogeneous nanocomposites remains a technical challenge, because of the nano-particles natures of easily agglomerate [6]. Surfactant has been successfully applied to address this challenge and enhance the dispersion of nano-particles or carbon nanotubes in epoxy resin matrix and improve the interfacial interaction between the nano-particles and matrix [7–9]. Several studies have contributed to studying the effects of surfactant on dispersibility and cured processing and other property changes of nano-particles/epoxy composites. The surfactants studied previously include non-ionic surfactants such as polyoxyethylene octylphenylether (Triton X-100), nonylphenol ethoxylate (Tergitol NP-7) [6]; anionic surfactants such as sodium dodecyl sulfate (SDS), sodium dodecylbenzenesulfonate (SDBS), poly(styrene sulfate) (PPS); cationic surfactants dodecyl tri-methyl ammoniumbromide (DTAB) and cetyltrimethylammounium 4-vinylbenzoate (CTVB) [8].

Sodium carboxymethyl cellulose (CMC) is a kind of surfactant with several hydroxyl groups. It is also a type of cellulose derivative bound to some of the hydroxyl groups of the glucopyranose monomers that make up the cellulose backbone, which is widely used in detergents, oil-drilling, food-making, paper, textile industries and dyeing industry [10]. CMC is used in textile and dyeing industry as sizing agent (glass fiber or carbon fiber) and dying adjuvant to make stock limpidity and transparence. It is also a good stabilizer of the stock. Aqueous solutions CMC have also been used to disperse carbon nanotubes (CNTs) [11–14]. It is thought that the long CMC molecules wrap around the nanotubes, allowing them to be dispersed in water or other matrix [9,11,12,15]. The

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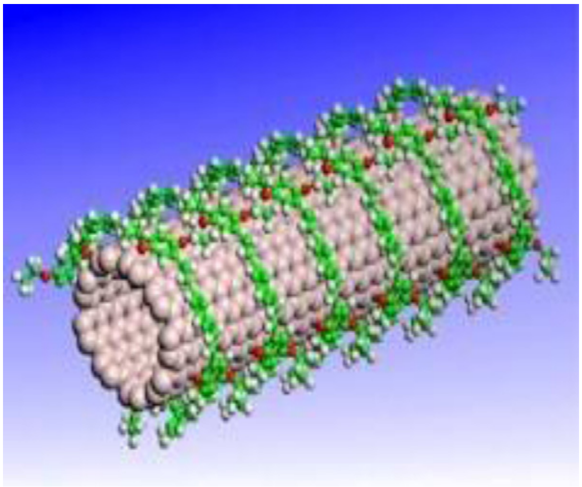

Fig. 1. Schematic of CNT wrap structure by the surfactant such as CMC. Copyright 2010, Composites: Part A 41, 1353.

possible schematic representation is shown in Fig. 1. It can form a double helical structure with CNTs by self-organized process. For this reason, CMC have potential applications in fabrication of the CNTs/epoxy or CNTs/epoxy/carbon fiber composites, so the influence of CMC on the epoxy resin curing process are worth investigating.

It is known that the properties of cured epoxy resin polymers depend on the curing conditions such as the time and the temperature of curing. On the other hand, to trace exactly the structure–property relationships for an epoxy resin system, understanding of the cure process is essential in order to get a better control of the reactions and optimize the physical properties of the final product. Kinetic analysis is applied to understand structure/property/processing relationships for the preparation of high performance epoxy resin matrix composites. Cure kinetics of epoxy resins can be studied by different techniques, such as differential scanning calorimetry (DSC) and infrared spectroscopy (IR). In this work, DSC technique was used to investigate the cure kinetics of epoxy resins with CMC under non-isothermal conditions.

Cure kinetic models can be classified into two categories, phenomenological and mechanistic models [16]. Mechanistic models obtain from the chemical reaction processing according the balance of chemical species. In many cases, it is not easy to obtain the mechanistic model especially when the cure reaction is very complicated. Phenomenological models, were proved to be more appropriate in these cases [17]. Among these models, the *n*th-order model and autocatalytic model were used extensively in the description of the kinetics of epoxy resin cure. Autocatalytic models mainly include SB model which is deduced by non-isothermal DSC and Kamal model which is obtained by isothermal DSC. Autocatalytic model have been intensively and extensively used to study the curing systems of bisphenol A type epoxy and curing agents containing active hydrogen groups such as hydroxyl, amino and mercapto group [18–20]. According to the literatures, a most probability method supported by Málek was widely used to obtain the kinetic parameters [1,19–21].

In this work, the curing reaction kinetics of diglycidyl ether of bisphenol A (E51) epoxy resins and 4,4′-diamino diphenyl methane (DDM) with and without CMC were studied by the non-isothermal DSC. A two-parameter (m, n) autocatalytic model (Šesták–Berggren equation) was used to describe the cure kinetics of epoxy resins system. The model parameters was tried to obtain by two different methods that one is the most probability method supported by Málek and the other is the least square regression (LSR) method. Furthermore, this work attempts to analyze and model the cure behaviors of the CMC/E51/DDM system in order to develop an optimal cure process for the CNTs/epoxy composite with CMC system. To the best of our knowledge, this is the first time that the curing kinetics of CMC/E51/DDM system was researched.

2. Experimental

2.1. Materials

The diglycidyl ether of bisphenol A type (E51) epoxy resin was provided by Deyuan Chemistry Plant, China (epoxide equivalent weight of 0.48–0.53). The curing agent was 4,4′-diamino diphenyl methane (DDM), which was provided in analytical grade by Shanghai crystal pure reagent Co. (Aladdin Reagent Co., China). The CMC was supplied by Suzhou Yiming Chemical Plant in China.

2.2. DSC measurements

Studies on the curing kinetics of CMC/E44/DDM system were carried out by DSC in different heating rates. E51 epoxy resin and CMC were mixed at mass ratio of 100/3 at room temperature. The DDM were added to the mixed CMC/E51 system. The mass ratio of E51 to DDM was set at 100:25. The CMC/E51/DDM system was stirred until a homogeneous mixture was obtained. The sample of CMC/E51/DDM was refrigerated in the fridge for 24 h, after that it was measured by DSC. This treatment can guarantee the stability of the measurement. In the same way, the E51/DDM system was done.

Dynamic DSC analysis was done by DSC Q200 (TA, USA) which was calibrated with high purity indium and zinc standards. The samples (4–5 mg) were added to aluminum pans and analyzed dynamically with heating rates at 5 K/min, 10 K/min, 15 K/min, 20 K/min in nitrogen atmosphere. Nitrogen was purged at rate of 40 ml/min to minimize oxidation of the sample. Measurements were always carried out with an empty cell as reference from 318.15 K up to 553.15 K.

3. Results and discussion

3.1. Basic assumptions of dynamic DSC analysis

DSC is one of the thermal analysis methods. Kinetics can be characterized with DSC by measuring heat generated during the curing reaction as a function of temperature and time. The DSC curves were analyzed on the basis of the following assumption: the area under the curves was proportional to the conversion α. The conversion α could be defined as [3]:

$$a(t) = \frac{H(t)}{\Delta H_T} \tag{1}$$

where ΔH_T is the total heat of curing reaction and $H(t)$ is the partial heat of reaction at time t. For both isothermal and non-isothermal conditions, the extent of cure, $a(t)$ is estimated by integrating DSC curves from the cured initial point to end point.

The distribution of heat of reaction $H(t)$ for non-isothermal curing is given by:

$$H(t) = \int_0^t Q(t)dt \tag{2}$$

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

A general expression is for the reaction rate as a function of temperature:

$$r_a = \frac{da}{dt} = k(T)f(a) \tag{3}$$