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Study on the effect of poly(oxypropylene)diamine modified organic montmorillonite on curing kinetics of epoxy nanocomposties

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ABSTRACT

The effects of poly(oxypropylene) diamine modified organic montmorillonite (modified MMT) on the curing kinetics of epoxy (EP) were investigated by means of differential scanning calorimetry (DSC). The curing kinetic parameters of pure epoxy and the EP/modified MMT were obtained by Kissinger method and autocatalytic model. The in total heat of reaction ΔH, peak temperature T_p, activation energy Ea and the overall order of reaction $m+n$ were enhanced due to the incorporation of modified MMT in the epoxy. Results on the calculation of EP/modified MMT revealed the activation energy was much higher at the beginning and decreased all the way in the curing process, while in the neat epoxy, the variation of activation energy is limited. Comprehensive kinetic analyses indicated that the incorporation of modified MMT brought in an effect of inhibition on curing process especially for MMT with disordered and puffed clay sheets and the possible curing mechanism and reaction pathways were proposed to provide a reasonable explanation.

1. Introduction

Epoxy is one of the most important thermosetting polymers, widely used in adhesives, coatings, electronics, high performance composite materials and aerospace industries due to its the excellent mechanical and chemical properties, such as high tensile and compressive strength, good chemical resistance and high heat distortion temperature [1,2]. However, epoxy resins are brittle and have poor resistance to the crack propagation due to the high degree of molecular crosslinking [3]. In general, the properties of epoxy resins are always determined by the chemical structure of the resin itself, the hardener and the fillers added, as well as the cross-linked network achieved after curing [4]. In order to make up the weak point of the epoxy resins and get more excellent properties, various of nano-particles have been used to modify the epoxy resins [5]. Adding montmorillonite (MMT) into polymer matrix, namely Polymer/layered silicate (PLS) nano-composites, have aroused intense attention of material investigators for their unique and perfect properties resulted from the combining characteristics of both components at nanometer scale [6].

Because of the small basal spacing, hydrophilicity and lack of affinity for the hydrophobic organic compounds, pristine MMT interlayers cannot be well penetrated by polymer, and so cannot exert its advantages on polymer matrix [7,8]. Therefore, the MMT must be modified with organic chemicals in order to expand its interlayer spacing and improve its compatibility with polymer. Among various organic chemicals used in modification of MMT, a number of studies have been carried out on the use of poly (oxypropylene) amine as an intercalating agent in the last decades [9–12]. Compared to the most common surfactants of alkylammonium salts, the application of poly(oxypropylene) amine to modify MMT could further expand the basal spacing and the modified MMT with a basal spacing of up to 8.5 nm have been obtained [13]. On the basis of the significantly expanding interlayer spacing and improving compatibility with polymer matrix, the exfoliated nanocomposites can be prepared readily, including epoxy/MMT nanocomposites [14].

Generally, improvement in the properties of epoxy nanocomposites filled with MMT depends on the formation of the crosslinked molecular network, which is often influenced by the mechanism and kinetics of epoxy resin curing that involves various chemical reactions. Nano-particles used to modify the kinetics of curing reaction have been reported [15,16]. In this sense, a clear understanding of reaction kinetics of epoxy resin plays an extremely important role in determining the curing condition

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and thus to optimize the physical properties of the final product [17]. Curing process of epoxy resins can be studied by different techniques, such as differential scanning calorimetry (DSC) [18,19]. Fourier transform infrared spectroscopy (FTIR) [20] and near infrared spectroscopy (IR) [21]. Among these techniques, differential scanning calorimetry (DSC) is the most widely used technique covering the most common kinetic methods such as model-free methods and mode-fitting methods [22]. Some studies have reported long-chain alkylammonium salts modified MMT was incorporated in the epoxy matrix to facilitate the curing reaction and kinetics of epoxy nanocomposites [23,24]. Meanwhile, a large expanding of basing spacing of MMT modified by poly(oxypropylene) diamine and its mechanical properties of epoxy/MMT nanocomposites were studied in some references [25–27]. However, few studies have depicted the curing behavior, especially merging on the curing mechanism and kinetics, of epoxy/MMT nanocomposites when MMT is modified by poly (oxypropylene) amine.

In our study, organic MMT was modified by poly(oxypropylene) diamine with two different molecular weight ($M_w = 400$ g/mol or $M_w = 2000$ g/mol) respectively. Compared with neat epoxy system, the aim of the present work was to investigate the effect of poly(oxypropylene) diamine modified MMT on the cure mechanism and cure kinetics of epoxy resin. Furthermore, the relationship between cure kinetic and disperse state of clay leaded by modification was also taken into consideration. For this propose, non-isothermal DSC measurement was carried out to reveal the curing behavior and some empirical approaches were used to model the kinetics of the curing reaction.

2. Expermental

2.1. Materials

The diglycidyl ether of bisphenol A type (E51) epoxy resin was provided by Deyuan Chemistry Plant, China, with an epoxide equivalent weight of 184–210 g/equiv. The density is 1.18 g/cm^3 at 25°C and the viscosity is 2500 mPa s at 40°C. The curing agent was 4, 4-diamino diphenyl methane (DDM), which was provided in analytical grade by Shanghai crystal neat reagent Co. (Aladdin Reagent Co., China). The pristine Na$^+$-MMT was provided by America Nanocor Inc., with a cation exchange capacity of 145meq/100 g. Poly(oxypropylene) diamine were obtained from Huntsman Corporation (The Woodlands, Texas, USA), including two kinds of diamine (D400, D2000), with average weight molecular weights of 400 g/mol and 2000 g/mol, respectively.

2.2. Preparation of modified MMT by poly(oxypropylene) diamine

The modified MMT by poly(oxypropylene) diamine was prepared through ion-exchanging reaction with distilled water as a dispersing medium at 70°C for 6 h. Stoichiometric amounts of the diamine and dilute aqueous HCl to ensure the acidification ratio of H^+/NH_2 to be 1:1. Similarly, POP ammonium ion to Na$^+$ is also at the molar ratio of 1:1. More detailed procedure was described in previous work [13]. The modified MMT were labeled according to the poly(oxypropylene) diamine as given below: D400-MMT and D2000-MMT.

2.3. Epoxy/MMT nanocomposites preparation

Weight ratio of epoxy/hardener (DDM) was 4:1(stoichiometric). The EP and modified MMT were mixed at a mass ratio of 100/5 using a high speed mechanical stirrer at 2500 rpm until a homogeneous mixture was obtained. Then the mixture of EP, modified MMT, and DDM was stirred for 30 min and subsequently degassed under vacuum for about 30 min. Three samples were designated as EP (neat epoxy), EP/D400-MMT (MMT modified by D400), EP/D2000-MMT (MMT modified by D2000). The curing behavior of samples was carried out on the DSC equipment as listed below.

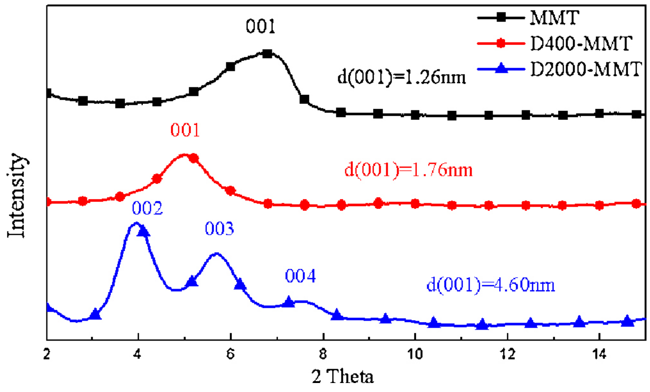

Fig. 1. XRD patterns of pristine MMT and modified MMT.

2.4. Characterization methods

2.4.1. X-ray diffraction (WXRD) analyses

Wide-angle X-ray diffraction (WXRD) analyses were performed on Dutch Philips X-ray DY-1291 diffractometer with Ni filtered CuKα (40 kV, 35 mA) from 2 to 15°2θ at a speed of 3°2θ min^{-1}.

2.4.2. TGA measurement

The TGA analysis of MMT intercalated by poly(oxypropylene) diamine (D400 and D2000) was carried out using a thermo analyzer TG209F1(NETZSCH, USA). Samples of 6–8 mg were heated from room temperature to 800 °C at a heating rate of 10 K/min under a nitrogen flow (40 ml/min).

2.4.3. DSC measurements

Calorimetric studies were carried out on DSC Q200 (TA, USA) which was calibrated with high purity indium and zinc standards. Samples of about 10 mg were put in aluminum pans under nitrogen atmosphere at the heating rate of 5, 10, 15 and 20 K/min respectively. Measurements were always carried out with an empty cell as reference from 323.15 K up to 523.15 K.

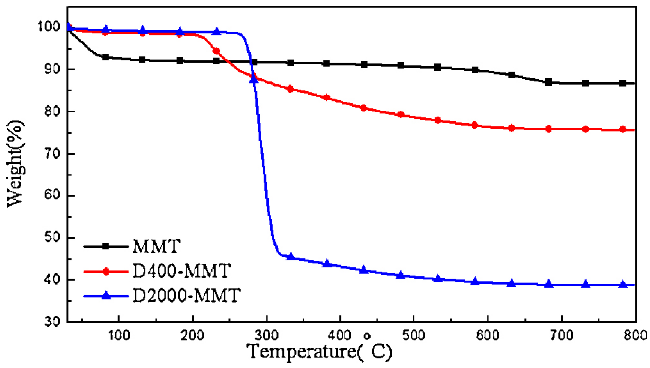

Fig. 2. TGA curves of MMT and modified MMT(D400-MMT, D2000-MMT).