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Study on the effect of aminosilane functionalized nanoclay on the curing kinetics of epoxy nanocomposites

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ABSTRACT

The curing kinetics of epoxy nanocomposites prepared by incorporating pristine (P-MMT) and functionalized montmorillonite clay (S-MMT) was studied using non-isothermal differential scanning calorimetry (DSC) experiments. Loading of S-MMT in epoxy matrix resulted in the decrease of peak exotherm temperature (T_p) at all heating rates corroborating the enhanced curing reactions, when compared to neat or P-MMT filled epoxy system. The kinetic parameters of the curing processes of the neat, pristine and functionalized MMT filled epoxy were determined using isoconversional methods viz. Kissinger and Friedman methods. In comparison to P-MMT filled epoxy system, epoxy nanocomposites loaded with S-MMT showed lower activation energy (E_α) over the range of conversion (α) revealing the enhanced curing reactions in these system. Besides E_α, the overall order of reactions ($m+n$) does not vary significantly in comparison to neat or P-MMT loaded epoxy corroborating the fact that the curing mechanism is autocatalytic in nature. The predicted curves determined using the kinetic parameters fit well with the non-isothermal DSC thermograms revealing the proposed kinetic equation clearly explain the curing kinetics of the prepared epoxy nanocomposites.

1. Introduction

Epoxy resin is one of the most important thermosetting polymers, widely used in adhesives, coatings, electronics, high-performance composite materials, and aerospace industries due to the excellent mechanical and chemical properties, such as high tensile and compressive strength, good chemical resistance, and high heat distortion temperature [1,2]. Epoxy resin reinforced with nanoscopic layered silicates has received increasing attention recently because of the possibility of obtaining improved properties in terms of stiffness, strength, fire resistance, dimensional stability, shrinkage, etc. [3,4]. Generally, high aspect ratio and high strength of these layered silicate such as montmorillonite clay (MMT) plays a major role in improving the properties of any polymer nanocomposites prepared using these materials [5]. However, montmorillonite clay (MMT) have neither good surface energy nor good interaction characteristics with epoxy matrices, resulting in the poor dispersion and a weak interface. To solve this issue, the ion-exchange behaviors of the Na^+ cations in MMT are typically employed to expand the layer distances by using intercalants that improves the interfacial interaction between the nanoclay platelets and epoxy matrices. Alkyl ammonium ions are the well known intercalant material capable of expanding the MMT layer distance [6]; moreover, as reported by several researchers, they help in the dispersion and exfoliation of the layered silicates in the epoxy matrices that results in the improvement of the properties [7–12].

Generally, improvement in the properties of the epoxy nanocomposites filled with MMT depends on the formation of the crosslinked molecular network, which is often influenced by the mechanism and kinetics of the epoxy resin curing that involves various chemical reactions. Understanding the cure process in the epoxy system is the essential part in order to get better control of the cure reactions and in consequence to optimize the physical properties of the final product. One of the most widely used techniques for studying the kinetics of the cure reaction of epoxy system is thermal analysis by differential scanning calorimetry (DSC) in isothermal or dynamic modes followed by kinetic analysis using phenomenological models [13]. Among these models, Borchardt–Daniels [14], Ozawa and/or Flynn and Wall [15], Kissinger [16], isoconversional [13,14,17,18], and autocatalytic cure rate methods [19,20,21] are widely applied to understand the curing mechanism of thermosetting resins. Significant studies have been conducted on the curing reaction kinetics of the thermosetting epoxy resins by employing various techniques, experimental procedures and data analysis methods [22–26]. Loading of the alkyl ammonium ion modified MMT in the epoxy matrix facilitates the curing reaction and kinetics of the epoxy nanocomposites [27–29]. Surface modification of MMTs using traditional modifier, such as long-chain alkyl ammonium, is a physical modification

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and it cannot provide any sort of chemical interaction between polymer and MMTs. Alternatively, chemical grafting of the aminopropyltriethoxysilane on clay platelets have been prepared and characterized by various research groups and its influence on the properties of polymer nanocomposites have also been investigated [30–32]. Very recently, Choi et al. [33] reported that by the addition of aminosilane grafted MMT, the mechanical properties such as tensile strength and toughness of the epoxy matrix are significantly improved, when compared to the pristine or organically modified MMT loaded epoxy system. However, no research report has been published that depicts the curing mechanism and kinetics of these epoxy nanocomposites.

The aim of the present work is to study the effect of silane functionalized nanoclay on the cure mechanism and kinetics of the epoxy resin (diglycidyl ether of bis-phenol A, DGEBA) cured with polyamidoamine (G-A0533) so as to understand the structure-property relationship. For this purpose, non-isothermal DSC measurements has been carried out to reveal the cure behavior of these epoxy systems and the empirical approaches are used to model the kinetics of the curing reactions.

2. Experimental

2.1. Materials

The epoxy resin used in this study, YD-115, was provided by Kukdo Chemical Co., Korea., Kukdo YD-115 consists of diglycidyl ether of bisphenol-A (DGEBA) with a epoxide equivalent weight of 180–190 g equiv^{-1}. The resin was cured with G-A0533, supplied by Kukdo Company, Korea. G-A0533 is a liquid polyaminoamine resin with an amine hardener equivalent of 95–115 g equiv^{-1}. Commercial grade montmorillonite clay (MMT) was purchased from southern MMT products Inc., USA. 3-aminopropyltriethoxysilane was obtained from Aldrich Chemical Company Inc., USA.

2.2. Nanocomposite preparation

Cloisite Na$^{\oplus}$ (P-MMT) and silanized MMT (S-MMT) was incorporated at concentrations (2 wt%) relative to the epoxy resin. Aminosilane functionalized MMT was prepared with distilled water as a dispersing medium and detailed procedure was described in a previous work [31]. Acetone was used as a solvent to facilitate the mixing. Weight ratio of epoxy (DGEBA)/hardener (PAA) was 2:1. DGEBA and MMT with solvent were mixed for 3 min at 25 °C using a high speed mechanical stirrer at 2500 rpm. Then hardener was added and mixed for 5 min. Mixture was dried for 3 h at 25 °C under vacuum to remove the solvent. Prepared samples are designated as EP0 (unfilled epoxy system), EP-MMT2 (epoxy/pristine MMT nanocomposites) and ES-MMT2 (epoxy/silane functionalized MMT nanocomposites).

2.3. Instruments

Calorimetric studies were carried out on a Mettler-Toledo DSC-821 thermal analyzer in covered high pressure stainless steel pans under nitrogen atmosphere at the heating rates of 5, 10, 15 and 20 °C/min. The instrument was calibrated for temperature and enthalpy using indium and zinc prior to the experiments. Samples of about 10 mg of the reactive systems were put in hermetically sealed aluminum DSC pans (Mettler). The cure process and the glass transition temperature of the partially cured and fully cured samples were determined in non-isothermal experiments.

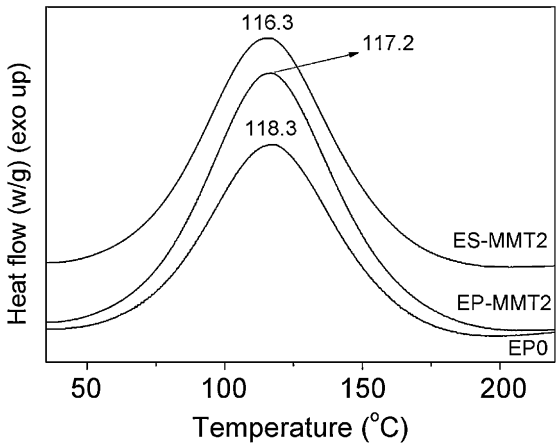

Fig. 1. DSC thermograms of neat (EP0) and clay filled epoxy nanocomposites (EP-MMT2 & ES-MMT2).

3. Results and discussion

The non-isothermal differential scanning (DSC) thermograms of neat (EP0) and montmorillonite clay filled epoxy (EP-MMT2 & ES-MMT2) measured at the heating rate of 10 °C/min are shown in Fig. 1. Dynamic DSC experiments of all epoxy system exhibit a single exotherm peak revealing the epoxy-amine ring opening addition reaction during the curing reaction. The total area of the exothermal peak (the region between the exotherm and the baseline) is directly proportional to the molar heat of the reaction ΔH_{cure} released during the whole cure reaction. Neat epoxy (EP0) showed a single exothermic peak, T_p at 118.3 °C with the heat of curing reaction, ΔH_{cure} of 300.9 J/g. Epoxy nanocomposites loaded with the pristine MMT (EP-MMT2) resulted in the shift of the peak temperature, T_p to 117.2 °C with the ΔH_{cure} value of 307.5 J/g. Similarly, loading of the silane functionalized MMT in the epoxy matrix (ES-MMT2) showed the peak temperature shift, T_p to 116.5 °C with the ΔH_{cure} value of 306.2 J/g. Slightly higher value of ΔH_{cure} with the decrease in peak temperature for clay filled system (EP-MMT2 & ES-MMT2) is corroborated to the better curing characteristics near the peak exotherm temperature, when compared to the neat epoxy matrix. As expected, increasing the heating rate leads to a gradually increased peak areas and reaction temperature for all the epoxy systems (EP0, EP-MMT2 and ES-MMT2). Representative DSC thermograms (ES-MMT2) at various heating rates viz. 5, 10, 15 and 20 °C/min that clearly depict the gradual rise in peak areas and temperature are shown in Fig. 2. The total heat of reaction, ΔH_{cure},

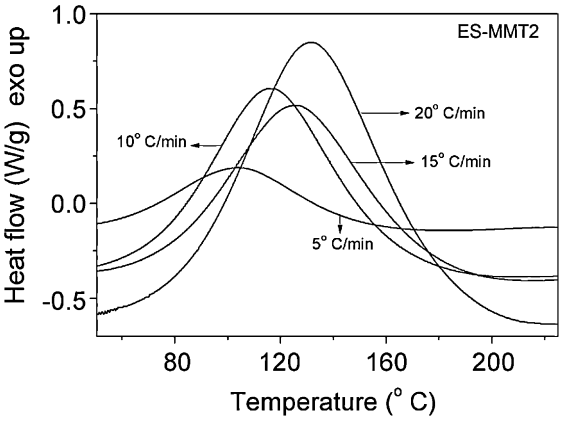

Fig. 2. DSC thermograms of silane functionalized clay filled epoxy nanocomposites at various heating rates.