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Isothermal curing behavior and thermo-physical properties of epoxy-based thermoset nanocomposites reinforced with Fe_2O_3 nanoparticles

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ABSTRACT

A new nanocomposite was synthesized by curing of diglycidyl ether of bisphenol A (DGEBA)/polypropylenimine octaamine dendrimer (PPOD) involving various percentages of Fe_2O_3 nanoparticles using ultrasonic dispersion protocol. DSC and DMTA studies revealed that high percentage of the nanofiller, i.e., 10%, results in improved cross-link density as evidenced by increasing in the glass transition temperature. Morphology studies using AFM and TEM showed that the nanoparticles were homogeneously dispersed into the entire volume of the resin. From the experimental data, the nanocomposite exhibited increase in storage modulus and degradation temperature from the neat epoxy system. The isoconversional method was utilized to describe the isothermal curing reaction of epoxy nanocomposite. Kinetics of DGEBA/PPOD/nano-Fe_2O_3 cure was studied by DSC measurements at isothermal mode. Isothermal kinetic parameters, including k_1, k_2 and n, were determined and it was shown that the reaction kinetics could be described well by the Horie model.

1. Introduction

The processing of polymer nanocomposites reinforced with various nanofillers is believed to become a key technology on advanced materials for next generation, in that the unique characteristics of nanoparticles made it possible for them to be used as promising nanofillers in polymer nanocomposites. In this regard, much research has been performed on the practical realization of excellent properties of nanoparticles for advanced composite in a broad range of industrial applications [1–4]. However, because of their high cost and limited availability, only a few practical applications in industrial fields have been realized to date. Considering these aspects, it is very instructive to fabricate polymer nanocomposites based on conventional cheap thermoset polymers and very small quantity of nanoparticles at lower manufacturing cost, from an industrial perspective. Inorganic–organic composite materials are increasingly important due to their extraordinary properties, which arise from the synergism between the properties of the components. There are several routes to these materials, but probably the most prominent one is the incorporation of inorganic building blocks in polymers. These materials have gained much interest due to the remarkable change in properties such as mechanical [5], thermal [6–9], electrical [10,11], and magnetic [12] compared to pure epoxy polymers. Inorganic additives and fillers are known to affect the cure kinetics of thermosetting polymers.

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 [13–17]. The development of epoxy nanocomposites during the past decade has revolutionized research into composites technology. The incorporation of inorganic fillers was achieved long ago to enhance the properties of neat epoxy nanocomposites, and they are specialty products where these inorganic fillers are dispersed in the nanoscale, and with at least one dimension of the filler phase being less than 100 nm. In recent researches, the epoxy nanocomposites based on a wide variety of nanometer fillers including SiO_2 particles [18], TiO_2 particles [19], ZnO particles [20], layered silicate [21,22] etc. have been investigated. Among various nanomaterials, those based on nano-Fe_2O_3 are a promising candidate for practical

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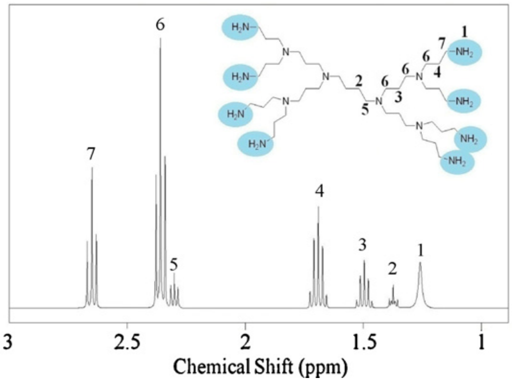
applications because these Fe_2O_3 particles are readily available and cheaper than other nano-scale fillers and also exhibit multi-functional properties. For example, the nanocrystalline Fe_2O_3 would have potential applications in the fields [23–26] such as solar energy conversion, electrochromism, optical and magnetic materials. Also, iron oxide nanoparticles are of special significance because of their application in catalysis, as gas sensors, magnetic storage, ferrofluids, magnetic refrigeration and colour imaging. The influence of ferric oxide nanoparticles on the thermal properties of polymer nanocomposites has been widely studied [27–34]. Also, polymer magnetic nanocomposites have potential applications in high density information storage media, wave absorbers, optical-magnetic media, cell separation and medical diagnosis [35–40]. Few studies have been concerned with the application of nano-Fe_2O_3 in epoxy coatings system with multi-properties.

On the other hand, curing agents play a very important role in determining reaction mechanisms, curing conditions, processability, network structures, final properties, and applicability of epoxy resins. Aliphatic-amine curing agents have high reactivity and low melting temperatures, accounting for their applications in room-temperature-cure epoxy coatings and adhesives. Aliphatic-amine curing agents of low molecular weights have the defects of the strong volatilization, high toxicity, skin irritation and sensitization, fast absorption of carbon dioxide and vapor in air, and strict stoichiometry with respect to epoxy resins [14]. As a result, sometimes they are chemically modified to form corresponding amine adducts of increased molecular weights to reduce the unfavorable odor, extend stoichiometry, decrease toxicity and improve surface appearance of epoxy resins [14,41]. But, some of these modifications will decrease desired properties of epoxy resins such as crosslink density, thermal stability and resistance, processability, reactivity and mechanical properties. For this purpose, amine acids have been used to cure epoxy resins, which take the advantages of the reduced toxicity and environmental friendliness [42,43]. Since, high melting points, poor compatibility and low reactivity of amine acids are some of their disadvantages, therefore greatly limiting their potential applications in epoxy formulations, especially, room-temperature-cure epoxy coatings and adhesives. One way to solve this problem is to develop new aliphatic-amine curing agents with high reactivity and good compatibility, which needs appropriate design of their molecular compositions and topology. Research studies on aliphatic-polyamine curing agents with nonlinear structures (i.e., branched, starlike and dendritic) show a great promise, since lowered bulk viscosity and reduced toxicity can be achieved without much sacrificing other suitable properties such as the high reactivity, fast compatibility and crosslink density of cured epoxy resins [44–47]. Using different nonlinear aliphatic-polyamines as curing agent to cure epoxy resins were sparsely reported [48–59]. Therefore, to reach to more and more practical applications, we need to perform more researches. So, we used the polypropylenimine octaamine dendrimer as a curing agent in this work.

Therefore, using nano-Fe_2O_3 and nonlinear polyamine as a curing agent at the same time, can affected on reaction kinetics and thermo-physical properties of epoxy resin with them from fundamental and practical application perspectives, which stimulates us to conduct the current work. The aim of this work is to analyze the kinetics of cure in isothermal mode and to assess the mechanical, thermal, and morphological properties of diglycidyl ether of bisphenol A/polypropylenimine octaamine dendrimer system reinforced with Fe_2O_3 nanoparticles as potential materials for the coating industry. These characterizations are extremely important since the degree high-performance of epoxy nanocomposite depends on formulation, final properties and used curing procedure.



Scheme 1. Molecular structure of curing agent and its ^1H NMR spectrum.

2. Experimental

2.1. Materials

The epoxy system used in this work was diglycidyl ether bisphenol A (D.E.R 332) with an epoxy equivalent weight of 175 g equiv^{-1}. The hardener was polypropylenimine octaamine dendrimer having molecular weight of 773.28 g mol^{-1} with CAS number of 154487-83-9. Chemical structure and ^1H NMR spectrum of curing agent are shown in Scheme 1, where assignments of chemical shifts for different kinds of protons are indicated by numbers. The epoxy resin and hardener were obtained from Sigma Aldrich. The materials were used without further treatments. Fe_2O_3 nanopowder with a mean size of <50 nm were purchased from Sigma Aldrich.

2.2. Specimen preparation

The nano-Fe_2O_3 was used as the filler to prepare epoxy nanocomposites. Various amounts of the nanofiller (0, 1, 5 and 10%) was mixed with the proper value of epoxy resin and stirred for 16 h. The mixture was sonicated for 60 min (two stages of 30 min) using an ultrasound bath. Then a stoichiometric amount of PPOD was added to the composition and about 20 mg in size samples used for DSC analyses. To provide the samples of TGA, DMTA, TEM and AFM analyses, 10% nano-Fe_2O_3 was mixed with the proper value of epoxy resin and stirred for 16 h. The mixture was sonicated for 60 min; then a stoichiometric amount of PPOD was added to the composition and composition was mixed about 30 min. Finally, the samples were cured isothermally at 120 °C for 90 min and then undergo a postcuring treatment at 160 °C for 30 min to produce nanocomposites.

2.3. Characterization

^1H NMR spectra were recorded on a BRUKER Spectrometer operating at 400 MHz. Tetramethylsilane was used as internal standard and $CDCl_3$ employed as the solvent. DSC experiments were made at under high purity nitrogen (45 cm^3 min^{-1}) using a DSC-60 (Shimadzu, Japan) calorimeter. The samples were heated from 20 to 250 °C at heating rate of 10 °C min^{-1} to record the heat evolution due to the thermal polymerization and to determine the appropriate concentration of the nanofiller. The cured sample was then cooled to 25 °C at the same heating speed. Finally, the samples were reheated to 250 °C in order to determine the glass transition temperature (T_g) and to confirm the absence of any residual curing. For isothermal measurements, the temperature was raised from 25 °C to the curing temperature at the maximum heating rate. The isothermal cure temperatures of 60, 65, 70, 75 and 80 °C were selected from the dynamic heating experiments. The effect