Progress in Organic Coatings 77 (2014) 1316–1324

Contents lists available at ScienceDirect

Progress in Organic Coatings

journal homepage: www.elsevier.com/locate/porgcoat

Thermo-mechanical behaviors of epoxy resins reinforced with silane-epoxide functionalized α-Fe_2O_3 nanoparticles

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ARTICLE INFO

Article history:
Received 9 December 2013
Received in revised form 4 March 2014
Accepted 2 April 2014

Keywords:
α-Fe_2O_3 nanoparticles
Surface modification
Organic coating
Nanocomposite
Mechanical properties

ABSTRACT

In this work, α-Fe_2O_3 nanoparticles was synthesized, terminal-epoxide functionalized by using 3-glycidoxypropyltrimethoxysilane (GPS) coupling agent, characterized by FT-IR, X-ray diffraction, TGA and particle size analyzer and used in preparation of nanocomposites with epoxy resin (DGEBA) using different weight fractions (2–11 wt%). TEM and SEM were used to observe particle dispersion in the resin matrix and to investigate the fractured surface of nanocomposites for evidence of extrinsic toughening mechanism. The mechanical and thermo-mechanical properties of nanocomposites prepared from DGEBA and modified epoxide-terminated α-Fe_2O_3 were compared with the properties of untreated α-Fe_2O_3/DGEBA nanocomposites and neat DGEBA. The modified α-Fe_2O_3/DGEBA nanocomposites showed improvement in properties such as glass transition temperature (T_g) and tensile, flexural and impact strength. These improvements are due to better dispersion of epoxide-terminated α-Fe_2O_3 particles in the resin matrix and enhanced interfacial adhesion between DGEBA and α-Fe_2O_3 phases.

1. Introduction

Epoxy resins are considered to be one of the most important classes of versatile thermosetting polymers and are characterized by high strength, high modulus, low shrinkage, and excellent heat, chemical and corrosion resistance with low impact strength. Attempts were made to improve the toughness of cured epoxy resins using rubber materials [1–3], although it may sacrifice the stiffness of epoxy significantly and decrease the T_g. An alternative approach for toughening is to incorporate some dispersed inorganic nanoparticles as second phase into cross-linked polymer to achieve nanocomposite. Numerous papers have been reported enhancing the physical and mechanical properties of epoxy resins by adding small amount of nanoparticles. Various types of nano-fillers like TiO_2 [4], Al_2O_3 [5], SiO_2 [6,7], ZnO [8], ZrO_2 [9], SiC [10], aluminum [11] and clay [12,13] are used to improve the toughness of the epoxy resin. However, nanoparticles-reinforced polymer nanocomposites suffer some problems, for example, the interfacial bonding between polymer resin and reinforced particles is weak, and for this reason, particles are agglomerated in the polymer [14]. Moreover, under force, cracks propagate from the weak sites, hence reducing the resultant mechanical properties of the nanocomposites. Therefore, much research has sought to develop effective methods for the dispersion of particles in the polymer matrix. Surface modification of particles by organic compounds is used to disperse them in the polymer matrix and can be achieved via several procedures [15,16]. One attractive approach to obtain proper dispersion of nanoparticles in polymer matrix and to yield better compatibility, via formation of a durable chemical junction between two incompatible phases, is the direct silanization of particles by using organofunctional coupling agents such as trialkoxy silanes [17,18].

Iron oxide nanoparticles are superior to the conventional bulk iron oxide and their applications in catalytic reactions, electronic devices and paint formulations [19–21], and also their influence on the mechanical and thermal properties of polymer nanocomposites have been widely investigated [22,23]. Although, a distinct link between particle–matrix adhesion and overall mechanical properties of the polymer composites has been established, as expected, but the use of organofunctional silane on the surface modification of Fe_2O_3 nanoparticles and its use in epoxy resin nanocomposites has not been received attention. In general, particle size, dispersion and silane treatment, all play an important role in determining the enhancement of fracture toughness.

The present work focuses on the performance of epoxy composites containing chemically bonded silane modified α-Fe_2O_3 nanoparticles and to understand what role these inorganic fillers play on the nanometer scale. α-Fe_2O_3 nanoparticles were synthesized via a wet chemical approach using iron (II) chloride

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http://dx.doi.org/10.1016/j.porgcoat.2014.04.001

tetrahydrate and iron (III) chloride. To achieve uniform dispersion of α-Fe_2O_3 nanoparticles in the epoxy resin and enhance particle-matrix adhesion, the surface of nanoparticles were treated with epoxide functionalized 3-glycidoxypropyltrimethoxysilane (GPS). The effect of GPS treated α-Fe_2O_3 nanoparticles on the fracture mechanism, mechanical properties such as tensile, flexural and impact strength, and also dynamic-mechanical properties of nanocomposites were investigated and compared with the properties of untreated α-Fe_2O_3/DGEBA nanocomposites.

2. Experimental

2.1. Materials

Diglycidyl ether of bisphenol A (DGEBA) type epoxy resin, (Epiran 6 and an epoxy equivalent weight of 187 eq/g), was purchased from Khuzestan Petrochemical Co. (Iran). The curing agent used was triethylenetetramine (TETA) with a purity of 99.5%, supplied by Fluka. 3-Glycidoxypropyltrimethoxysilane (GPS) was purchased from Merck and used as coupling agent. $FeCl_3$ (99%), $FeCl_2{\cdot}4H_2O$ (98%), HCl (37%) and NH_4OH (25–30%) were purchased from Merck Chemicals and used for the synthesis of α-Fe_2O_3 nanoparticles.

2.2. Synthesis of α-Fe_2O_3 nanoparticles

The α-Fe_2O_3 nanoparticles were prepared by wet chemical method according to the reported procedures [24], as follows: $FeCl_3$ and $FeCl_2{\cdot}4H_2O$ were dissolved in 2 M hydrochloric acid to form a solution with the concentration of 1 M for $FeCl_3$ and 2 M for $FeCl_2.4H_2O$. The NH_4OH solution (2 M) was dropped to this solution with vigorous stirring at room temperature for 2 h. The brown precipitate was then collected by filtration and rinsed several times with deionized water. The precipitate was dried at 60 °C overnight. Finally, the brown γ-Fe_2O_3 particles were calcined in air at 500 °C and held at this temperature for 1 h in a muffle furnace to obtain red α-Fe_2O_3 nanoparticles.

2.3. Surface modification of α-Fe_2O_3 nanoparticles

Surface modification was performed as follows: in the first stage, 6 g of α-Fe_2O_3 nanoparticles were kept in a vacuum chamber for 75 min at 110 °C and then dispersed in 200 mL acetone via stirring for 1 h at ambient temperature and sonicated (Elma, TRANSSONIC T890) for 20 min. In the second step, 50 wt% (3 g) GPS was gradually added to the dispersed solution and stirred for further 24 h at ambient temperature. Finally, it was centrifuged and the residue washed with acetone. The washing procedure was repeated for three times and the remained precipitate was dried in a vacuum oven at 50 °C for 72 h.

2.4. Preparation of α-Fe_2O_3/epoxy nanocomposites

The α-Fe_2O_3 nanoparticles (surface modified or unmodified) were kept in a vacuum oven at 80 °C for 1 h to remove physically absorbed moisture and were then used to prepare nanocomposites at different weight percentages (2, 5, 8, 11 wt%). The fabrication processes of the treated and un-treated α-Fe_2O_3/epoxy nanocomposites were as follows. The preheated nanoparticles directly added to acetone (25 ml acetone per gram of nanoparticles), the mixture was agitated for 1 h using an ultrasonic bath to give a homogeneous dispersion. This particle-solvent dispersion was introduced to epoxy resin slowly using mechanical mixing. Further ultrasonic irradiating and mechanical mixing were employed for several times alternatively. The mixture was heated at 70 °C for 3–4 h with continuous mechanical agitation to drive out the remained acetone. To ensure that all solvent was removed, constituent weights were monitored at all steps. Once the proper dispersion was attained, a stoichiometric amount of curing agent (TETA) was added and mixed for 5–10 min by hand mixing. After degassing, the mixture was poured into pre-prepared casting mold and cured for about 24 h at room temperature and postcured at 75 °C for 4 h and at 110 °C for 90 min.

2.5. Characterization

FT-IR spectroscopy was performed in KBr pellet on a Bruker Vector 22 FTIR spectrometer in the range of 400–4000 cm^{-1}. The thermal behavior of the untreated and treated nanoparticles was evaluated with thermal gravimetrical analysis (TGA) (PL-1500) from room temperature up to 600 °C with the heating rate of 10 °C min^{-1}. To determine the size distribution of treated and untreated α-Fe_2O_3 particles, the prepared particles were dispersed in distilled water, and measurements were performed using a particle size analyzer (PSA) (Scatteroscope I, Qudix, Korea). The crystalline structure of α-Fe_2O_3 nanoparticles was characterized by X-ray diffraction (Philips Analytical X-ray B.V.) using Cu Kα ($\lambda = 1.54$ Å) radiation. Dispersion stability of untreated and treated α-Fe_2O_3 nanoparticles was assayed in an organic solvent (acetone). Suspensions of nanoparticles in acetone were prepared and sonicated for 30 min and stirred further 1 h. Then, the dispersion states of nanoparticles were visually evaluated at 20 min, 1 h, 24 h and 144 h. The tensile properties of the samples were determined on dog-bone shaped samples according to ASTM D 638 at room temperature using an Instron Universal Testing Machine (Model DBBP 500, BONGSHIN). Dimensions of specimen were chosen according to the type I of this standard and a 2 mm/min cross-head speed was used. Five specimens were tested for each sample. Un-notched specimens with the dimensions of 63.5 mm × 12.7 mm × 7.2 mm as indicated in ASTM D 256 were broken by an Izod impact tester (Resil Impactor Junior) for obtaining the corresponding impact properties. To measure flexural strength and flexural modulus, the three-point bend tests were performed using a universal testing machine (Gotech Testing Machines Inc. U60) according to ASTM D 790. The support span was 50 mm with a cross-head speed of 1 mm/min at room temperature. Five specimens of each composition were tested to evaluate each of the mechanical tests. Scanning electron microscopy (SEM) (Leo 1455 VP, Germany) was used to evaluate the morphology of fractured interfaces obtained from flexural test. Dispersion state of α-Fe_2O_3 with and without treatment was also examined by SEM. The sample was placed in vacuum chamber of the instrument and then was examined at various magnifications and the images were recorded photographically. Transmission electron microscopy imaging of the samples was performed using a TEM instrument (model EM10C, Zeiss Co.). A dynamic mechanical thermal analyzer (DMTA) was conducted to measure the dynamic mechanical thermal properties of prepared epoxy/α-Fe_2O_3 nanocomposites. The neat epoxy and nanocomposite samples with dimension 50 mm × 10 mm × 1 mm were tested in tree point bending at varying temperature between room temperature and 160 °C at a heating rate of 5 °C/min and a frequency of 1.0 Hz in a nitrogen atmosphere. The storage modulus and tan δ curves were recorded and analyzed. The peak position of tan δ curve was regarded as the T_g of the samples.

3. Result and discussion

3.1. Characterization of Fe_2O_3nanoparticles

3.1.1. XRD curve

Fig. 1a shows X-ray diffraction patterns of α-Fe_2O_3 nanocrystals. The peaks in XRD pattern could be in consistent with the