Polymer grafted graphene oxide: For improved dispersion in epoxy resin and enhancement of mechanical properties of nanocomposite

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ABSTRACT

In this work, poly(vinyl imidazole) (PVI) chains have been grafted from the methacrylate functionalized graphene oxide (GO) nanosheets surface via radical polymerization yielding nanocomposite PVI-g-GO. The homogeneous stable dispersion of PVI-g-GO in epoxy resin (EP) has been cured using triethylene-tetramine (TETA) curing agent. In-depth structural characterization of resulting PVI-g-GO was carried out using Fourier transform infrared spectroscopy (FTIR), thermal gravimetrical analysis (TGA), X-ray diffraction (XRD), and transmission electron microscopy (TEM). The exfoliation and dispersion of PVI-g-GO sheets in the EP matrix was investigated by XRD and scanning electron microscopy (SEM). The kinetic parameters of the curing process were determined using non-isothermal Kissinger and Ozawa methods. The PVI-g-GO enhanced the curing rate via decreasing the activation energy (E_a) of the reaction. The mechanical properties of the nanocomposites were investigated by using tensile tests. Comparing with the neat EP, the tensile strength and modulus of the nanocomposite contains 0.25 wt% of PVI-g-GO increased 59.6% and 45.5%, respectively. The fracture surfaces were analyzed by SEM showing tough-ening structure with rough surfaces confirming the enhanced tensile strength. The thermal stability of the nanocomposites was investigated by using TGA and differential scanning calorimetric (DSC).

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1. Introduction

Epoxy resins are a very important class of thermoset polymers due to their excellent engineering properties such as good stiffness, specific strength, dimensional stability, and chemical resistance. The main drawback of epoxy resins for structural applications may be its inherent brittleness. Several research works have been devoted to the reinforcement of epoxy matrices with carbon nanotube [1,2], graphene [3,4], graphene oxide (GO) [5–8], and with three different types of carbon nano-fillers [9]. GO has attracted the attention of a growing number of scientists from several disciplines due to its remarkable physical properties and chemical functionalization capabilities. One of the most promising applications of GO is in the preparation of polymer nano-composites. This is due to the substantial enhancements in the mechanical, thermal, dielectric and rheological, and gas barrier properties of polymeric nanocomposites at much low loadings compared to the polymer composites prepared with conventional micron-scale fillers [10–13]. The dispersion of GO nanosheets in polymer matrix is difficult due to the aggregation and strong forces between the sheets [5]. This can limit load transfer from the polymer matrix to the GO sheet and thus prevent improvement in the mechanical properties of the composite [4]. Therefore, the main problem with polymer nanocomposites is the prevention of parti-cles aggregation. This problem can be overcome by surface modi-fication of GO nanosheets. The modification improves the interfacial interactions between the nanosheets and the polymer matrix. There are two ways to modify the surface of nanomaterials. The first can be accomplished via surface absorption or reaction with small molecules, such as silane coupling agents, and the sec-ond method is based on grafting polymeric molecules through covalent bonding to the functional groups existing on the surface. The advantage of the second procedure over the first lies in the fact that the polymer-grafted nanomaterial can be designed with the desired properties through a proper selection of the species of the grafting monomers and the choice of grafting conditions [14]. There are plenty of oxygen-containing groups on GO sheet surface such as hydroxyl and epoxy groups on their basal planes, and carbonyl and carboxyl groups located at the sheet edges. These groups not only allow the good dispersion of GO in aqueous medium, but also

provide active sites to form covalent functionalization, acting as an ideal interface between the GO nanosheets and polymers matrix [5,15,16]. Imidazole derivatives were often used as hardeners in a variety of epoxy resin systems to initiate the homopolymerization of epoxide groups, the esterification reaction in the epoxy-anhydride systems, and catalyze the homopolymerization of epoxide groups in epoxy-phenol systems [17,18]. In another study, in order to enhance the interaction between GO and epoxy resin, the GO was linked covalently to the imidazole via isophorone diisocyanate and used as curing agent [19].

In the present work, an attempt has been made in this direction to prepare composite from epoxy resin (EP) and polyvinyl imidazole grafted-GO (PVI-g-GO) with improved dispersion and strong interfacial adhesion leading to the enhancement of mechanical properties. Therefore, vinyl imidazole (VI) was selected as a suitable monomer to polymerize on the surface of GO nanosheets to obtain PVI-g-GO. In the first step, GO nanosheets were functionalized with the methacrylate groups through reaction with γ-methacryloxypropyltrimethoxysilane (MPS) (I-GO). Then, VI was polymerized on the surface of I-GO nonosheets via radical polymerization. The PVI matrix as a host material has unique characteristics such as processability, miscibility with epoxy resin, and hetero-aromaticity with amine-functionality. In this study, the effect of PVI on dispersion of GO nanosheets, on the mechanism and kinetics of curing, and on the mechanical and thermal properties of composite has been investigated.

2. Experimental

2.1. Materials

Diglycidyl ether of bisphenol A (DGEBA) type epoxy resin(EP) (Epiran 6, epoxy equivalent weight of 187 g eq^{-1}) was purchased from Khuzestan Petrochemical Co.(Iran). Benzoyl peroxide (BPO), γ-methacryloxypropyltrimethoxysilane (MPS), 1-Vinylimidazole (VI) and Triethylenetetramine (TETA, as a curing agent) were purchased from Sigma-Aldrich (Germany). Graphene oxide nanosheets were supplied by US Research Nanomaterials, Inc.(USA), with a purity of 99%. The thickness of GO nanosheets was 3.4–7 nm. Toluene and tetrahydrofuran (Merck, Germany) were purified with sodium.

2.2. Synthesis of I-GO

Surface modification of GO was performed as follows: 1.00 g GO was dispersed in 100 mL dried toluene via sonication (Elma, TRANSSONIC T890) for 1 h. 1.00 g MPS was gradually added to the dispersed GO solution under nitrogen atmosphere and stirred for further 24 h at 80 °C. Finally, the mixture was centrifuged and the residue washed with toluene. The black solid was filtered and dried overnight under vacuum at 50 °C.

2.3. Synthesis of PVI-g-GO

Typically, 0.25 g I-GO was placed in a 100 mL three-necked flask containing 50 mL THF and the mixture was sonicated for 1 h. Then, 4.50 g VI was added to the prepared suspension and purged with argon gas for 30 min. The temperature was raised to 80 °C and a solution of BPO (1.00 × 10^{-3} M) was added to initiate the graft polymerization of VI onto I-GO. The reaction was proceeded at 80 °C for 24 h. After completion of the reaction, the precipitate was filtered and washed with THF and then extracted with hot methanol for 24 h to remove the non-grafted PVI. The filtrate was then dried overnight under vacuum at 50 °C. The schematic of functionalization reaction of GO is shown in Fig. 1.

2.4. Preparation of nanocomposites

Epoxy nanocomposites containing different weight percentages (0.10, 0.25 and 0.50 wt%) of PVI-g-GO (0.1, 0.25 or 0.5 PVI-g-GO/EP/TETA) were prepared by the following procedure. First, a certain amount of PVI-g-GO was dispersed in THF by sonication at room temperature for 1 h. The suspension solution was mixed with a certain amount of EP by sonication for 30 min and then stirred further by magnetic stirring to obtain highly dispersed/exfoliated PVI-g-GO/EP dispersions. Then, the mixture was degassed at 70 °C for 6 h to remove the solvent. Once the proper dispersion was attained, a stoichiometric amount of the curing agent TETA was added and mixed for 10 min. After degassing, the mixture was poured into a pre-prepared casting mold and heated from room temperature to 80 °C at the rate of 2 °C min^{-1} and remained at this temperature for 4 h, then post-cured at 100 °C for 90 min. The nanocomposites of pristine GO (0.25 GO/EP/TETA),and I-GO(0.25 I-GO/EP/TETA) were also prepared under the same experimental conditions for comparison.

2.5. Characterization

FT-IR spectroscopy was performed in KBr pellet on a Bruker Vector 22 FTIR spectrophotometer in the range of 400–4000 cm^{-1}. The thermal behavior of materials was evaluated with thermal gravimetrical analysis (TGA, Rheometric Scientific) from room temperature up to 600 °C under nitrogen with the heating rate of 10 °C min^{-1}. The TGA test was repeated twice for each sample. The structure of GO, I-GO, PVI-g-GO and the composites was verified by X-ray diffraction (Philips Analytical X-ray B.V., Netherlands) using Cu K$_\alpha$ radiation (λ = 1.54 Å). The samples were scanned in the range of 5–60 2θ at a scan rate of 2°min^{-1} operating at a generator voltage of 40 kV and applied a current of 35 mA. The morphology of GO and PVI-g-GO sheets were examined by a transmission electron microscopy (TEM, modelEM10C, Zeiss Co.). The nanosheets were dispersed in water and or ethanol by sonication for 15 min, and some pieces were then collected on copper grids for TEM observation. The tensile properties were determined on rectangular shaped samples (with the dimensions of 80 × 12 × 3 mm) using an Instron Universal Testing Machine (Model DBBP 500, BONGSHIN). Five tests were carried out for each sample. Scanning electron microscopy (SEM) (VEGA\\TESCAN) was used to evaluate the morphology of the fractured interfaces obtained from the tensile test. Dispersion state of GO with and without functionalization in the epoxy matrix was also examined by SEM. Evaluation of cure kinetic parameters was performed by differential scanning calorimetric analysis (DSC, METTLER TOLEDO). About 10 mg of the uniform viscous mixture was placed in a DSC sample pan and covered with an aluminum lid and closed tightly under pressure. The sample pan was placed in the DSC sample cell at ambient temperature and an empty pan was also placed in the DSC reference cell, and it was heated according to the program of constant heating rates(5, 10, 15, and or 20 °C min^{-1}) under nitrogen purge gas from room temperature to 200 °C. Glass transition temperature (T_g) of EP and the nanocomposites was determined by DSC at the heating rate of 10 °C min^{-1}.

3. Results and discussion

3.1. Characterization of modified GO nanosheets

FT-IR spectra of GO, I-GO and PVI-g-GO are presented in Fig. 2a. The spectrum of GO demonstrates the characteristic oxygen-containing groups: O−H stretching vibration at 3428 cm^{-1}, C=O stretching vibration at 1710 cm^{-1},unoxidized sp^{2}C=C stretching