



Interfacial microstructure and properties of poly (phenylene benzobisoxazole) fiber grafted with graphene oxide via solvothermal method

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ARTICLE INFO

Article history:

Received 19 November 2012

Received in revised form 4 December 2012

Accepted 5 December 2012

Available online 13 December 2012

Keywords:

PBO fiber

Graphene oxide

Solvothermal method

Surface grafting

Interfacial property

ABSTRACT

An effective approach for grafting graphene oxide (GO) onto poly (phenylene benzobisoxazole) (PBO) fiber surface through ethanediamine as linkage using solvothermal method was proposed. Grafting GO onto the PBO fiber surface was an attempt to improve the interfacial properties between PBO fibers and epoxy matrix. Experimental results reveal that GO was grafted uniformly on the PBO fiber surface through chemical bonds. The polar functional groups and surface energy of PBO fiber were obviously increased after the grafting process. Results of the mechanical property tests show the interfacial shear strength increased obviously and single fiber tensile strength have not any discernable decrease after the grafting process. GO effectively enhanced the interfacial adhesion of PBO fiber-reinforced composite by increasing chemical bonding, improving wettability and mechanical interlocking.

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1. Introduction

Poly (phenylene benzobisoxazole) (PBO) fiber-reinforced composites are used in a wide variety of applications, ranging from aerospace and military to sport apparatus due to high-stiffness, high-strength, light-weight and excellent thermal resistance [1–7]. The properties of the PBO fiber-reinforced composites are, to a large extent, controlled by the interfacial properties between fibers and matrix. Strong interfacial adhesion guarantees efficient load transfer from the soft organic matrix to stiff fibers with high strength and modulus, which helps to reduce internal stress concentration and improves overall mechanical properties [8–10]. However, just as many advanced fibers, smooth and chemically inert fiber surfaces limit the further application of PBO fiber. Consequently, scientists have paid many efforts on surface modification of PBO fiber for the interfacial adhesion strength of PBO fiber-matrix interface, including chemical oxidation, γ -ray irradiation, plasma treatment and electronic beam [11–13].

In the previous research, carbon nanotubes, polyhedral oligomeric silsesquioxanes and nano-TiO₂ have been used to modify the PBO fiber, which demonstrated the grafting of these materials could effectively increase the interfacial properties of

the resulting PBO fiber-reinforced composites [14–16]. Graphene oxide (GO) containing reactive oxygen functional groups has larger specific surface area and more excellent properties than above materials, which opens more opportunities on the preparation of new hierarchical reinforcement [17–21]. This provide further enhancement of the interfacial properties effectively, because the larger area of GO improves pull-through and delaminating resistance in composites. However, to make GO uniformly grafted on the PBO fiber surface and obtain good interfacial bonding between GO and PBO fiber is still a key challenge.

The use of a particular environment is essential to maximize the interactions between the GO and PBO in order to obtain the most stable and hierarchical structure. Recently, solvothermal synthesis has been proved to be effective to prepare a variety of materials such as metals, semiconductors, ceramics, including novel macromolecules, which can prepare thermodynamically stable and metastable states that cannot be easily formed from other synthetic routes [22–30]. In our study, solvothermal method was used to graft GO onto the PBO fiber surface. In solution, thermal motion provides the major part of the motion required to bring the GO into contact PBO fibers. At the interface, interactions between GO and PBO fiber are maximized because of the drastic changes in the polarity of the solvents. At surfaces, depending on the hydrophilic nature of the GO and hydrophobic of PBO substrate, GO was firstly adsorbed to the surface of PBO fiber via electrostatics and further grafted, the interactions between GO and PBO substrate can lead to interesting morphological. Here, the effective use of solvothermal strategy for the fabrication of GO-grafted PBO fibers ensures

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the mobility of the GO for occurring on PBO fiber surface. The feasibility of using GO to improve the interfacial properties of PBO fiber composite was firstly investigated. Atomic force microscopy (AFM) was used to determine the lateral size and layer thickness of GO. X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared spectroscopy (FTIR) were carried out to characterize the surface chemical composition change of PBO fibers before and after grafting GO. Field emission scanning electron microscopy (FESEM) and transmission electron microscope (TEM) were used to observe the surface morphologies after grafting GO. Dynamic contact angle (DCA) measurement was carried out to investigate the wettability and surface free energy of PBO fibers. Interfacial shear strength (IFSS) was used to evaluate the interfacial properties between PBO fibers and epoxy resin.

2. Materials and methods

2.1. Raw material and processing

2.1.1. Materials

In the research, high-modulus PBO fibers were purchased from Toyobo Co., Ltd. (Japan). PBO fibers were continuously washed with acetone solvent for 24 h by a Soxhlet extractor in order to remove the surface contaminants, then dried at 80 °C in a vacuum oven. The GO was prepared from graphite according to modified Hummers method [31] using 20% SO₃ fuming H₂SO₄. The rest used chemicals were analytical reagent grade and were purchased from Beijing Chemical Works and used after removing water treatment.

2.1.2. Grafting procedure

The PBO fibers were refluxed and oxidized in HNO₃ (15.3 M, 100 mL) at 80 °C for 0.5 h. Then the carboxyl functionalized PBO fibers were taken out and washed several times with deionized water until the pH of the wash water was neutral and dried under vacuum. The carboxyl functionalized PBO fibers, ethanediamine (EDA), GO and DMF were transferred into a Teflon-lined autoclave, which was then heated at 180 °C for 12 h to produce GO-grafted PBO fibers using EDA as linkage. The Teflon-lined autoclave were cooled to room temperature, the obtained GO-grafted PBO fibers were took out and rinsed in excess THF under sonication to remove the DMF and unreacted EDA. Finally, the prepared GO-grafted PBO fibers were dried at 180 °C for 24 h under vacuum (Fig. 1).

2.2. Characteristics

2.2.1. FTIR

The surface functional groups of the PBO fibers were determined by FTIR spectrophotometer (Nicolet, Nexus 670, USA) using powder-pressed KBr pellets. Specimens were prepared by mixing 10 mg of the sample powder with 100 mg of KBr and pressing the mixture into pellets for the measurements. FTIR spectra were obtained at a resolution of 2.0 cm⁻¹ in the range of 4000–400 cm⁻¹ wavenumbers at room temperature.

2.2.2. XPS

In this research, surface elemental composition was characterized by XPS (PHI 5700 ESCA system, Physical Electronics, Inc., USA). XPS analysis was performed on a mono-chromated Al K α radioactive source (1486.6 eV) at a base pressure of 2 × 10⁻⁹ mbar. Wide scan spectra for element detection were obtained over the range of 0–1000 eV, using pass energy of 187.85 eV. High resolution spectra were measured at a perpendicular take-off angle, using pass energy of 20 eV. Surface chemical elemental composition was analyzed by the XPS Peak version 4.1 program software.

2.2.3. AFM

The dimension of GO was determined by using an AFM (Bruker Dimension Icon-PT). A silicon pellet with area of 1 cm × 1 cm was immersed into GO water dispersed solution for 10 min, then taken out to dry. The scanning force constant of 1–5 N/m and scanning resonant frequency of 70–150 kHz were selected. The scanning scope was 5 μm × 5 μm. At last, the thickness result of GO was evaluated by the NanoScope Analysis software.

2.2.4. FESEM

Surface morphologies of GO and different treated PBO fibers were observed by using FESEM (S-4300, Hitachi, Japan). The filaments of PBO fiber fixed on the smooth aluminum sheet with conductive adhesive were coated with gold using United States Gatan 682 ion etching plating instrument for 12 min before FESEM observation in order to obtain stable and clear images of fiber surface.

2.2.5. SEM

To further study hierarchical structure, GO and ultrathin sections of GO-grafted PBO fiber have been observed by TEM (Hitachi H-7650). The sample of GO was prepared through infiltration method by placing one drop of aqueous GO solution on the copper net coated with carbon. The ultrathin sectioning sample for PBO fibers was prepared according to Ref. [32].

2.2.6. Interfacial properties and mechanical properties

Interfacial properties of PBO fibers were estimated with surface wettability, surface free energy and IFSS. Surface wettability of PBO fibers was evaluated by Dynamic Contact Angle meter and Tensiometer (DCAT21, DataPhysics Instruments, Germany). This measurement was performed through dynamic capillary method. Advanced contact angle (θ) was determined from the mass change during immersion of fiber into test liquid using Wilhelmy's equation (Eq. (1)) [33]. The surface energy (γ_f), dispersion component (γ_f^d) and polar component (γ_f^p) of the testing PBO fibers were estimated from the measured dynamic contact angles of the test liquids with known surface tension components and calculated according to the Owens–Wendt model described in Eqs. (2) and (3).

$$\cos \theta = \frac{mg}{\pi d_f \gamma_l} \quad (1)$$

$$\gamma_l(1 + \cos \theta) = 2\sqrt{\gamma_l^d \gamma_f^d} + 2\sqrt{\gamma_l^p \gamma_f^p} \quad (2)$$

$$\gamma_f = \gamma_f^d + \gamma_f^p \quad (3)$$

Where θ is the contact angle between PBO fibers and the testing liquid, °; d_f is the fiber diameter, m; g is the gravitational acceleration, 9.8 m/s²; γ_l , γ_l^d , γ_l^p are the testing liquid surface tension, its dispersion and polar component, mJ/m², respectively. Deionized water ($\gamma = 72.8$ mJ/m², $\gamma^d = 19.9$ mJ/m², $\gamma^p = 52.2$ mJ/m²) and diiodomethane ($\gamma = 50.8$ mJ/m², $\gamma^d = 48.5$ mJ/m², $\gamma^p = 2.3$ mJ/m², 99% purity, Alfa Aesar, USA) were used as the testing liquids. Each type of fiber was measured at least 10 times, and then the average value was calculated.

Single-filament pull-out test was carried out by pulling out a fiber from the cured epoxy resin droplet, which was usually regarded as the most quick and efficient method to evaluate the IFSS between fibers and matrix. The PBO fiber or GO-grafted PBO fiber monofilament was fastened to aluminum holder with double sided adhesive tap. Some epoxy droplets were applied to the monofilament with the embedded length of 50–70 μm using a fine-point applicator. The samples were cured at 75 °C for 2 h, at 120 °C for 2 h and at 150 °C for 4 h. After curing, the single fiber IFSS test was performed on an interfacial strength evaluation instrument (Tohei

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