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Facile fabrication of hierarchically structured PBO-$Ni(OH)_2$/NiOOH fibers for enhancing interfacial strength in PBO fiber/epoxy resin composites

Lei Chen [a], Yunzhe Du [b], Yudong Huang [b], Pui Fai Ng [a], Bin Fei [a, *]

[a] Nanotechnology Centre, Institute of Textiles & Clothing, The Hong Kong Polytechnic University, Hong Kong, China
[b] School of Chemical Engineering and Technology, Harbin Institute of Technology, Harbin, China

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A new hierarchical reinforcement was fabricated by depositing honeycomb-like $Ni(OH)_2$/NiOOH coating onto poly(*p*-phenylene benzobisoxazole) (PBO) fibers using a facile chemical bath deposition (CBD) method. The crystal structure of $Ni(OH)_2$/NiOOH deposited PBO fiber, denoted as PBO-$Ni(OH)_2$/NiOOH, was characterized by X-ray diffractometer (XRD). Scanning electron microscopy (SEM) was employed to characterize the surface morphologies of PBO fibers and the de-bonding surface morphologies of their composites. Atomic force microscopy (AFM) and contact angle (CA) testing results demonstrated that the surface roughness (R_a) and wettability of PBO fibers increased obviously after $Ni(OH)_2$/NiOOH deposition due to the unique honeycomb structure of the coating. Monofilament pull-out tests showed that the interfacial shear strength (IFSS) of PBO/epoxy composite increased by 46.3%. Moreover, the possible interfacial property enhancing reasons were explored. Thermogravimetric analysis (TGA) and hydrothermal aging tests revealed that PBO-$Ni(OH)_2$/NiOOH had excellent thermal stability and hydrothermal aging resistance. Notably, the $Ni(OH)_2$/NiOOH coating on the fiber surface can be easily reduced to Ni, resulting in a highly conductive PBO fiber. Our design starts from simple chemistry and inexpensive materials, and may offer a versatile and scalable method for fabricating hierarchical reinforcements.

1. Introduction

Poly(*p*-phenylene benzobisoxazole) (PBO) fibers have been widely used as reinforcements of advanced composites in aerospace and industrial fields owing to their excellent properties, such as high tensile strength, high modulus, high thermal stability and light weight [1–3]. However, the smooth and chemically inert surface of PBO fibers makes them difficult to form strong interfacial adhesion and high compatibility with resin matrix. Hence, the surface modification of PBO fibers has been a topic of great interest. For instance, Liu et al. [4] reported that the interlaminar shear strength (ILSS) of PBO/bismaleimide composite increased by 39.7% after argon plasma treatment. However, the modification effects degraded with the increase of storage time in the air. Gu et al. [5] proposed a "three-step approach" of methanesulfonic acid/γ-aminopropyl triethoxy silane/glycidylethyl polyhedral oligomeric silsesquioxane (MSA/KH550/POSS) to modify the surface of PBO fibers, and found that the IFSS of PBO/epoxy composite increased by 26.6%. However, this chemical grafting approach is complex and time-consuming. Therefore, it remains a challenge to improve the interfacial properties of PBO fiber composites via a simple and effective approach [6–8].

It is well known that PBO fiber reinforced polymer composites contain three parts including PBO fiber reinforcement, hosting matrix and interphase between the fibers and the matrix. The mechanical properties of the PBO fiber composites depend not only on the intrinsic characteristics of the fibers and of the matrix but also on the physicochemical properties of the interphase [9–11]. An optimum interphase can significantly improve the mechanical properties and environmental stability of the composites, and efficiently transfer the stress from the matrix to the PBO fibers [12,13]. Many kinds of micro-molecules or nanomaterials with controlled, ordered and active structures are introduced into PBO fiber composites as interphases to enhance their interfacial properties through physical coating and chemical grafting treatments [14,15]. Recently, hierarchical reinforcements composed of high-

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* Corresponding author.
E-mail address: tcfeib@polyu.edu.hk (B. Fei).

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performance fiber (e.g., carbon fiber, PBO fiber, and aramid fiber) and micro-/nano-filler have attracted wide attention due to their excellent interfacial properties [16,17]. Nevertheless, almost all of the reported hierarchical structures are made of carbon nanotubes (CNTs) and graphene oxide (GO) [8,10,13,18], with limited options. Normally, surface coating and chemical grafting are used to introduce them onto the surface of PBO fiber. In the process, CNTs and GO are functionalized to improve their dispersion in sizing agent and their reactivity with PBO fiber, whereas high cost and tedious preparation procedure restrict their practical applications.

Chemical bath deposition (CBD) as a traditional and effective coating method has attracted a lot of attention due to the useful properties imparted to substrates. In addition, CBD is considered as an inexpensive technique that is suitable for large-scale production [19]. Highly porous nickel oxide film with interconnected nanoflakes has been employed as a supercapacitor electrode due to its well-defined electrochemical redox reactions, large specific surface area, tunable morphology by modifying synthetic conditions, environmental friendliness, and comparatively low cost of its precursors [19,20]. Very recently, our group provided a potential application to fabricate highly efficient oil-water separators by depositing nickel oxide coating onto metal meshes [21]. The mesh surface modified with the honeycomb-like coating exhibits superhydrophilic and underwater superoleophobic properties. Considering the unique nature of the coating, it is reasonable to infer that the coating may increase not only the R_a and rigidity but also the wettability of PBO fibers, resulting in a great enhancement of the interfacial properties of their composites.

In this study, through a simple CBD method, we fabricated new hierarchically structured $Ni(OH)_2$/NiOOH-deposited PBO fibers to enhance the interfacial properties of PBO/epoxy composite for the first time. The microstructure of $Ni(OH)_2$/NiOOH coating were systematically characterized. To substantiate the superior performance of the interfacial properties of PBO-$Ni(OH)_2$/NiOOH composite, a direct comparison is made with untreated and acid-treated PBO fibers. The thermal stability of different PBO fibers and hydrothermal aging resistance of their composites were investigated. PBO-$Ni(OH)_2$/NiOOH was further reduced by $NaBH_4$, resulting in a highly conductive fiber.

2. Experimental

2.1. Materials

The PBO fibers (Zylon, HM) with a filament diameter of 12 μm were supplied by Toyobo Ltd., Japan. Nickel (II) sulphate hexahydrate ($NiSO_4 \cdot 6H_2O$), potassium persulphate ($K_2S_2O_8$, 99.5%), sodium borohydride ($NaBH_4$), ammonia solution (25%) and sulfuric acid (H_2SO_4, 98%) were purchased from Sigma–Aldrich Co., USA. Epoxy resin (E–51) and 4, 4′-methylene-bis(2-ethylaniline) (H-256) were received from Shanghai Research Institute of Synthetic Resins, China, used at a weight ratio of 100: 32. All chemicals and solvents were used as received.

2.2. Fabrication of PBO-$Ni(OH)_2$/NiOOH

Experiments were conducted on a bundle of PBO fibers cut to length of 40 cm, then wound around a glass frame to prevent the separation of monofilaments. Afterwards the fibers were etched in 80 wt% H_2SO_4 for 20 s to increase the R_a and wettability [22]. Finally, the acid-treated fibers were submersed in a chemical bath containing 40 mL of 1 M $NiSO_4 \cdot 6H_2O$, 30 mL of 0.25 M $K_2S_2O_8$, 10 mL of ammonia solution, and 20 mL of deionized water. The deposition process was carried out at 25 °C for 15 min with a mild stirring (200 rpm). The obtained fibers, denoted as PBO-$Ni(OH)_2$/NiOOH, were rinsed with deionized water for several times and dried under vacuum.

2.3. Fabrication of PBO-Ni

The PBO-$Ni(OH)_2$/NiOOH were submersed in 0.3 M $NaBH_4$ solution at room temperature for 1 h. The resultant fibers, denoted as PBO-Ni, were rinsed with deionized water for several times and dried under vacuum.

2.4. Characterization of PBO fibers

Various PBO fibers were observed by a field emission scanning electron microscopy (FE-SEM, JEOL JSM-6335F, Japan). The adhesion durability of the $Ni(OH)_2$/NiOOH coating was evaluated by ultrasonic exposure test, which was carried out in water at 50 °C for 15 min with an ultrasonator (Branson 2510, USA). The crystal structure of PBO fibers was studied by a X-ray diffractometer (XRD, Rigaku Smartlab, Japan) with Cu Kα radiation (k = 1.5406 nm) generated at 40 kV and 100 mA. The R_a of PBO fibers was determined in an area of 4 μm × 4 μm by an atomic force microscopy (AFM, Solver-P47H, NT-MDT, Russia).

Dynamic contact angle (DCA) was measured by a CA meter (DCAT21, Data-Physics Instrument, Germany). Deionized water (γ_f = 72.8 mJ/m^2, γ_f^d = 21.8 mJ/m^2) and diiodomethane (γ_f = 50.8 mJ/m^2, γ_f^d = 50.8 mJ/m^2) were used as the testing liquids. Four PBO monofilaments are immersed into the liquids with an insertion depth of 5 mm and an insertion speed of 0.008 mm/s. Advanced CA (θ) was determined from the mass change during immersion of PBO fibers into the testing liquids using Wilhelmy's Eq. (1):

$$\cos\theta = \frac{mg}{\pi d_f \gamma_\iota} \tag{1}$$

The surface free energy (γ_f), dispersive component (γ_f^d) and polar component (γ_f^p) of the testing PBO fibers were calculated according to the Owens-Wendt model described in Eqs. (2) and (3):

$$\gamma_\iota(1+\cos\theta) = 2\sqrt{\gamma_\iota^d \gamma_f^d} + 2\sqrt{\gamma_\iota^p \gamma_f^p} \tag{2}$$

$$\gamma_f = \gamma_f^d + \gamma_f^p \tag{3}$$

where θ is the DCA between the PBO fibers and the testing liquids; m is the weight of PBO fibers; d_f is the monofilament diameter; γ_l, γ_l^d and γ_l^p are the surface tension of testing liquids, its dispersive and polar component, respectively.

Static contact angle (SCA) was examined by a CA meter (SCA 20, Data-Physics Instrument, Germany) using the sessile drop method at room temperature. A water droplet (2.0 μL) was dropped onto the surface of PBO fiber bundles, and the pictures were captured immediately once the droplet escaped from the needle.

Thermogravimetric analysis (TGA) was tested by a simultaneous thermal analyzer (Mettler Toledo TGA/DSC1, Switzerland) with the temperature increasing from 25 to 800 °C under nitrogen atmosphere at a heating rate of 10 °C/min.

Monofilament tensile tests were conducted on a universal testing machine (Instron 5566, USA) according to the ASTM D3379-75 with a load cell of 50 N, a gauge length of 10 mm, and a crosshead speed of 10 mm/min. The tensile strength (TS) results were analyzed by a Weibull statistical method.

Monofilament pull-out tests were performed to determine the interfacial shear strength (IFSS) of PBO/epoxy composites using an interfacial strength evaluation equipment (Tohei Sanyon Co Ltd,