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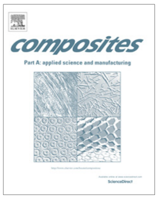

Hierarchical poly(*p*-phenylene benzobisoxazole)/graphene oxide reinforcement with multifunctional and biomimic middle layer

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ABSTRACT

A new hierarchical reinforcement developed by coating biomimic polydopamine (PDA) on the surface of poly(*p*-phenylene benzobisoxazole) (PBO) fibers, which served as a platform for the graphene oxide (GO) grafting, using branched polyethyleneimine (b-PEI) as a bridging agent. The surface morphologies and chemical structures of PBO fibers were characterized for confirming the formation of covalent bond between GO and PBO fibers. The surface roughness (R_a) and wettability of the obtained fibers, denoted as PBO@PDA-PEI-GO, were obviously increased in comparison with those of untreated one. The reinforcement offered a 68.8% enhancement in the interfacial shear strength (IFSS) without degrading the base fiber. The PDA layer on the PBO fiber surface led to improved UV resistance. The hydrothermal aging resistance of PBO/epoxy composite was also greatly improved. This biomimic surface modification approach is facile to prepare, highly efficient to enhance interface, adaptable to all high-performance fibers, and meaningful in multifunctional applications.

1. Introduction

Poly(*p*-phenylene benzobisoxazole) (PBO) fibers, characterized by excellent mechanical and thermal properties, have been as the king of organic fibers and widely used as reinforcements of advanced composites in aerospace, marine and automobile industries [1–5]. An optimum interface ensures efficient load transfer from the matrix to the reinforcement, which reduces stress concentration and improves overall mechanical properties [6,7]. However, due to the surface smoothness and chemical inertness, PBO fibers have poor interfacial adhesion with resin matrix. To overcome the problem, numerous researches have been devoted to the surface modification of PBO fibers, including chemical oxidation, plasma treatment, high-energy irradiation, whiskerization and chemical grafting [8–14]. Nevertheless, the conventional surface treatments (or pretreatments) with oxidation procedure, which etches the fiber surface, would deteriorate the mechanical properties of PBO fibers to some extent [8,15,16]. Therefore, searching for a mild and effective approach for surface modification of PBO fibers is still a challenge.

Recently, Lee et al. reported a surface chemistry for functional coatings inspired by the adhesive proteins secreted by mussels [17]. They found that dopamine, a small-molecule compound, could self-polymerize under mild conditions and form polydopamine (PDA) layer onto almost all types of substrates. Furthermore, the catechols of PDA layer can react with amines and thiols via Michael addition or Schiff base reactions, which makes it a versatile and robust platform for further functionalization [18–23]. Based on the superior natures, dopamine chemistry has been employed to modify the surface of carbon fibers for improving the interfacial properties of their composites [24,25]. PBO fibers are sensitive to long-term ultraviolet (UV) and high humidity exposure, which seriously deteriorate their mechanical properties [26,27]. Thus, steps must be taken to improve the environmental stability of PBO fibers. The chemical structure of PDA is similar to melanins, whose major function is to protect human skin against sunlight by absorbing energetic UV part and quenching reactive radicals [28,29]. Many recent reports have also disclosed that PDA is an anti-oxidant [30–32]. To the best of our knowledge, the use of PDA as a photoprotective agent for high-performance fibers has not been investigated.

Compared to the modification effect of multifunctional-group macromolecules on the interfacial properties, a hierarchical reinforcement, such as carbon nanotubes (CNTs) or graphene oxide (GO), is more significant [14,33–38]. Especially for GO, its excellent mechanical properties and large specific surface area support possible to assemble new hierarchical reinforcement. Although the

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hierarchical composites with GO reinforcement have been fabricated by some researchers, its effect on the hydrothermal aging resistance has not been reported so far.

In the present study, we reported a mild and effective approach to fabricate multifunctional PBO fibers with simultaneously enhanced interfacial properties and environmental stability. Biomimic PDA was first coated onto PBO fibers through self-polymerization, subsequently functionalized by branched polyethyleneimine (b-PEI). Then, GO was chemically and uniformly grafted onto the PBO fibers, between which b-PEI acted as the “bridge”. This biomimic surface modification approach may greatly extend the application areas of PBO fibers.

2. Experimental

2.1. Materials

The PBO fibers (HM) with a monofilament diameter of 12 μm were supplied by Toyobo Ltd., Japan. Prior to use, sizing agent of PBO fibers were removed by Soxhlet extraction with acetone at 70 °C for 48 h. Graphite powder, sodium nitrate ($NaNO_3$, $\geqslant$99%), and potassium permanganate ($KMnO_4$, $\geqslant$99.5%) were received from Sinopharm Chemical Reagent Co., Ltd., China. Sulfuric acid (H_2SO_4, 98%), methanesulfonic acid (MSA, 99%), hydrochloric acid (HCl, 37%), hydrogen peroxide (H_2O_2, 30%), hydroxyphenethylamine hydrochloride (dopamine, 98%), tris(hydroxy-methyl)aminomethane (Tris, 99.8%), branched polyethyleneimine (b-PEI, M_w = 25,000 g/mol), N,N′-dicyclohexylcarbodiimide (DCC, 99%), 4-dimethylaminopyridine (DMAP, 99%) and N,N′-dimethylformamide (DMF, 99.9%) were purchased from Sigma–Aldrich Co., Ltd., USA. E-51 epoxy resin and 4,4′-methylene-bis(2-ethylaniline) (H-256) were provided by Shanghai Research Institute of Synthetic Resins, China. All chemicals and solvents were used as received.

2.2. Fabrication of PBO@PDA-PEI-GO

The PBO@PDA-PEI-GO hierarchical reinforcements were fabricated through several steps as illustrated in Fig. 1. PBO fibers (0.1 g) were immersed in an aqueous solution of dopamine (2.0 g/L) for 24 h. The pH of the dopamine solution was monitored with a pH meter and buffered to 8.5 by adding Tris (1.2 g/L). The PBO fibers changed from yellow to dark brown, which were denoted as PBO@PDA. Being rinsed thoroughly with deionized water, The PBO@PDA were immersed into the b-PEI aqueous solutions (4.0 g/L with 10 mM HCl-Tris) at room temperature for 12 h. Then the resulting fibers, denoted as PBO@PDA-PEI, were rinsed thoroughly with deionized water and dried under vacuum. GO was prepared using a modified Hummers method [39]. The details are described in Supporting Information. Afterwards the PBO@PDA-PEI and GO (0.1 g) were placed into DMF (50 mL) and were subject to intense ultrasonic treatment for 30 min. Then, DCC (1.5 g) and a catalytic amount of DMAP (0.1 g) were added. After reaction at room temperature for 24 h, the modified PBO fibers, denoted as PBO@PDA-PEI-GO, were rinsed with DMF for several times and dried under vacuum.

2.3. Characterization of GO and PBO fibers

Field emission scanning electron microscope (FE-SEM, JEOL JSM-6335F, Japan) and transmission electron microscope (TEM, Hitachi H-7650, Japan) were used to characterize the morphology and structure of the samples. Atomic force microscope (AFM, Solver-P47H, NT-MDT, Russia) were used to assess the surface roughness (R_a) of PBO fibers. X-ray diffractometer (XRD, Rigaku Smartlab, Japan) was used to examine the condensing structures of graphite and GO. Fourier-transform infrared spectrometer (FT-IR, Perkin-Elmer Spectrum 100, USA) and X-ray photoelectron spectroscopy (XPS, Kratos Axis Ultra DLD, USA) were used to measure the surface chemical composition of PBO fibers.

Contact angle meter (DCAT21, Data-Physics Instrument, Germany) was used to investigate the surface wettability of PBO fibers. Deionized water (γ = 72.8 mJ/m^2, γ^d = 21.8 mJ/m^2) and diiodomethane (γ = 50.8 mJ/m^2, γ^d = 50.8 mJ/m^2) were used as the testing liquids. Dynamic contact angle (θ) was determined from the mass change during immersion of PBO fibers into testing liquids using a Wilhelmy's Eq. (1):

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

where θ is the dynamic contact angle between PBO fibers and the testing liquids; m is the weight of PBO fibers; g is the gravitational acceleration; d_f is the fiber diameter and γ_l is the surface tension of testing liquids.

The surface free energy (γ_f), dispersive component (γ_f^d) and polar component (γ_f^p) of the PBO fibers were estimated from the measured dynamic contact angle of the testing liquids with known surface tension components and calculated according to the Owens–Wendt model described in the following Eqs. (2) and (3):

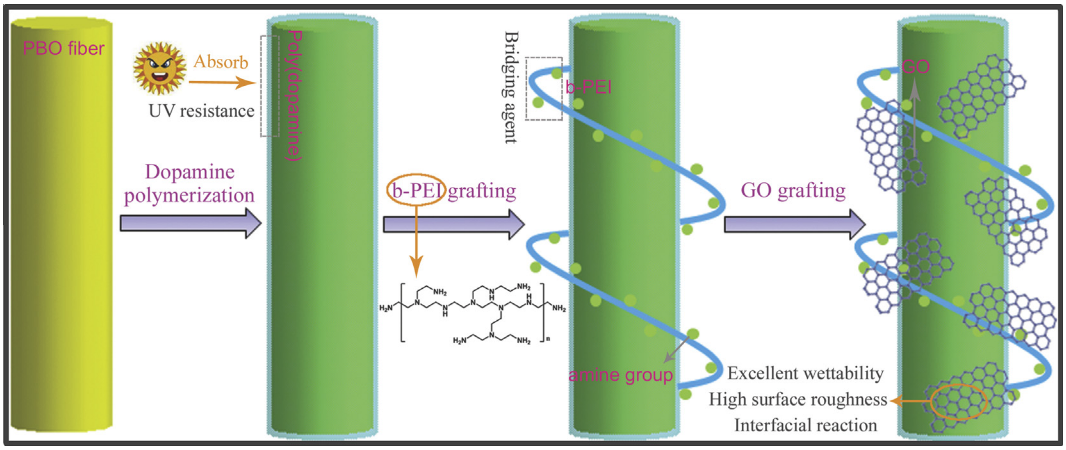

Fig. 1. Schematic of the fabrication of PBO@PDA-PEI-GO. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)