



Full Length Article

A facile one-pot fabrication of polyphosphazene microsphere/carbon fiber hybrid reinforcement and its effect on the interfacial adhesion of epoxy composites

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ABSTRACT

Introducing nanoscale reinforcements into the interface between carbon fiber (CF) and resin is an effective approach to improve the interfacial adhesion of CF composites. In this paper, a facile one-pot polymerization process provides a rapid and efficient method for preparing polyphosphazene microspheres/CF hybrid reinforcement using hexachlorocyclotriphosphazene (HCCP) and bis(4-hydroxyphenyl) sulfone (BPS) as monomers. By the *in situ* polymerization modification, HCCP and BPS were successfully cross-linked and deposited on the CF surface. Scanning electron microscope and atomic force microscopy images show that poly(cyclotriphosphazene-co-4,4'-sulfonyldiphenyl) microspheres were introduced onto the CF surfaces and the surface roughness of fibers is enhanced obviously. Fourier transform infrared spectroscopy and X-ray photoelectron spectroscopy confirm that the polymerization between HCCP and BPS has been successfully carried out. The surface modification can significantly increase the fiber roughness, polarity, wettability and surface energy, thus improving the interfacial shear strength of CF/epoxy composites. Meanwhile, the single fiber tensile strength of CF also shows an increase after modification.

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1. Introduction

Carbon fiber (CF) reinforced polymer composites have been widely used in many areas such as aerospace, vehicles, defense and sports utilities, due to their excellent properties including high strength, high modulus, light weight, superior chemical resistance and outstanding thermal stability [1–3]. In general, the mechanical properties of CF reinforced epoxy (CF/EP) composites highly depend on the interface between CF and resin matrix [4]. An appropriately engineered interface is essential to ensure the efficient load transfer from matrix to reinforcements, which helps to relieve internal stress concentrations effectively and enhance the mechanical behavior and environmental stability of composites significantly [5,6]. However, CF has poor wettability and interaction with resin matrix because of the smooth, non-polar and chemically inert fiber surface [4]. To satisfy with the various technological demands, several modification techniques for CF surface

treatments have been proposed to enhance the interfacial adhesion between CF and matrix such as sizing [3,7–9], coating [10,11], oxidation [12,13], chemical grafting [14,15], plasmas treatment [16,17], electrophoretic deposition [18,19] and high-energy irradiation [20,21].

Recently, some new trends have emerged to improve the interfacial properties of composites by introducing the secondary nanoscale reinforcements (e.g., graphene, carbon nanotubes) into the interface between fiber and matrix [1,5,22–27]. Kamae et al. [1] prepared CF/EP composites by coating CF with carbon nanotubes (CNTs) and resulted in an effective enhancement in interfacial shear strength (IFSS). Qian et al. [22] introduced a layer of CNT on the CF surface via chemical vapor deposition (CVD) method, constructing a CNT/CF multi-scale hybrid structure and improving IFSS of CF/EP composites significantly. Peng et al. [24] grafted CNTs onto CF using poly(amido amine) as coupling agent to form the CNT/CF hierarchical reinforcements. The surface roughness, surface chemical activity and surface energy of CF were improved, and the hierarchical structure resulted in remarkable improvement of interfacial properties. Therefore, introducing micro/nano scale reinforcements onto CF surface can improve the interfacial strength

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by increasing fiber surface area, creating mechanical interlocking and local stiffening at the fiber/matrix interface.

Although the high potential application of secondary nano-reinforcements to improve interfacial properties of CF reinforced composites has been demonstrated in many works [5,22–27], the functionalization conditions are always harsh [15,28], and some defects can be created on fiber surfaces under harsh conditions. For example, in the process of CNT growth onto CF surface via CVD, the outer layers of CF were severely damaged by the etching effect of metal catalyst, leading to a reduced tensile strength (about 55%) [22]. Therefore, developing a facile and efficient method to prepare multi-scale hybrid CF reinforcements simultaneously improve the interfacial properties of CF/EP composites and preserve other mechanical properties of CF (such as tensile strength) is attractive and challenging.

Hexachlorocyclotriphosphazene (HCCP) as a novel organic-inorganic hybrid material has recently attracted great scientific interest owing to the unique P=N structures with remarkably active P-Cl groups. HCCP can readily react with diol, diamine compounds under mild reaction conditions, obtaining cyclomatrix-type polyphosphazene materials with different forms, such as microsphere [29–31], nanotube [32,33] and nanofiber [34]. These novel micro/nano particles can work as reinforcing fillers in polymer nano-composites [35]. Zhou et al. [35] prepared poly(cyclotriphosphazene-co-4,4'-sulfonyldiphenol) microspheres (PZSMs) using HCCP and bis(4-hydroxyphenyl) sulfone (BPS) as monomers by one-step precipitation polymerization and then added PZSMs into polyurethane matrix, obtaining polyurethane/PZSMs composites with higher tensile strength and thermal stability. The organic/inorganic microspheres also may be incorporated into CF surface to fabricate novel multi-scale hybrid reinforcement, thereby enhancing the interfacial adhesion of CF reinforced polymer composites. However, up till now, the relevant studies have not been reported.

In this work, we focus on developing a facile one-pot method for the preparation of polyphosphazene microsphere/CF hybrid reinforcement for the aim of enhancing the interfacial adhesion of CF reinforced polymer composites. Polyphosphazene microspheres were first deposited on CF surface by *in situ* polymerization of monomers HCCP and BPS under a mild condition. The modified CF can obtain a uniform poly(cyclotriphosphazene-co-4,4'-sulfonyldiphenol) (PZS) coating and numerous PZS microspheres (PZSMS) are dispersed well on the fiber surfaces. The effects of the new hierarchical structure on the interfacial properties of CF/EP composites and the tensile strength of CF were investigated respectively. In terms of interfacial shear strength of CF/EP composites, CF-PZSMS shows an obvious increase of 22.98% compared to untreated CF. Moreover, the tensile strength of fibers increased distinctly after modification.

2. Experimental

2.1. Materials

T700S CF (12K, average diameter of 7 μm and density of 1.80 g cm⁻³), supplied from Toray, Japan. Epoxy resin (E51) based on bisphenol-A and the curing agent ZH-593 were obtained from Hubei Zhenzhengfeng new material Co., Ltd., Hubei, China. Resin and curing agent was used at a weight ratio of 100:26. HCCP was purchased from Zibo Lanyin Chemical Co., Ltd., China. Anhydrous acetonitrile was obtained from Aladdin Industrial Inc., Shanghai, China. BPS and triethylamine (AR, 99.0%) were obtained from Sinopharm Chemical Reagent Co., Ltd., China. All other chemicals (acetone, concentrated nitric acid and absolute alcohol) obtained from Sinopharm Chemical Reagent Co., Ltd., which are of reagent-

grade. Triethylamine (TEA) was redistilled for purification prior to use.

2.2. Surface treatment of carbon fibers

T700 carbon fibers (CFs) were extracted in acetone for 48 h to remove the sizing agent and pollutants (denoted as untreated CF). Then, the extracted fibers were oxidized at 373 K for 2 h in concentrated HNO₃ to generate hydroxyl groups (CF-OH) and carboxyl groups (CF-COOH), and then washed with deionized water until pH was 7, dried at 353 K for 6 h under vacuum (denoted as CFO). Subsequently, the CFO was reacted with HCCP (0.3 g) and TEA (3 mL) in anhydrous acetonitrile (40 mL) and kept stirring at 313 K for 1 h to yield HCCP functionalized fibers. Then BPS (0.65 g) was added into the above reaction mixture and kept stirring for 5 h under N₂ atmosphere to obtain PZSMS coated fibers. At last, the modified fibers were extracted with acetonitrile for 8 h to remove unreacted and physically-absorbed monomers and byproduct, and then dried at 333 K for 6 h under vacuum, named CF-PZSMS. The functionalization process is schemed in Fig. 1.

2.3. Characterization

The surface morphologies of CFs with and without surface treatment were examined by scanning electron microscope (SEM) (S-4800, Hitachi, Japan), operating at an accelerating voltage of 8 kV. The surface roughness values (Ra) of fibers were observed by atomic force microscopy (AFM) (Dimension 3100 V Veeco, USA) with the tapping mode. All AFM images of CF used the tapping mode to obtain the scan area of 5 μm × 5 μm.

The surface compositions of fibers were analyzed by X-ray photoelectron spectroscopy (XPS) using an Axis Ultra XPS instrument (Shimadzu, Japan) equipped with a monochromatic Al Kα source (1486.6 eV) at a base pressure of 2 × 10⁻⁹ mbar. The binding energy was calibrated by placing the principal C 1s peak at 284.8 eV. The CASA XPS program was used for data analysis. Fourier transform infrared spectroscopy (FTIR) (Nicolet, Nexus-6700, USA) was applied to detect the molecular structure of hybrid coating using powder-pressed KBr pellets. The FTIR spectra were acquired by scanning the specimens for 32 times in the wave number range of 400–4000 cm⁻¹ with the resolution of 2 cm⁻¹.

The surface wettability of CFs with and without surface modification were evaluated by using a dynamic contact angle meter and tensiometer (DCAT21, DataPhysics, Germany). Deionised water (γ = 72.8 mN m⁻¹, γ^d = 21.8 mN m⁻¹, γ^p = 51.0 mN m⁻¹) and diiodomethane (γ = 50.8 mN m⁻¹, γ^d = 44.1 mN m⁻¹, γ^p = 6.7 mN m⁻¹) were used as testing liquids. The advancing contact angle (θ) was examined by using Wilhelmy equation:

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

Where θ is the contact angle (°) between CF and the test liquids, d_f is the fiber diameter (μm), g is the gravitational acceleration (ms⁻²), and γ_l is the surface energy of the test liquid (mN m⁻¹). The dispersive and polar components of fibers can be easily determined according to the Owens-Wendt equations:

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

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

Where γ_l, γ_l^p and γ_l^d are the surface tension of test liquid, its polar and dispersive component, respectively. The subscript f means the test fibers. Each measurement was repeated 5 times and the results were averaged.

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