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Material Behaviour

The architecture of carbon fiber-TiO_2 nanorods hybrid structure in supercritical water for reinforcing interfacial and impact properties of CF/epoxy composites

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ABSTRACT

To improve the interfacial properties of carbon fiber (CF)/epoxy composites, the growth of titanium dioxide nanorods (TiO_2 NRs) on CF surface was obtained by hydrothermal and supercritical methods. The microstructures, morphologies and mechanical properties of CF-TiO_2 NRs before and after architecture were investigated, which indicated that TiO_2 NRs were grown uniformly onto CFs. The polarity, roughness and wettability of CF-TiO_2 NRs were increased distinctly in comparison with those of untreated CF, especially in supercritical water, indicating that supercritical water has ameliorated the growth efficiency and promoted the TiO_2 NRs onto the CF surface more compactly. The interfacial shear strength (IFSS) and impact strength of composite could be increased as high as 50.7% and 50.0% without deteriorating fiber tensile strength in supercritical water. Meanwhile, the interfacial reinforcing and toughing mechanisms of hybrid fiber composite have also been elaborated. It is believed that the effective method would offer a novel interface design ideology for developing high performance composites.

1. Introduction

Carbon fiber reinforced polymer (CFRP) composites have exhibited tremendous applications in aerospace, automotive and numerous industrial fields on account of their light, high specific strength, high rigidity, durability and chemical resistance [1–3]. However, the performance of CF composites is often confined due to the weak interface between fiber and polymer matrix [4]. This is ascribed to the smooth and inert surface of CF that hardly reacts with the active groups of polymer matrix. Therefore, the study of CF surface modification is an increase in importance project, which plays a critical role in determining the overall performance of composites [5].

In general, the interfacial adhesion between CF and matrix is typically improved by increasing the chemical interaction with the matrix or enhancing the fiber surface area to benefit the load transfer in composites. Various approaches of CF surface treatments have been reported to strengthen the interface property of CF composites, for instance, chemical oxidation, plasma treatment and high-energy irradiation. Compared to those techniques [6–10], whiskerization is an effective method by growing high strength single crystals such as carbon nanotubes (CNTs), silicon carbide (SiC) and zinc oxide nanowires (ZnO NWs) directly onto CF to increase fiber specific surface area, mechanical interlocking, or locally stiffen in the interfacial region. In addition, the addition of nanoparticles to polymers matrix may also provide the nucleation effect for earlier crystallization, which may promote to enhance the mechanical performance [11].

However, many efforts have been investigated that increasing the interfacial strength by CNTs and SiC, which was at the cost of tensile strength due to the destruction of CF surface exposure to high-temperature or whisker growth conditions [12–17]. Afterwards, some researchers attempted to grow ZnO NWs on CF surface in aqueous solutions below 90 °C to maintain the fiber tensile strength, the interfacial strength enhancement primarily could attributed to the appetency of ZnO NWs with carboxylic acid [18–20], which gave rise to strong bond between CF and ZnO NWs as well as enhanced load transfer ascribed to mechanical interlocking.

Titanium dioxide nanorods (TiO_2 NRs) have been drew considerable attention on account of their strong hydrophilicity, high specific surface area, excellent optical and electrical properties, low toxicity and cost. Therefore, TiO_2 NRs play a critical role in various fields, such as dye-sensitized solar cells, lithium ion batteries, gas sensors, and photocatalysts [21–25]. The growth of TiO_2 NRs on CF surface would

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improve the interfacial strength of CF/epoxy composite. Moreover, it is expected that it will exploit the applications of CF and nanocomposites as well as provide more potential materials for some popular fields. However, no other research effects have been reported in literature that TiO_2 NRs have been utilized to enhance the interface strength of CF composites.

The hydrothermal method has become the hotspot which is investigated extensively for growing TiO_2 NRs on substrate owing to its mild reaction condition, simple equipment and high purity [26]. It is well-known that supercritical fluids have admirable peculiarities such as low viscosity, high diffusivity and solvation power [27]. If supercritical water is adopted as the reaction medium to prepare TiO_2 NRs, it would combine all advantages of supercritical fluid and hydrothermal method, which could improve reaction efficiency, selectivity and conversion efficiency, as well as the crystallinity of products. Some papers have reported on the investigation of supercritical fluid treatment of the CF surface, mainly CF cleaning, oxidation and grafting, however, the growth of whiskerization on CF surface in supercritical fluids has not yet been reported on [28–30].

In the present work, the growth of TiO_2 NRs with controlled length and diameter on CFs in hydrothermal and supercritical water were obtained, and how these properties affect the interfacial strength and impact toughness were investigated. The supercritical water can work as an availably medium to improve efficiency, and would offer an approach to efficiently design the interphase to optimize load transfer from the matrix to the fiber, which indicates that our strategy has a promising future in the functional material field.

2. Experimental

2.1. Materials

Polyacrylonitrile-based CFs (T300, diameter 7 μm and density 1.76 g cm^{-3}) were purchased from Sino Steel Jilin Carbon Co., China. E−51 epoxy resin and 4, 4′-methylene-bis(2-ethylaniline) (H-256) as curing agent were supplied by Shanghai Research Institute of Synthetic Resins, China, used at a weight ratio of 100:32. Titanium *n*-butoxide [Ti $(OC_4H_9)_4$], Potassium persulfate ($K_2S_2O_8$) and silver nitrate ($AgNO_3$) was obtained from Aladdin Co., Shanghai, China. All other chemicals, such as acetone, methanol, diethanol, polyethylene glycol and hydrochloric acid (HCl) were supplied by Tianjin Bodi Organic Chemicals Co. Ltd., China and were of reagent grade.

2.2. Growth of TiO_2 NRs onto CF

Growth of TiO_2 NRs onto the CF surface was fabricated via the sol-gel and supercritical water technologies. A typical experimental procedure was described in Fig. 1.

2.2.1. CF cleaning and oxidizing

CFs were extracted in supercritical water/acetone at 633 K for 20 min [28], and were denoted as untreated CF. In order to lay a firm foundation on enhancing the interfacial strength, the desized CF was oxidized in 0.01 mol/L $AgNO_3$/0.1 mol/L $K_2S_2O_8$ solution at 343 K for 1 h to introduce carboxylic acid groups (CF-COOH) [31].

2.2.2. Preparation of TiO_2 sol

Firstly, a semitransparent TiO_2 Sol was formed through continuously stirring a mixed solution, composed of titanium *n*-butoxide (as matrix), ethanol (as solvent), diethanol (as inhibitor), water and polyethylene glycol (W_{PEG} = 1 wt%, as surfactant) in the volume ratio of 5:20:1:20:1 for 1 h [26]. Secondly, after being soaked in the resultant sol for 1 min under ultrasonic, the CF-COOH were pulled up and placed vertically in the oven at 373 K for half hour. Such sol-gel cycles were repeated for four times.

2.2.3. The growth of TiO_2 NWs onto CF in hydrothermal method

$Ti(OC_4H_9)_4$ (1 mL) was dissolved in 15 mL HCl by stir, then H_2O (15 mL) was added to this solution and stirred at room temperature for 3 h, which formed precursor solution. CFs coated with TiO_2 gel were put into an teflon autoclave (40 mL) containing the [Ti $(OC_4H_9)_4$]-HCl-H_2O solution and hydrothermally treated at 423 K for 4 h to obtain the hierarchical TiO_2 NRs arrays on CFs. The TiO_2 NRs-grown CFs were removed, washed thoroughly and sequentially with water, ethanol and sonication three times (10min, 150 W), dried at room temperature, and was denoted CF-COOH-TiO_2 NRs.

2.2.4. The growth of TiO_2 NRs onto CF in supercritical water

The [Ti $(OC_4H_9)_4$]-HCl-H_2O precursor solution mentioned above and the CFs coated with TiO_2 gel were transferred into a teflon autoclave (40 mL) with a high pressure valve. The autoclave was heated to 648 K and pressure was above 22.5 MPa, which was kept for 15 min, then the autoclave was taken out and cooled to room temperature, and the supercritical water dropped slowly to normal pressure. Afterwards, the TiO_2 NRs-grown CFs were removed. The cleaning method is in accordance with that mentioned above, and it was denoted as CF-COOH-s-TiO_2 NRs.

2.3. Characterization techniques

The CFs crystal structure was detected via X-ray diffractometer (XRD, RIGAKU D/MAX-rβ, Japan) with Cu Kα radiation generated at 40 kV and 100 mA. The elemental composition of CFs before and after decoration were determined by X-ray photoelectron spectroscopy (XPS, Thermofisher Scienticfic, USA).

The CFs surface morphology and roughness (Ra) were tested by atomic force microscopy (AFM, NT-MDT Co., Moscow, Russia) using tapping mode. and field-emission scanning electron microscopy (FESEM, Quanta 200FEG, Inc. Japan) accompany with gold plating and energy dispersive spectrometer (EDS), analyzing elemental compositions of the TiO_2 NRs-grown CFs. The interphase sections of single fiber/epoxy composites were observed using transmission electron microscopy (TEM, Hitachi H-7650, Japan) at an accelerating voltage of 100 kV. To prepare TEM sample, the CFs were moulded in a room temperature curing epoxy resin. These samples were cross sectioned to a relatively thin section (< 100 nm) using a microtome.

Dynamic contact angle tests were performed by a dynamic contact angle meter (DCAT21, Data Physics Instruments, Germany). Test liquids are deionised water (γ^d = 21.8 mN m^{-1}, γ = 72.8 mN m^{-1}) and diiodomethane (γ^d = 50.8 mN m^{-1}, γ = 50.8 mN m^{-1}), respectively. The polar and dispersive components can be acquired by the following equations:

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

$$\gamma_f = \gamma_f^p + \gamma_f^d \tag{2}$$

whereγ_l, γ_l^p and γ_l^d are the surface tension of the immersion liquid, and its polar and dispersive components, respectively.

Single fiber tensile tests were carried out on a testing machine (5569, Instron, USA) according to ASTM D3379-75. The gauge length (distance between papers) was 20 mm. The results were analyzed by Weilbull statistical methods.

The interfacial shear strength (IFSS) was used to estimate the interfacial properties between CFs and epoxy resin by interfacial evaluation equipment (FA620, Japan). The microdroplets include epoxy resin (E−51) and curing agent (H-256) mixed with 100:32 mass ratio, and then cured at 363 K for 2 h, 393 K for 2 h and 423 K for 3 h. The IFSS values were determined from:

$$IFSS = \frac{F}{\pi dl} \tag{3}$$