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Zirconia doped in carbon fiber by electrospinning method and improve the mechanical properties and corrosion resistance of epoxy

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ABSTRACT

Zirconia(ZrO_2) was uniformly doped in the carbon fiber (CNF) through the electrospinning method. In addition, the as-prepared zirconia doped carbon fiber (ZrO_2-CNF) were modified with γ-(2,3-epoxypropoxy)propytrimethoxysilane (KH560) in order to improve the dispersion in the epoxy resin, then the ZrO_2-CNF/epoxy composite coatings were prepared. The morphology and structure of ZrO_2-CNF composites fiber were characterized through SEM, EDS-Mapping, TEM, FT-IR and XPS. Besides, the mechanical properties of ZrO_2-CNF/epoxy composite coatings were tested by Tensile test, and the corrosion resistance properties of the composite coatings were characterized by means of electrochemical impedance spectroscopy (EIS) and polarization curves analysis. The results show that the ZrO_2 could be doped on the CNF uniformly, and fiber with uniform size can be obtained. Then the corrosion resistance properties and mechanical properties of the ZrO_2-CNF/epoxy composite coatings were enhanced effectively due to excellent hardness and corrosion resistance of ZrO_2.

1. Introduction

Carbon fiber mostly consists of carbon atoms and has advantage of high strength relative to its light weight and it is widely utilized as a reinforcing material. Therefore, the carbon fiber frequently be considered as a benchmark reinforcement in many structural composite applications [1–8]. Up to now, many related studies show its excellent mechanical properties. Feng Xu et al. [9] indicated that the toughness improvement of the modified carbon fiber/epoxy(CNF/E) composites displaying similar through-the-thickness reinforcing mechanism to that of the 2.5 dimensional fabric reinforced composites. Lei Xiong et al. [10] demonstrate that the flexural strength and tensile strength of fiber/epoxy composites has increased by 32.3 and 39.6% after grafting with nano-TiO_2. However, the corrosion resistance is also very important for epoxy coatings, and the enhancement of carbon fiber is mainly focused on the flexibility of reinforced composites. Zirconium dioxide(ZrO_2) is one of the most promising nanoparticles employed in anticorrosion coatings [11–18] due to its high strength, high fracture toughness, excellent wear resistance, high hardness. Wei Zhang et al. [19] prepared the ZrO_2 Films on Stainless Steel Surface by the Sol − Gel Method and showed that the corrosion and wear resistances of the stainless steel surface were enhanced. M. Behzadnasab et al. [20] indicated that the epoxy coatings with 2–3 wt% ZrO_2 nanoparticles possessed the best corrosion performance among the coating specimens.

Recently, electrospinning has drawn widespread attention due to it is a simple, versatile and convenient approach to create nanowire composites. Moreover, the nanowires prepared by electrospinning exhibit many remarkable characteristics, including large surface areas, strong mechanical performance and homogeneity [21–26]. In order to obtain nanowires with uniform morphology and excellent performance, we prepared carbon fiber(CNF) and zirconia doped carbon fiber(ZrO_2-CNF) through electrospinning method in this study, the as-prepared fiber was modified with γ-(2,3-epoxypropoxy)propytrimethoxysilane (KH560), and then the CNF/epoxy and ZrO_2-CNF/epoxy was prepared. The corrosion performance of composite coatings in 3.5% NaCl solution was studied by electrochemical method, and the mechanical properties was characterized through tensile test.

2. Experimental

2.1. Materials and equipments

The following are the materials acquired: polyvinylpyrrolidone (PVP, Mv = 1,300,000 g/mol), zirconium acetate, *N,N-*

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dimethylformamide(DMF), anhydrous ethanol, γ-(2,3-epoxypropoxy) propytrimethoxysilane (KH560), deionized water with a resistance of 18.0 MW, syringe(10 ml), metal needle with an inner diameter of 3.2 mm, SS-2535H Model Electrospun instrument (Positive power supply: 0 ~ + 50 kV; negative power supply: 0 ~ −30 kV; Beijing Yongkang Industry Technology Development Co. Ltd.), SK-G06123 K Model Tubular electric furnace (Tianjin middle ring electric furnace Limited by Share Ltd).

2.2. Experimental method

2.2.1. Fabrication of ZrO2-CNF composite fiber

ZrO_2-CNF were strictly prepared according to the following steps: 15 g zirconium acetate (15%) solution was firstly added in a vial contain 2 ml of *N,N*-dimethylformamide(DMF) and 2 ml of anhydrous ethanol. Then, 0.7 g of PVP powder was gradually added to the above solution. A clear and homogeneous precursor solution of PVP/ zirconium acetate composites was obtained after 12 h stirring at 25 °C. Subsequently, this precursor solution was loaded into a 10 mL glass syringe. A syringe pump was used to squeeze out the homogeneous precursor solution through a needle with an inner diameter of 0.32 mm at a speed of 1 mL/h with a positive voltage of 20 kV applied to the tip. The distance between the needle tip and spinning collector was 17 cm. The PVP/ zirconium acetate composite nanowires were collected on aluminum foil at 200 rpm. The obtained nanowire was firstly dried at 60 °C in vacuum oven to ensure full vaporization of the solvents. Then, the calcination procedure was performed by calcinating under argon (Ar_2) at 400 °C for 2 h with a low heating rate of 2 °C/min, after which the temperature was increased to 600 °C, the heating rate was decreased to 1 °C/min and maintained for another 3 h. The ZrO_2-CNF was obtained after gradually cooling down to room temperature. In addition, the preparation method of carbon fiber is similar to the above steps, the only difference is to not adding zirconium acetate. The preparation principle is shown in Fig. 1.

2.2.2. The modification of ZrO_2-CNF composite fiber

The as-prepared carbon fiber(CNF) and zirconia doped carbon fiber (ZrO_2-CNF) were added into two beakers separately, which contained deionized water/ethanol mixture solution. The liquid mixture was dispersed for 30 min by numerically controlled ultrasonic cleaners. The same proportion of γ-(2,3-epoxypropoxy)propytrimethoxysilane (KH560) was added into the two beakers, respectively. The previously mentioned solution was then transferred into three flasks with a mechanical stirrer after oscillation. Subsequently, the solution was stirred for 8 h under 85 °C, filtered in vacuum, and dried.

2.2.3. Materials characterization

The morphology of the as-prepared ZrO_2-CNF materials was obtained by the Scanning Electron Microscope (FE-SEM, the acceleration voltage was 5–30 kV, the surface of the sample was sprayed with gold and then its surface morphology was magnified 1000 times and 5000 times). Its surface morphology was further characterized through transmission electron microscopy (TEM) (JEM-2100 F, Japan Electron Optics Laboratory Co., Ltd.). The chemical composition of modified hybrid materials was characterized by FT-IR spectroscopy (WQF520 spectrometer; the test wavelength range was 500–4500 cm^{-1}, the resolution was 4 cm^{-1} and the number of scans was 32). The phase analysis of hybrid materials was tested by X-ray diffraction (XRD, PANalytical, Shanghai, China, the X-ray emission source was copper Ka (wavelength l = 0.154 nm), the tube voltage was 40 kV and the slit was 0.15 mm. The tube flow was 100 mA, the emission slit was 1/6° and the antiscattering slit was 1/6°. The scanning rate was 5°/min, the scanning range was about 5–90° and the scan length is 0·02°). The chemical composition of hybrid materials was characterized by X-ray Photoelectron Spectroscopy (XPS, KRATOS XSAM 800, Al Kα ray). The element distribution of ZrO_2-CNF composites fiber was tested by EDS-mapping.

2.2.4. Tensile test of composite coatings

The tensile dumbbell samples were made using a PTFE mold, with

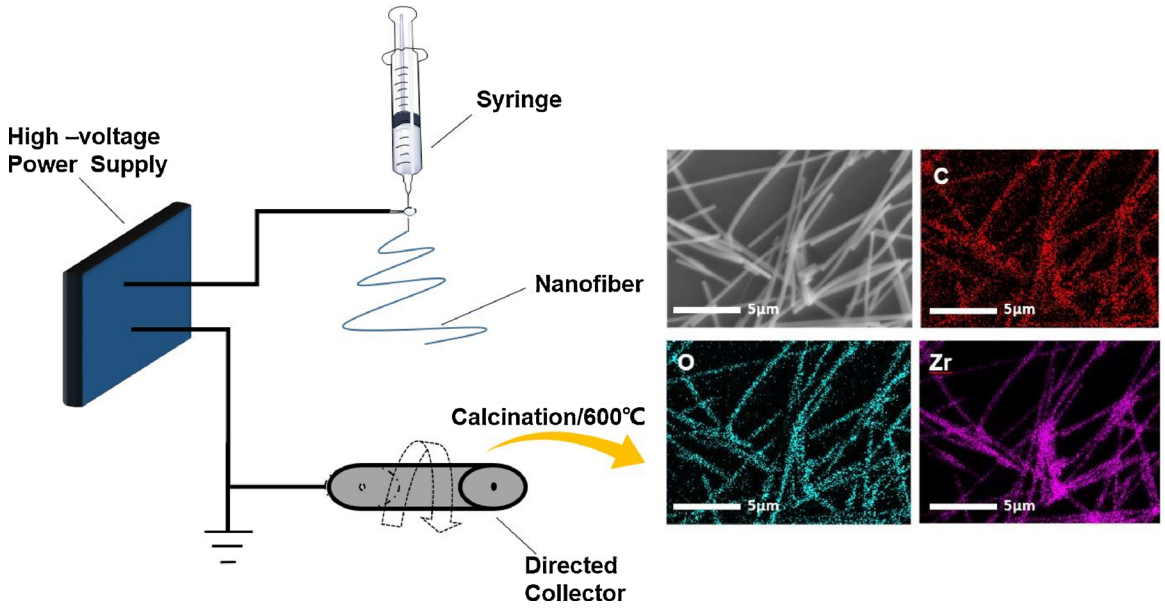

Fig. 1. The preparation principle of ZrO_2-CNF nanowires.