Applied Surface Science 362 (2016) 341–347

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Carboxyl functionalization of carbon fibers via aryl diazonium reaction in molten urea to enhance interfacial shear strength

Yuwei Wang[a,b], Linghui Meng[a], Liquan Fan[a,b], Guangshun Wu[a], Lichun Ma[a], Min Zhao[a], Yudong Huang[a,*]

[a] School of Chemical Engineering and Technology, Harbin Institute of Technology, Harbin 150001, PR China
[b] College of Materials Science and Engineering, Qiqihar University, Qiqihar 161006, PR China

ARTICLE INFO

Article history:
Received 26 August 2015
Received in revised form
25 November 2015
Accepted 26 November 2015
Available online 28 November 2015

Keywords:
Carbon fiber
Aryl diazonium reaction
Benzoic acid group
Interfacial property
Urea

ABSTRACT

Using molten urea as the solvent, carbon fibers were functionalized with carboxylic acid groups via aryl diazonium reaction in 15 min to improve their interfacial bonding with epoxy resin. The surface functionalization was quantified by X-ray photoelectron spectroscopy, which showed that the relative surface coverage of carboxylic acid groups increased from an initial percentage of 3.17–10.41%. Mechanical property test results indicated that the aryl diazonium reaction in this paper could improve the interfacial shear strength by 66%. Meanwhile, the technique did not adopt any pre-oxidation step to produce functional groups prior to grafting and was shown to maintain the tensile strength of the fibers. This methodology provided a rapid, facile and economically viable route to produce covalently functionalized carbon fibers in large quantities with an eco-friendly method.

1. Introduction

On account of their high modulus, enlarged tensile strength and low density, carbon fibers (CFs) have been widely used in aerospace, marine and automobile industries over the past few decades [1]. The combination of CFs and polymer often leads to the generation of high specific strength materials for structural composites [2]. However, carbon fibers contain a high fraction of graphitic carbon, which gives the fibers high strength, but also makes them less reactive. The non-polar nature of the graphitic bonds as well as inertness prevents the fibers from covalently crosslinking or interacting with the surrounding matrix [3]. The interface between the fibers and matrix plays an important role in determining the macroscopic shear properties of a composite [4].

As a result, both physical coating treatment and chemical grafting have emerged as viable techniques for surface functionalization of graphitic carbon [5–8]. However, a lot of processes typically employ strong oxidizing chemicals or oxidizing atmospheres to create polar oxygen groups from the existing carbon in the fibers at the expense of tensile strength for base carbon fibers. Oxidation also can create a mixture of C—OH, C=O and COOH functional groups [9,10], which is difficult to be separated. Hence, an ideal functionalization process will create uniform functional groups on the surface of the fibers without any negative impact on the tensile strength.

With plenty of examples indicating the effectiveness of the diazonium reaction for surface grafting of graphene and carbon nanotube materials [11–13], this method is suitable for the modification of carbon fibers with no additional defects on the surface or losing fiber tensile strength. Although we have developed an environmentally protocol "on water" reaction, this functionalization protocol requires lengthy reaction times [14]. Here we present a rapid, facile and environmental friendly protocol to surface functionalization, which attaches polar carboxylic acid groups onto the surface of carbon fibers in molten urea without any pre-oxidation (Fig. 1).

2. Materials and methods

2.1. Materials

Polyacrylonitrile (PAN)-based carbon fibers (3×10^3 single filaments per bunch, average diameter 6.5 μm, density 1.76 g cm^{-3}) were obtained from Sino steel Jilin Carbon Co., China. Urea was purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). Sodium nitrite (analytically pure) was supplied by

---

* Corresponding author.
E-mail address: ydhuang.hit1@yahoo.com.cn (Y. Huang).

http://dx.doi.org/10.1016/j.apsusc.2015.11.232
0169-4332/

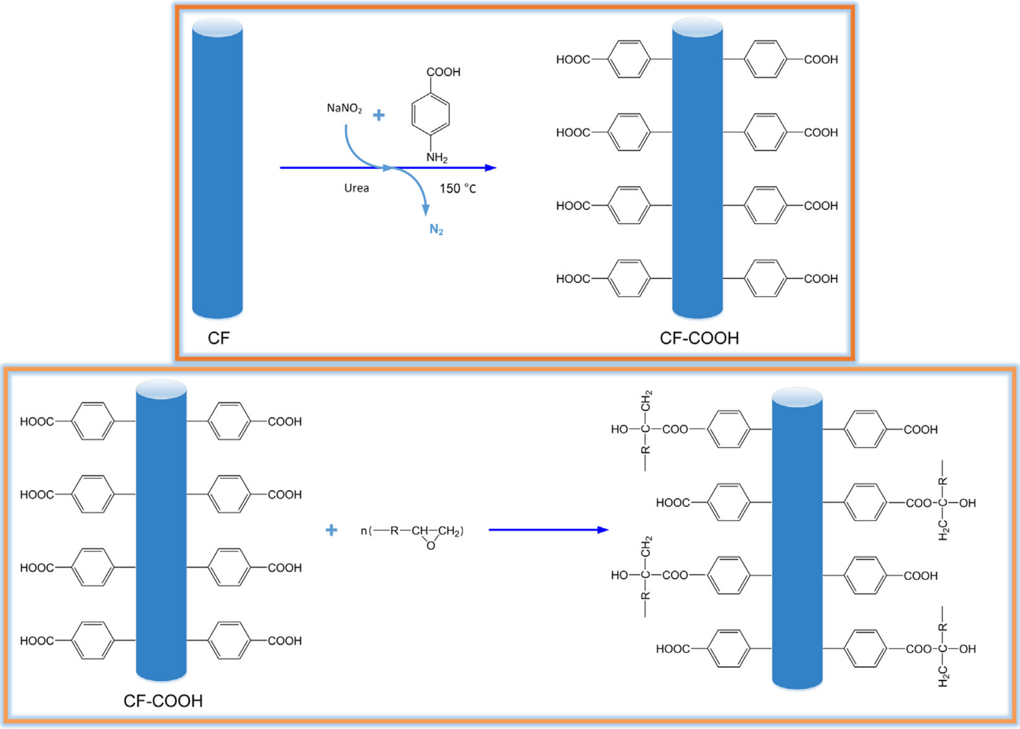

Fig. 1. Schematic image of aryl diazonium functionalization of carbon fibers in molten urea.

Tianjin Bodi Chemicals Co. Ltd. *p*-aminobenzoic acid (analytically pure) was purchased from Guangfu Fine Chemical Research Institute (Tianjin, China). All other chemicals (acetone, dimethylformamide (DMF) and ethanol) obtained from Tianjin Bodi Chemicals Co. Ltd. were of reagent-grade.

2.2. Experimental method

The CFs were firstly treated in Soxhlet extractor with acetone for eliminating the polymer sizing and contaminants from the surface of CFs. Then the CFs were extracted with supercritical acetone/water (25 mL acetone and 5 mL deionized water) at 633 K for 20 min, and then were desized in acetone again (denoted as bare CFs) [15].

Appropriate proportion of a bunch of bare carbon fibers, *p*-aminobenzoic acid and sodium nitrite were precisely weighed. The experimental parameters are given in Table 1. The carbon fiber bunch was bound on a glass frame (3.3 mm × 20.0 mm × 50.0 mm) and added into a 100 mL three-neck flask with *p*-aminobenzoic acid and excess urea. The glass frame was placed flatwise in the flask. Meanwhile, a magnetic stirbar was placed under the glass frame. Then the reaction unit was heated to 423 K in an oil bath. The appropriate amount of sodium nitrite was slowly introduced. At the same time, the whole reaction unit was agitated drastically with the magnetic stirbar at 423 K for 15 min. After reaction, the deionized water and DMF were added into the reaction unit in order to remove any urea and unreacted *p*-aminobenzoic acid from the product respectively, then dried in a drying oven at 393 K for 24 h.

2.3. Characterization methods

Raman spectroscopy was conducted on an Invia Renishaw 2000 spectrometer using an Ar$^+$ laser at ambient temperature. An excitation source with a wavelength of 514.5 nm was used. Raman focusing and imaging was conducted using a confocal microscope with an objective of 50× with a spot diameter of 1–2 mm. The wavenumber range of Raman spectra was 800–2000 cm^{-1}. The spectra acquired from experiment were analyzed using a Lorentzian curve fitting with a linear baseline to determine the peak areas in the software of WIRE 3.3.

The surface functional groups of the carbon fibers were characterized by Fourier transform infrared (FT-IR) spectrometer (Nicolet, Nexus 670, USA). Before the surface analysis, the carbon fibers samples were dried under vacuum at 423 K for 2 h. In order to obtain accurate spectra, a very thin KBr layer was introduced between the prism and the carbon fibers by using a KBr pelletize. The FT-IR spectra were acquired by scanning the specimens for 64 times in the wavenumber range of 400–4000 cm^{-1} with the resolution of 2 cm^{-1}.

The chemical composition of the fiber surface was conducted on an X-ray photoelectron spectrometer (XPS, ESCALAB 220i-XL, VG, UK). XPS analysis was performed on a monochromated Al Kα source (1486.6 eV) at a base pressure of 2×10^{-9} mbar and was calibrated to the C1s peak of graphite at 284.6 eV. The CasaXPS version 2.3.13 program was used for data analysis.

The morphologies of the carbon fibers were observed by a FEI Quanta 200FEG scanning electron microscope (SEM) using a field emission gun (FEG) at an accelerating voltage of 20 kV. The samples were coated with a thin gold layer by sputter prior to the SEM observation in order to capture a stable and clear image.

Dynamic contact angle (DCA) analyses were performed using a dynamic contact angle tensiometer (DCAT21, DataPhysics Instruments, Germany). The advancing contact angle θ was determined from the mass change during the immersion of fibers in each test liquid using Wilhelmy's Eq. (1) [16]

$$\cos\,\theta = \frac{mg}{\pi d_f \gamma_1} \quad (1)$$

where d_f is the fiber diameter, g is the gravitational acceleration, and γ_1 is the surface tension of the test liquid. The surface energy (γ_f), dispersion component ${\gamma^d}_f$ and polar component ${\gamma^p}_f$ of the CFs were estimated from the measured dynamic contact angles of the