

# Influence of deposited CNTs on the surface of carbon fiber by ultrasonically assisted electrophoretic deposition

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**Abstract.** The surface property of carbon fiber directly affects the interface performance between carbon fiber and matrix. To improve the surface property of carbon fiber, we proposed a simple method to prepare carbon nanotubes /carbon fiber hybrid fiber via ultrasonically assisted electrophoretic deposition (EPD). Surface morphologies and surface functional group of carbon fibers were examined by atomic force microscopy (AFM), scanning electron microscopy (SEM) and fourier transform infrared spectrometer (FTIR), respectively. The results show that the deposition of carbon nanotubes changed the surface morphologies of carbon fibers and introduced polar groups (C=O and C-O) to carbon fiber surface. Comparing the results with EPD-only, ultrasonically assisted EPD increased the uniformity of carbon nanotubes coatings whereas only sparse and not uniformly deposition formed without ultrasonic.

## 1. Introduction

Carbon fiber (CF) reinforce composites with their favorable mechanical properties has widely used in aviation industry. Mechanical properties of carbon fiber reinforce composite is closely related to its interfacial bond strength of carbon fiber and matrix. However, the interface performance related to the carbon fiber surface properties, the interface bonding of untreated carbon fiber that has large surface inertia and resin matrix is weak which affects the carbon fiber composite material's excellent performance into full play [1, 2]. As a result, a lot of studies have been devoted to the surface treatment of CF to improve surface properties of CF, such as electrochemical method [3], sizing process [4], plasma treatment [5], preparation of carbon nanotubes (CNTs)/CF hybrid fiber [6]. Among these methods, CNTs with their excellent properties have caused enough attention on hybrid fiber. Grafting CNTs onto fiber surface is a practical method to improve fiber surface area, forming mechanical interlocking on the interface between fiber and matrix, which may improve stress transfer and interfacial properties [7].

Recently, many grafting methods have been proposed such as chemical vapor deposition (CVD) [8] and electrophoretic deposition (EPD) [9]. Both methods reported to deposited CNTs on the fiber surface successfully. However, high temperatures and predeposited catalysts for CVD, seriously limits the practical application of this technique for the fabrication of CNTs/CF hybrid fiber. EPD is known to be one of the most promising manipulation techniques to produce large-scale reinforcement of

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nano-particles in composite applications, which have several advantages over other surface coating process, such as simple process, homogeneity of the deposited films and easy control of the deposited thickness [10]. All these characteristics can be used for the preparation of CNTs/CF hybrid fiber to avoid these problems.

Most research reported improved properties of composites. However, limited attention has been paid to the influence of deposited CNTs on the surface of carbon fibers. In this study, a facile route is proposed to prepare carbon nanotubes/ carbon fiber hybrid fiber via electrophoretic deposition (EPD) without complex chemical reactions. Special emphasis has been put on the influence of CNTs coatings on carbon fiber by ultrasonically assisted electrophoretic deposition on its surface property. Surface roughness and surface morphologies of the fibers were examined using atomic force microscopy (AFM) and scanning electron microscopy (SEM), changes in surface chemistry were studied using fourier transform infrared spectrometer (FTIR).

## 2. Experimental

### 2.1. Materials and processing

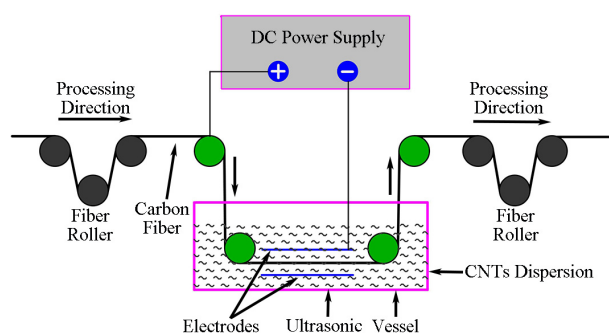
PAN-based CF tow (T700, 12 K and diameter about 7  $\mu\text{m}$ ) was purchased from Toray Industries, Japan. Carbon nanotubes (95% purity, diameter about 10–20 nm, length 10–30  $\mu\text{m}$ ) were purchased from Nanjing Xianfeng. Port. Co., Ltd. The epoxy resin was bought from Yueyang Chemical Reagent Co., Ltd. of China. The curing agent was supplied by Shanghai jingchun Chemical Reagent Co., Ltd. of China.

The CF tow was refluxed in acetone at 80°C for 72 h, then washed with deionized water repeatedly and dried under vacuum at 80°C for 3 h to remove sizing agent (labeling as desized CF).

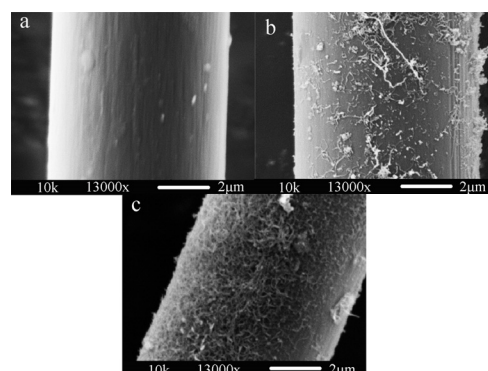
The carbon nanotubes was refluxed in a 3:1 (v: v) mixture of concentrated sulfuric acid and nitric at 100°C for 4h to introduce carboxylic acid groups, then diluted with deionized water and suction filtering, deionized water washing to neutral.

### 2.2. Preparation of CNTs/CF hybrid fiber

A schematic of the EPD setup is shown in figure 1. For the EPD of CNTs onto the CF, the CF tow was used as the deposition electrode, and two graphite plates were used as the counter electrodes. In order to obtain 0.05 mg/mL CNTs dispersions, we disperse CNTs in deionized water by ultrasonic. The EPD process was carried out at constant voltages of 20 V for 20 min; the sonicator (60 W, 40 KHz) used to provide ultrasonic during ultrasonically assisted EPD. After EPD process, sonicator was switched off and the samples were dried in air at room temperature.



**Figure 1.** Schematic for continuous EPD process of CNTs onto carbon fiber.



**Figure 2.** SEM images of the surface of carbon fiber; (a) desized; (b) CNTs deposited without ultrasonic; (c) CNTs deposited with ultrasonic.

### 2.3. Characterizations

**2.3.1. Scanning electron microscopy.** Surface morphologies of the CF was characterized using scanning electron microscope at 10 kV (JOEL, JCM-6000). Fiber samples were cut with scissors to observe a transverse cross-section for SEM observation

**2.3.2. Atomic force microscopy.** Surface roughness of CF was characterized by atomic force microscopy (Park, XE-100). All AFM images of CF used the tapping mode to obtain with the scan area of 4 mm×4 mm.

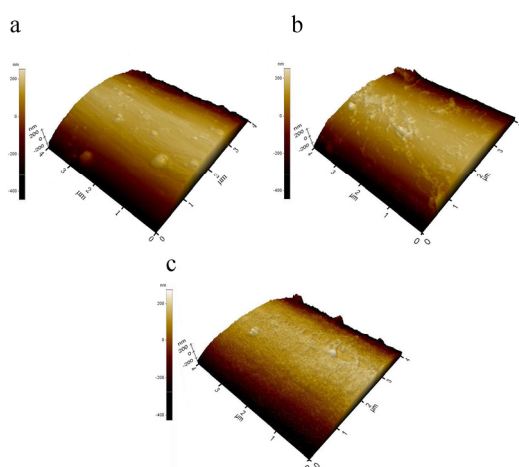
**2.3.3. Fourier transform infrared spectrometer.** Fourier transform infrared spectra (FTIR) were conducted on Nicolet 20DXB 60,000 spectrophotometer with the range of 450–4000  $\text{cm}^{-1}$  to evaluate the chemical structures using a KBr pellet.

## 3. Results and discussion

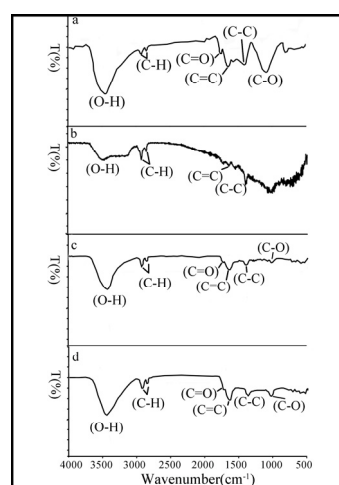
### 3.1. Surface roughness and surface morphologies of carbon fiber

Figure 2 shows typical SEM micrographs of the surface of CF at different process stages. Initially, the surface of desized CF was rough and there are some grooves on the surface of CF (figure 2a). Figures 2(b) and 2(c) shows that the surface of CF has been deposited CNTs. It also shows that EPD process can prepare CNTs/CF hybrid fiber successfully. Meanwhile, homogeneous CNTs films due to ultrasonic can be seen from the SEM images of CNTs/CF hybrid fiber, the surface of CF with CNTs deposited showed some slight concave pits and convex hills without ultrasonic (figure 2b), whereas the surface of the CF showed much more convex hills with ultrasonic and homogeneously cover the whole surface (figure 2c). It appears that ultrasonic during the EPD process can increase the quality and quantity of depositing CNTs.

In order to have better understanding of the surfaces, AFM studies have been carried out. Figure 3 shows the increased roughness of CF surface with the CNTs deposition. It can be found that desized CF (figure 3a) shows a smooth surface with streaks, as shown in figures 3b and 3c), the introduction of CNTs can increase the surface roughness of CF obviously. In addition, the surface roughness increased when introduce ultrasonic to deposition of CNTs on the CF surface (figures 3b and 3c). The increase of surface roughness is beneficial to enhance mechanical interlocking between the fiber and matrix [9].



**Figure 3.** AFM images of CF (a) desized; (b) CNTs deposited without ultrasonic; (c) CNTs deposited with ultrasonic.



**Figure 4.** FTIR spectra of (a) CNTs; (b) desized CF; (c) CNTs deposited without ultrasonic; (d) CNTs deposited with ultrasonic.

### 3.2. Surface functional group of carbon fiber

The FTIR was used to determine the functionalization during EPD process, as shown in figure 4. The spectrum of CNTs-COOH showed peaks at  $1731\text{ cm}^{-1}$ ,  $1628\text{ cm}^{-1}$ , and  $1042\text{ cm}^{-1}$ , which are assigned to C=O stretching vibration, C=C deformation vibration, C-O stretching vibration (figure 4a) [11], respectively. For the desized CF, four peaks located at  $3468\text{ cm}^{-1}$ ,  $2925\text{ cm}^{-1}$ ,  $1644\text{ cm}^{-1}$ ,  $1384\text{ cm}^{-1}$  in the FTIR spectrum are observed (figure 4b), which are allocated to  $\nu(\text{O-H})$ ,  $\nu(\text{C-H})$ ,  $\nu(\text{C=C})$ ,  $\nu(\text{C-C})$ . After depositing CNTs on the desized CF without ultrasonic,  $\nu(\text{C=O})$  at  $1731\text{ cm}^{-1}$  are visible (figure 4c), which means carboxyl are formed as a result of CNTs were successfully deposited on the surface of CF. For depositing CNTs on the desized CF with ultrasonic, the broader peaks of  $\nu(\text{C=O})$  at  $1731\text{ cm}^{-1}$  (figure 4d) indicate that the amount of carbon nanotubes were increased by ultrasonically assisted EPD process.

### 4. Conclusions

In summary, carbon nanotubes was successfully coated onto carbon fiber surfaces via ultrasonically assisted electrophoretic deposition, which avoids complex chemical reactions, therefore provides great potential for industrial applications. SEM and AFM analysis showed that carbon nanotubes film with high roughness is homogeneously formed on carbon fibers. Comparing the results with EPD-only, EPD with ultrasonic increased the amount and homogeneity of CNTs coatings, this comes from ultrasonic improves the dispersion of CNTs and inhibits water electrolysis reaction.

### References

- [1] Chand S 2000 Review carbon fibers for composites *J. Mater. Sci.* **35** 1303-13
- [2] Akbar D and Gungor U E 2014 Study of high radio frequency plasma discharge effects on carbon fiber using raman spectroscopy *Surf. Coat. Technol.* **240** 233-42
- [3] Cao H L, Huang Y D, Zhang Z Q and Sun J T 2005 Uniform modification of carbon fibers surface in 3-D fabrics using intermittent electrochemical treatment *Compos. Sci. Technol.* **65** 1655-62
- [4] Liu J, Ge H, Chen J, Wang D and Liu H 2012 The preparation of emulsion type sizing agent for carbon fiber and the properties of carbon fiber/vinyl ester resin composites *J. Appl. Polym. Sci.* **124** 864-72
- [5] Xie J F, Xin D W and Cao H Y 2011 Improving carbon fiber adhesion to polyimide with atmospheric pressure plasma treatment *Surf. Coat. Technol.* **206** 191-201
- [6] Bekyarova E, Thostenson E T and Yu A 2007 Multiscale carbon nanotube-carbon fiber reinforcement for advanced epoxy composites *Langmuir*. **23** 3970-4
- [7] Thostenson E, Li W, Wang D, Ren Z and Chou T 2002 Carbon nanotube/carbon fiber hybrid multiscale composites *J. Appl. Phys.* **91** 6034-7
- [8] Greef N D, Zhang L and Magrez A 2015 Direct growth of carbon nanotubes on carbon fibers: Effect of the CVD parameters on the degradation of mechanical properties of carbon fibers *Diamond. Relat. Mater.* **51** 39-48
- [9] Guo J H, Lu C X and An F 2012 Effect of electrophoretically deposited carbon nanotubes on the interface of carbon fiber reinforced epoxy composite *J. Mater. Sci.* **47** 2831-6
- [10] Subramanian P, Jonsson J N, Lesniewski A, Wang Q and Li M S 2014 Preparation of reduced graphene oxide-Ni(OH)<sub>2</sub> composites by electrophoretic deposition: application for nonenzymatic glucose sensing *J. Mater. Chem.* **2** 5525-33
- [11] Byrappa K, Dayananda A S, Sajjan C P and Basavalingu B 2008 Hydrothermal preparation of ZnO: CNT and TiO<sub>2</sub>: CNT composites and their photocatalytic applications *J. Mater. Sci.* **43** 2348-55