

THE METHOD TO IMPROVE INTERFACIAL PROPERTIES OF CFRP COATING NANO-CARBON-MATERIAL ON CF SURFACE

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ABSTRACT

To improve the interfacial performance of carbon fiber (CF) and epoxy resin, carbon nanotubes (CNTs) and graphene oxide (GO) were deposited on the electrochemically oxidized CF surface. The characterization of the CF surface properties were done before and after coating (surface chemistry, surface morphologies, and surface energy) which shows the oxygenated groups concentrations of the CF surfaces significant increasing from 14.41% to 28.93%. Moreover, the uniform and homogeneous of CNTs and GO were tightly attached on the surface of CF, and the surface wettability of CF were significant improved by enhanced surface free energy. In addition, CNTs coated, GO-coated and pristine unidirectional carbon fiber fabrics were used to manufacture CF/epoxy composites by vacuum assisted resin transfer molding method, and their moisture absorption and interlaminar shear strength were measured. The incorporation of nanomaterials enhanced interfacial properties of carbon fiber-reinforced epoxy composites. The ILSS of the CNTs/CF/epoxy composite rose by 58.6%, and the moisture absorption of the GO/CF/epoxy composite decreased by 63.6%.

1 INTRODUCTION

Due to the exceptionally high specific strength, high modulus, low density, and reasonable cost, CF reinforced composites are one of the most attractive materials for their wide use in aeronautical and aerospace applications, automobile, and many military applications. Mechanical properties of CF-reinforced composite are closely related to the properties of fiber–matrix interface. Good interfacial properties are essential to ensure efficient load transfers from polymer matrix to reinforcing fibers. However, the untreated CF surface has big inertia and small active specific surface area, which affects the CF composite material's excellent performance into full play [1–4]. As a result, over the last few decades, a great deal of scientific effort has been focused on the surface modification of CF for improving the interfacial properties of composites through many methods such as plasma etching treatment [5], sizing technique [6], chemical treatment [7], electrochemical oxidation treatment [8], etc. These methods have improved interfacial properties of composites to some extent, however, due to the different scales of the fiber and polymer matrix, they have barely gained the satisfying results[9–11].

In recent years, with the production and popularity of nano-materials, there has been significant interest in developing micro/nano composites where traditional fibers are integrated with diverse nanoparticles [12,13]. Nanoscale reinforcements have critical dimensions that are three orders of magnitude smaller than traditional fiber reinforcements, such an arrangement will have the advantage of having a complex, hierarchical structure—by having bonding between matrix and traditional fibers in addition to the smaller scale bonding between nanoparticles and matrix [14]. Many methods have been presented that incorporate chemical vapor deposition (CVD) [15], chemical grafting [16], electrophoretic deposition (EPD) [17,18], etc. These processes effectively attached nanoparticles to the surface of the fiber. However, the chemical grafting method is not practically applicable because of its long processing time and violent chemical reaction, and the CVD needs high temperatures and pre-deposited catalysts. The EPD technique has been widely utilized for surface modification to produce a large-scale nanoparticle reinforcement material for application in composites. EPD has several advantages over other techniques, including effortless control of film thickness, good surface homogeneity, high deposition rate and simplicity of scaling up, etc [19-22].

As typical one-dimension and two-dimension carbon-based nano-materials, carbon nanotubes and graphene nano-platelets are widely used as nanoscale reinforcements into the interphase region of composites to cause interfacial mechanical interlocking between fibers and the matrix for improving interfacial properties of composites [23]. Functionalized CNTs and GO are always used to modify CF because oxygen-containing polar groups can improve the surface wettability of CF. Additionally, these polar groups are useful in enhancing the interfacial adhesion through establishing covalent bonds with matrix in the curing step [24]. In this work, carboxylic-functionalized CNTs and GO were separately deposited on surface of CF by EPD technique. Although some work has been reported in the literature using these two separate nanomaterials, they have barely been compared before. This paper offers a comparison of the interfacial properties of CF/epoxy composites with CF modified with CNTs and GO.

2 EXPERIMENTAL

2.1 Materials and processing

PAN-based CF tow (T700, 12 K and diameter about 7 μm) was purchased from Toray Industries, Japan. Commercially available multiwall carbon nanotubes (length 10–20 μm , diameter about 10–20 nm, 95% purity) were purchased from Shenzhen Nanotech Port. Co., Ltd, and the natural graphite flakes (with a purity of 99% and a mean diameter of 25 μm) were purchased from Qingdao Huatai Co., Ltd. The matrix used in this work was a bisphenol. An epoxy resin (E-51) was bought from Nantong Xingchen Reagent Co., Ltd. The hardener was 3,3'-diethyl-4,4'-diaminodiphenylmethane (H-256) and was provided by Jiangsu Huifeng Co., Ltd.

The CF was refluxed in acetone for 48 h at 60 $^{\circ}\text{C}$ to remove sizing agents, and then repeatedly washed in deionized water and dried under ambient temperature to obtain the desized CF. All CF used afterwards in this study is desized CF unless otherwise specified.

The carboxylic-functionalized CNTs were prepared by a mixed acid treatment method [25], that the as-received CNTs (0.1 g) were refluxed in a mixture of concentrated sulfuric acid (98%, 25 ml) and concentrated nitric acid (65%, 75 ml) and stir at 98 $^{\circ}\text{C}$ for 4h. Then, the mixture was washed with deionized water for several times to neutral. The carboxylic-functionalized CNTs were dispersed in deionized water by sonication treatment for 1 h to get CNTs solutions. All CNTs used afterwards in this study are carboxylic-functionalized CNTs unless otherwise specified.

The GO was made by a modified Hummers method [26]. Briefly, graphite flakes (2 g) were mixed with concentrated sulphuric acid (98%, 50 ml) and sodium nitrate (2g), then potassium permanganate (4 g) was slowly added into the system. The mixture was magnetically stirred at 30 $^{\circ}\text{C}$ for 2 h, followed by the addition of deionized water (100 ml) and stir at 96 $^{\circ}\text{C}$ for 1 h. The mixture was further added with hydrogen peroxide (5%, 100 ml) and washed with deionized water for several times. The purified sample of GO was dispersed in deionized water by sonication treatment for 1 h, yielding GO dispersions. The typical transmission electron microscope images of carboxylic-functionalized CNTs and GO used in this work are presented in Fig. 1.

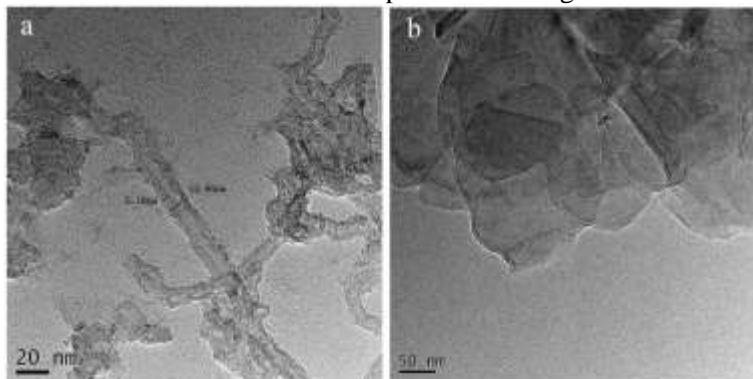


Figure 1: This is an example of a figure.

2.2 Preparation of CNTs/CF and GO/CF hybrid fiber

A schematic of the EPD setup is shown in Fig. 2. For the EPD of CNTs and GO on the CF, the CF tow was used as the deposition electrode, and two stainless steel plates were positioned opposite to carbon fibers as the counter electrode; pH of solutions was controlled 10, CNTs and GO concentration were 0.25 g/L; and pH was acquired by adding a 0.2 M sodium hydroxide solution. The EPD process was carried out at constant voltages of 20 V for 20 min, with a electrode distance of 2 cm. Ultrasonic assistance was provided by sonicator (60 W, 40 kHz) to remove the bubbles produced from the electrolysis of water. After the EPD process, the CFs were dried in an oven at 90 °C for 12 h, and the carboxylic-functionalized CNTs and GO were deposited on the CF to obtain the fibers, labeled as CNTs/CF and GO/CF, respectively.

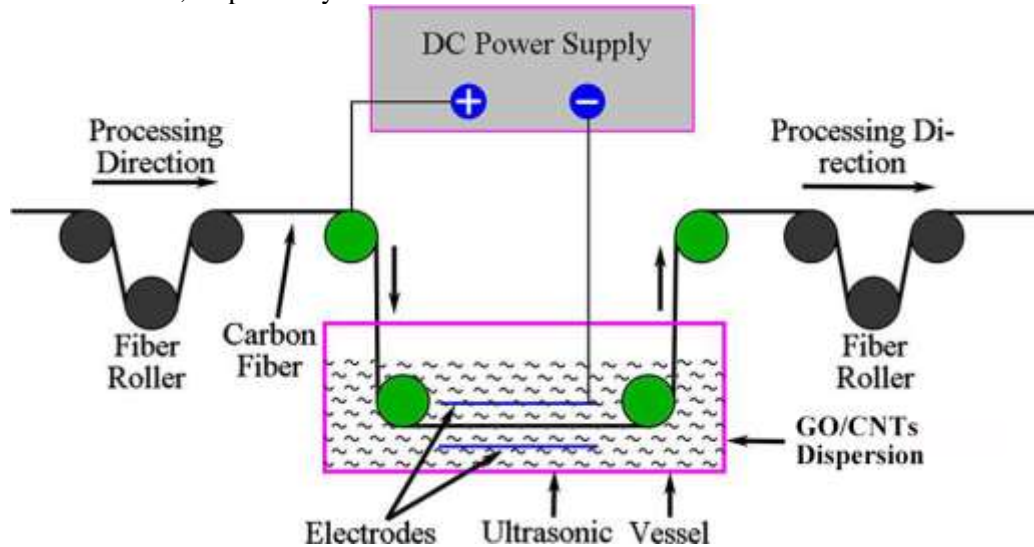


Figure 2: Schematic for continuous EPD process to make CNTs/CF and GO/CF hybrid fibers.

2.3 Preparation of CF/EP composites

The setup to prepare CF/EP composites is shown in Fig. 3. Carbon fiber fabrics were used as the base material to synthesize the CNTs&GO/CF/EP hybrid composites, and the fabrics comprised CNTs& GO/CF hybrid fiber. The CNTs&/CF performs were infiltrated with epoxy using vacuum-assisted resin transfer molding (VARTM) with the epoxy resin and curing agent at a ratio of 100/33 parts by weight. In the VARTM process, the epoxy resin is infused into the carbon fibers under vacuum. After the infiltration of epoxy, the composites were cured for 12h at 80 °C.



Figure 3: Schematic for preparation of CF/EP composites.

2.4 Characterizations

The morphologies of carboxylic-functionalized CNTs and GO were observed on transmission electron microscope (TEM, FEI, Tecnai-F30-G2, USA). The surface morphologies of the CFs were characterized by scanning electron microscope (SEM, JOEL, JCM-6000, Japan).

Surface roughness of CF was characterized by AFM (Bruker Corporation, Germany). All AFM images of CF used the tapping mode to obtain the scan area of 4 mm × 4 mm.

Fourier transform infrared spectra (FTIR) were conducted on Nicolet 20DXB 60,000 spectrophotometer with the range of 500-4000 cm⁻¹ to evaluate the chemical structures using a KBr pellet.

The dynamic contact angle meter (DCA, Data Physics Instruments, DCAT21, Germany) was used to carry out dynamic contact angle tests. Deionized water and glycol were used as the test liquids. The polar components, dispersive components and total surface energy can be calculated as following formulas:

$$\gamma_l (1 + \cos\theta) = \frac{4\gamma_l^d \cdot \gamma_s^d}{\gamma_l^d + \gamma_s^d} + \frac{4\gamma_l^p \cdot \gamma_s^p}{\gamma_l^p + \gamma_s^p} \quad (1)$$

$$\gamma_{\text{Total}} = \gamma_s^d + \gamma_s^p \quad (2)$$

where θ is the contact angle. And γ_l , γ_l^p and γ_l^d is surface tension of the testing liquid, its polar and dispersive component, that deionized water ($\gamma^d = 21.8 \text{ mNm}^{-1}$, $\gamma^p = 51.0 \text{ mNm}^{-1}$, $\gamma = 72.8 \text{ mNm}^{-1}$) and glycol ($\gamma^d = 29.3 \text{ mNm}^{-1}$, $\gamma^p = 19 \text{ mNm}^{-1}$, $\gamma = 48.3 \text{ mNm}^{-1}$). All measurements were performed at least eight times.

Short-beam shear tests were performed to determine the ILSS of CF/EP composite. The ILSS of the CF/EP composites was measured by short-beam shear test according to ASTM D 2344. The tests were performed on a universal testing machine with a constant cross head rate of 2 mm/min and a span thickness ratio of 5. The tests were carried out at 20°C and 50% relative humidity. Specimen dimensions were 25 × 6 × 2 mm³, the ILSS was calculated as follows:

$$\tau_{\text{ILSS}} = \frac{3P_b}{4b \cdot h} \quad (3)$$

where P_b represents the largest load, and h and b represent the thickness and width of the specimen, respectively.

The moisture absorption of hierarchical CF/epoxy composites were studied to evaluate the effect of CNTs and GO on interfacial adhesion of the composite. The test was performed following ASTM D 570. The weight measurements were made using an electronic analytical balance (Mettler-Toledo, MS105DU-700B, Switzerland). Percentage of moisture absorption can be calculated to the nearest 0.01% as following formula:

$$\text{Moisture absorption} = (W_t - W_0) / W_0 \times 100\% \quad (4)$$

where W_0 and W_t represent the initial mass and wet weight of the composite samples.

3 RESULTS AND DISCUSSION

3.1 Morphology of CF with CNTs and GO

The morphologies of different CF samples are presented in Fig. 4. As previously said, it can be seen that the surface of the desized CF was smooth (Fig. 4a & b). The EPD technique made a fairly uniform coating consisting of either CNTs or GO on the fiber surface. Fig. 4c & d shows connectivity of individual CNTs leads to a continuous CNTs network on the fiber surface. In contrast, the surface of GO/CF displays a number of convex hills and concave pits (Fig. 4e & f). These morphological differences derived from the structures of coatings: GO is two-dimension material and can be readily assembled layer by layer on the surface of fiber, conversely CNTs have a wire-like structure with a high aspect ratio [27].

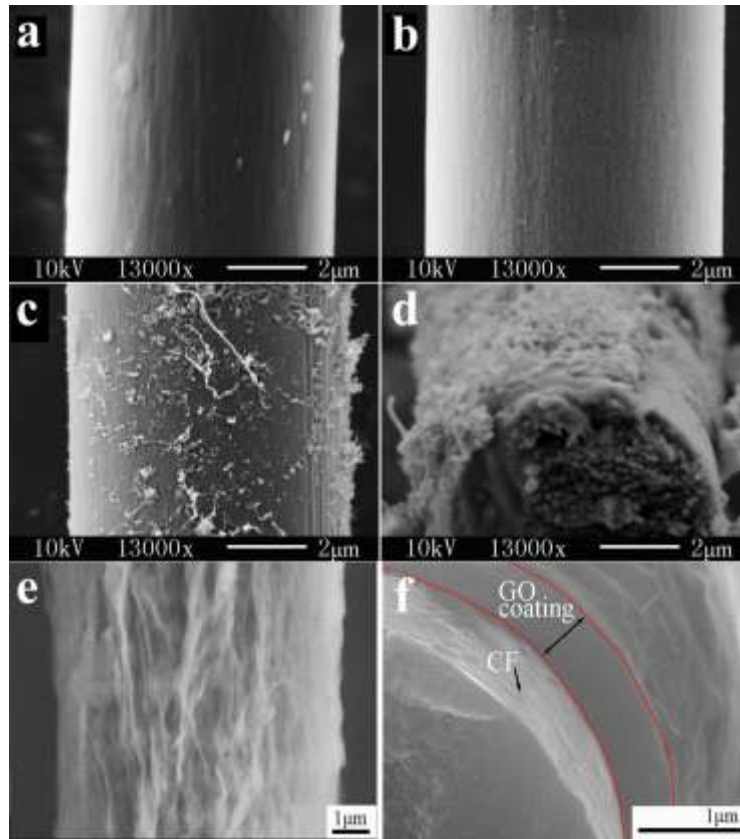


Figure 4: FE-SEM images of surface morphology and cross-sectional morphology of (a) desized CF; (b) oxidized CF; (c) CNTs/CF-oxidized hybrid fiber; (d) cross-section of CNTs/CF-oxidized hybrid fiber; (e) GO/CF-oxidized hybrid fiber; (f) cross-section of GO/CF-oxidized hybrid fiber.

3.2 Surface roughness of CF with CNTs and GO

In order to have better understanding of the surfaces, AFM studies have also been carried out. The CNTs and GO deposited on the CF surface contributed to the increased roughness as shown in Fig. 5; it can be found that desized CF and oxidized CF showed a smooth surface (Fig. 5a, b); as shown in Fig. 3c, many obvious convex hills are presented on the fiber surfaces. The results indicated that the surface morphologies of the CNTs and GO/CF-oxidized hybrid fiber became more complicated, which was beneficial to enhance mechanical interlocking between the fiber and matrix. Surface roughness of carbon fiber, which can be characterized by arithmetic mean roughness R_a and root mean square (RMS) roughness R_q , is shown in Table 1. For the desized CF, R_a and R_q were 59.2 and 75.72 nm, respectively. After depositing CNTs and GO on the oxidized CF, it was found that R_a of CF increased to 141.9 and 106.5 nm, and R_q of the carbon fiber went up to 188.6 and 140.1 nm. The results indicate that CNTs and GO deposition enhances the surface roughness of CF, which can improve the wettability and interfacial adhesion between carbon fibers and matrix.

	R_a (nm)	R_q (nm)
Desized CF	59.2	75.72
Oxidized CF	72.2	90.8
CNTs/CF-oxidized hybrid fiber	141.9	188.6
GO/CF-oxidized hybrid fiber	106.5	140.1

Table 1: Arithmetic mean roughness R_a and RMS roughness R_q of carbon fiber.

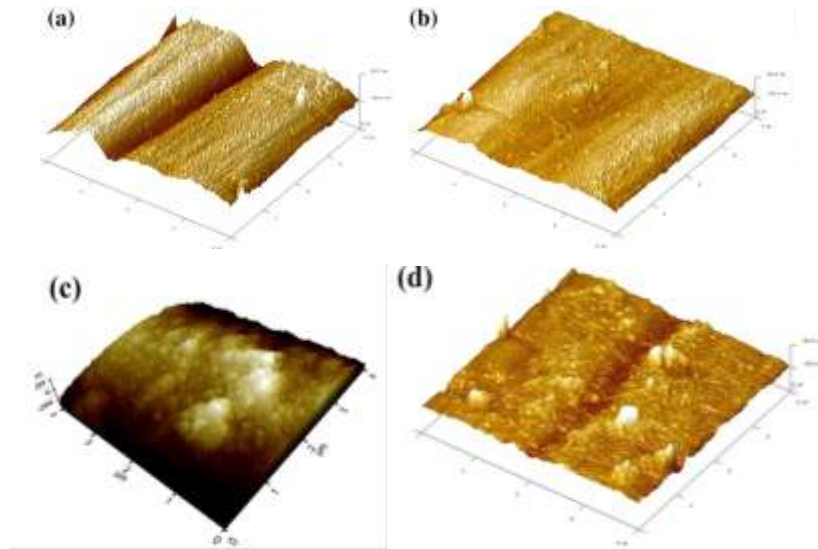


Figure5: AFM images of a desized CF, b oxidized CF, c CNTs/CF-oxidized hybrid fiber, d GO/CF-oxidized hybrid fiber.

3.3 Chemical groups and Surface chemical elemental composition of CFs analysis

The surface functional groups of the nano-particles and the fibers were examined by FT-IR, as presented in Fig. 6. It can be seen, the spectrum of carboxylic-functionalized CNTs shows peaks at ν (O-H) (3468 cm^{-1}), ν (C-H) (2925 cm^{-1}), ν (C=O) (1731 cm^{-1}) and ν (C-O) (1042 cm^{-1}), respectively. For the spectrum of GO, the characteristic peak of ν (O-H) and ν (C=O) are more broader, and a new peak ν (C-O-C) appear around 1250 cm^{-1} . The results reveal both functionalized CNTs and GO have a lot of oxygen-containing groups. After depositing CNTs and GO on fibers surface by EPD, the spectrum obviously change, the peak of ν (O-H) and ν (C-O) are obviously broader, which indicate that both CNTs and GO were successfully deposited on the surface of CF.

Fiber type	Surface elements abundance (%)					
	C	O	N	S	Si	O/C
CF	84.04	12.11	2.87	0.68	0.3	14.41
CNTs/CF	74.52	21.56	2.63	0.73	0.56	28.93
GO/CF	71.16	25.25	1.29	1.42	0.88	35.48

Table 2 Summary of element composition on carbon fiber surface.

To obtain a deep understanding of the differences that occur during deposition, XPS analysis was used to characterize the chemical compositions on the surface of the CFs. The global surface atomic compositions for all samples studied are presented in Table 2. Oxygen, carbon and nitrogen are the most abundant elements on the fiber surface. Other elements are present in concentrations of less than 2%. After carboxylic-functionalized CNTs deposition, the O/C ratio of the CF increased from 14.41% to 28.93%. GO deposition significantly increased the oxygen concentration on the fiber surface, and the O/C ratio of GO/CF increased to 35.48%. To quantify the differences and similarities among the studied samples, high-resolution XPS spectra of the C1s region were examined. Four peaks were found, which represent graphitic carbons (peak I, 284.6 eV); carbons present in alcohol, ether, or phenolic groups (peak II, 286.2-286.5 eV); carbons from quinone or carbonyl groups (peak III, 287.2-

287.7 eV); and carbons from ester or carboxyl groups (peak IV, 288.3-288.8 eV) [28]. The relative composition, expressed as the ratio of each peak area to the total peak area, is presented in Fig. 7. The desized CF showed four peaks related to C-O (16.47%), C=C (3.35%), C-C (75.03%) and O=C-O (4.95%) (Fig. 7a). After carboxylic acid-functionalized CNTs deposition, the O=C-O peak ratios increased from 4.95% to 11.41% (Fig. 7b). This result shows that more carboxyl groups appear on the fiber surface. Carbon fiber deposited with GO presented the concentrations of reactive oxygen-containing groups (II and IV) were 23.58% and 10.48% (Fig. 7c), respectively, which indicated that GO increasing polar groups on carbon fiber. These increased oxygenated groups are useful in enhancing the interfacial adhesion through increasing wettability of fibers and establishing covalent bonds with numerous sites on epoxy in the curing step [29].

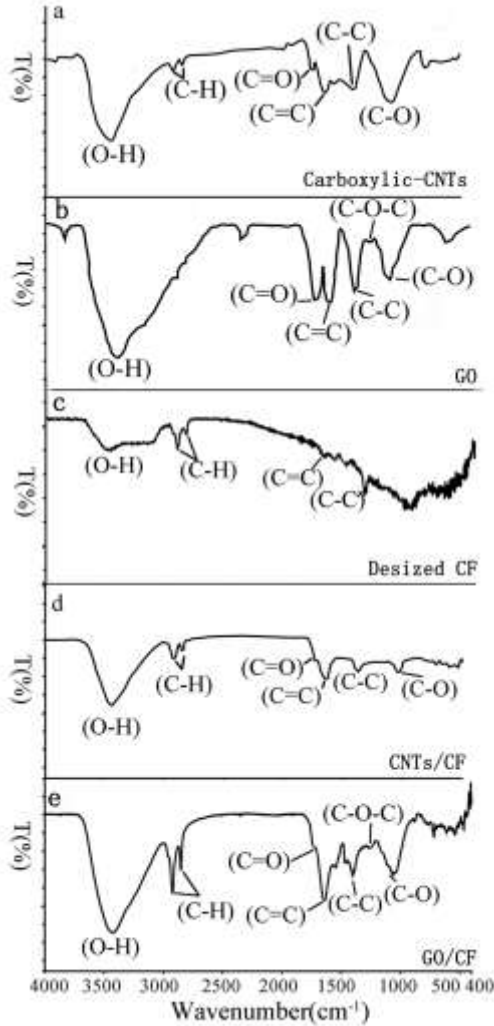


Figure 6: FTIR spectra of (a) carboxylic-functionalized CNTs, (b) GO, (c) desized CF, (d) CNTs/CF, (e) GO/CF.

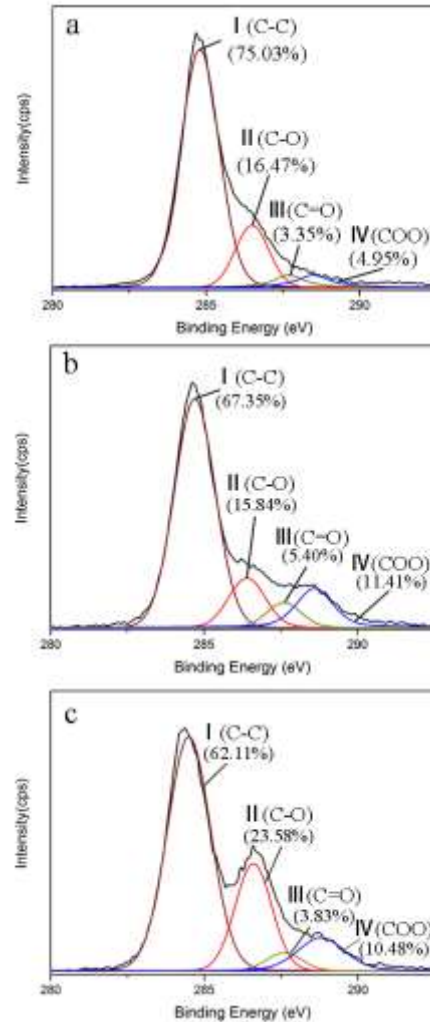


Figure 7. C1s spectra of (a) desized CF, (b) CNTs/CF, (c) GO/CF.

3.4 Surface wettability analysis

The surface wettability of the CFs was characterized using DCA and the results are presented in Table 3. The results of the contact angle measurements with glycol and deionized water for CF, CNTs/CF and GO/CF. The contact angles of water (θ_{water}) and glycol (θ_{glycol}) on the desized CF surface were 76.1° and 62.6° , respectively. In addition, θ_{water} and θ_{glycol} of CNTs/CF were 51.2° and

43.1 °, respectively. After depositing GO, θ_{water} and θ_{glycol} decreased to 45.8 ° and 39.1 °, respectively. The results revealed that although carbon nanotube was a super-hydrophobic material, but the hydrophilicity of carboxylic-functionalized CNTs increased significantly after acid-treatment of CNTs. In addition, GO-coated carbon fiber had excellent wettability.

As for the surface free energy of the CFs, the polar component (γ^p), the dispersive component (γ^d) and the total surface free energy (γ) of the desized CF were 23.2 mJ/m², 9.5 mJ/m² and 32.7 mJ/m², respectively. The γ^p , γ^d and γ of CNTs/CF were 39.4 mJ/m², 11.1 mJ/m² and 50.5 mJ/m², respectively. In addition, γ^p , γ^d and γ of GO/CF increased to 43.3 mJ/m², 11.5 mJ/m² and 54.8 mJ/m², respectively. In a nutshell, the new nanoscale coatings have a large influence on the wettability of CFs by increasing number of polar groups and the surface topography. The interfacial properties of the composites consequently increase due to the high number of polar components and the increased surface energy.

Fiber type	Contact angle (°)		Surface energy (mJ/m ²)		
	θ_{water}	θ_{glycol}	γ^d	γ^p	γ
Desized CF	76.1	62.6	9.5	23.2	32.7
CNTs/CF	51.2	43.1	11.1	39.4	50.5
GO/CF	45.8	39.1	11.5	43.2	54.8

Table2: The contact angles and the surface energy..

3.4 Interfacial properties of CF/epoxy composites

The interfacial bonding strength between the matrix and studied fibers was evaluated by examining the IFSS, and the results are shown in Fig. 8. Clearly, it can be observed that CNTs and GO increased the interfacial bonding strength of the composites significantly. The values of IFSS increased from 48.2 MPa (desized CF) to 91.3 MPa (CNTs/CF) and 78.6 MPa (GO/CF). The IFSS of the composites increased by 89.4% and 63.1% after depositing CNTs and GO on the fiber surface, respectively. The change in IFSS correlated directly with the CNTs and GO severally deposited onto the fiber surface.

The ILSS results are presented in Fig. 9. As can be seen, the ILSS of desized CF composite was 36.7 MPa. The ILSS of the GO/CF/epoxy composite was 56.9 MPa. And the maximum ILSS was 58.2 MPa, which belonged to CNTs/CF/epoxy composite. This result demonstrates that the interfacial and mechanical properties of the CF/epoxy composites could be enhanced by introducing CNTs and GO in the interphase of composites.

The moisture absorption of the composites relates to both the interfacial adhesion between fibers and the matrix and the porosity of the composites [30]. The damage of the interface in hygrothermal condition decreases mechanical properties of CF/epoxy composites. Thus, the moisture absorption of the composites shows the interface bonding situation of composites indirectly. The results of moisture absorption are as shown in Fig. 10. It can be seen, after two hours the moisture absorption of composites of desized-CF/epoxy, CNTs/CF/epoxy and GO/CF/epoxy were 0.362wt%, 0.167wt% and 0.142wt%, respectively. Furthermore, after 24 hours these values increased to 0.662wt%, 0.38wt% and 0.241wt%, respectively. For CNTs/CF and GO/CF epoxy composites, the moisture absorption declined by 42.6% and 63.6%. In brief, GO/CF/epoxy composite had better humidity resistance and lower porosity.

To further study the interfacial behavior of the composites, after performing the ILSS tests, SEM images of the fractured surface of the CF/epoxy composite were examined and are shown in Fig. 11. The matrix was completely detached from the fiber surface of the untreated composite because of the

weak bonding between the fibers and the matrix (Figure 11a). In contrast, for CNTs/CF and GO/CF, a number of resin fragments were attached on the fiber surface, which showed that the interfacial adhesion between the CFs and the matrix improved after depositing CNTs and GO onto the fiber surface, as shown in Fig. 11b,c.

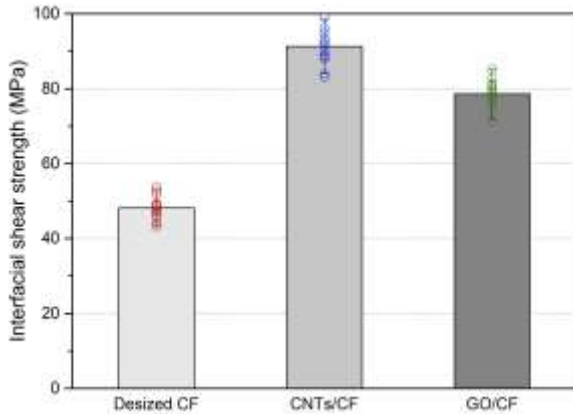


Figure8: Interfacial shear strength results of the composites.

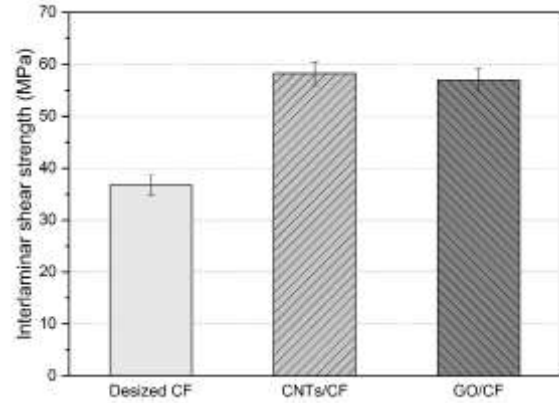


Figure 9. Interlaminar shear strength of the composites.

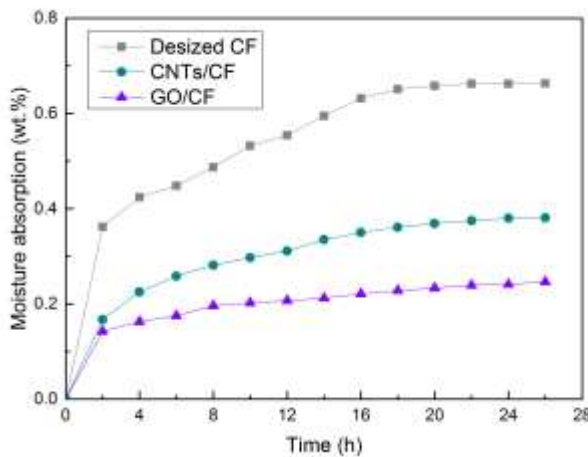


Figure10: Moisture absorption of the composites.

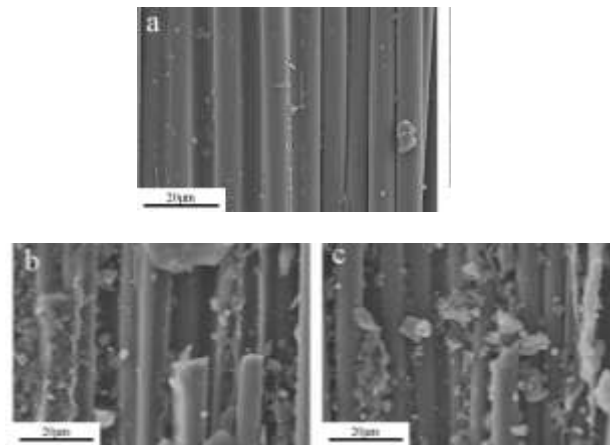


Figure 11. Fractured images of the composites (a) desized CF, (b) CNTs/CF, (c) GO/CF.

3.5 Interfacial reinforced mechanism of the composites

The test results of interfacial properties revealed that CNTs-coated CF composite had higher shear strength, and GO-coated CF composite had lower moisture absorption. The dissimilarities between CNT/CF/epoxy and GO/CF/epoxy may come from the different interphases generated between the matrix and fibers. Since carbon nanotube is a one-dimensional wire-like material, CNTs on the CF look like hair on the head, which is a loose and porous structure. When CNTs/CF contacted with the matrix, they synthesized a CNTs/epoxy nanocomposite in the interphase of CF/epoxy composites. In contrast, GO on the CF looks like hat on the head, and the GO coating with a layer by layer structure. When GO/CF contacted with the matrix, the matrix was attached on the GO coating, that built interfacial mechanical interlocking and chemical bonding. However, the outermost layer of the GO coating served as a barrier for the penetration of the matrix, which formed a CF-GO-epoxy structure in the composite. CNTs/epoxy nanocomposite can provide additional reinforcement to the interface and decrease the interlaminar stress concentration, which effectively improves the shear strength of the

composites. In contrast, GO/CF has a higher surface energy, which can increase the wettability and provides close molecular contact between fibers and the matrix; thus GO/CF/epoxy composite has better humidity resistance. The exact structure differences are illustrated in Fig. 12.

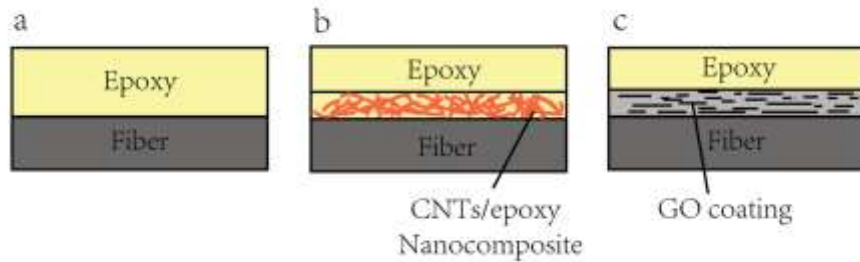


Figure 12. Schematic showing the interphase structures of the composites (a) CF/epoxy, (b) CNTs/CF/epoxy, (c) GO/CF/epoxy.

4 CONCLUSIONS

In summary, this work demonstrated that the electrophoretic deposition method is an efficient technique for the deposition of carboxylic-functionalized CNTs and GO on the surface of carbon fibers, which afford excellent potential for practical applications. The different morphologies and chemical compositions of fibers with CNTs and GO were studied and compared. The results of microdroplet test showed the interfacial shear strength of CNTs/CF increased by 89.4% compared with desized CF. The incorporation of nanomaterials enhanced interfacial properties of carbon fiber-reinforced epoxy composites. The ILSS of the CNTs/CF/epoxy composite rose by 58.6%, and the moisture absorption of the GO/CF/epoxy composite decreased by 63.6%. The differences on the dimension and structure of GO and CNTs endowed the formation of different interphase in CF/epoxy composites. For CF/epoxy composite with CNTs, the interphase was a nanocomposite consisting of CNTs and epoxy, while the one in GO/CF/epoxy composite was a CF-GO-epoxy structure.

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