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# Electrophoretic deposition of graphene oxide on continuous carbon fibers for reinforcement of both tensile and interfacial strength

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### A R T I C L E I N F O

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### 1. Introduction

Excellent tensile strength, high stiffness, light weight and great thermal resistance make carbon fiber reinforced composites an ideal structural material [1]. However, due to the smooth and chemically inert carbon fiber surfaces, the carbon fiber reinforced composites show a weak interfacial shear strength because of the poor wettability and adsorption between carbon fiber and matrix [2].

In the past decades, people have developed a lot of technologies to improve the interfacial properties of carbon fiber composites. Generally, surface modification of carbon fiber could be the favorite routine [3]. Recently, it is found that graphene can be used as the reinforcing phase in polymer composites because of its stress transfer behavior between the polymer matrix and carbon fiber [4–9]. Up to now, many methods have been developed to introduce GO onto the surface of carbon fibers, including coating [10], chemical grafting [11–13], chemical vapor deposition [14], supercritical [15] and solvothermal treatment [16]. However, the

### ABSTRACT

Carbon fiber reinforced composites have been attracting increasing attention due to their excellent mechanical properties. However, the interfacial properties of carbon fiber composites tend to be weak because carbon fibers naturally show a weak wettability and adsorption with most polymers matrix. Here, we proposed a method to improve the interfacial properties of carbon fiber composites together with the tensile strength of carbon fiber. Briefly, a layer of graphene oxide (GO) was deposited on continuous carbon fibers by electrophoretic deposition in isopropyl alcohol under ultrasonic treatment. After treatment at 150 °C, the tensile strength of carbon fibers and the interfacial shear strength (IFSS) of carbon fiber/epoxy composites were enhanced by 34.58% and 69.87%, respectively. This method is believed to have applications in continuous production of high-performance carbon fiber composites.

improvement of interfacial properties is often followed by a sacrifice of fiber tensile strength owing to the etching effect during the treatment. Therefore, it is meaningful to develop the technology to enhance both the tensile strength of carbon fiber and the interfacial properties of its composites.

Recently, electrophoretic deposition (EPD) is used to deposit carbon nanotubes and GO on carbon fibers. And it is found that EPD show no weakness on the tensile strength of carbon fiber [17–19]. Nevertheless, the GO layers coated on the carbon fiber show poor dispersibility [20], and they take a long time as 30 min to finish the deposition, which make it not suitable for continuous production of high-performance carbon fiber.

In this study, we proposed an efficient EPD method to deposit GO onto the surface of carbon fiber in a mild condition. Different from the previous studies [21,22], isopropyl alcohol, instead of water, was used as the electrolytic solution to avoid generation of big bubbles, which increased the dispersibility of GO on the surface of carbon fiber and the deposition efficiency. This new technology decreased the deposition time of GO to 1 min. Meanwhile, the tensile strength of carbon fiber was increased from 4.54 GPa to 6.11 GPa while the IFSS of carbon fiber/epoxy composites were enhanced from 46.8 MPa to 79.5 MPa.







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### 2. Materials and methods

### 2.1. Materials

Carbon fibers (T700SC-12000-50C, 12 K, tensile strength 4.9 GPa, diameter 7 µm, density 1.8 g cm<sup>-3</sup>) [23] were purchased from Toray Industries, Inc. Natural graphite flakes with an average diameter of 10 µm were supplied from Haida Graphite Factory (Qingdao, China). Concentrated sulfuric acid (95–98%), concentrated nitric acid (68%), hydrochloric acid (36–38%), isopropyl alcohol, potassium permanganate (KMnO<sub>4</sub>) and magnesium nitrate hexahydrate (Mg(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O) were supplied by Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Deionized water (DI water, the resistivity of water >18 MΩ cm) was used throughout the experiments. All chemicals were used as received unless stated otherwise.

### 2.2. Experimental procedure

### 2.2.1. EPD of GO sheets

Firstly, GO was prepared by chemical exfoliation of graphite of scaly nature by using a modified Hummer's method [13,15]. The obtained GO and  $Mg(NO_3)_2 \cdot 6H_2O$  were dispersed in isopropyl alcohol ( $C_{GO} = 0.1 \text{ mg mL}^{-1}$ ) with ultrasonic treatment for 1 h at room temperature [6]. The weight ratio of GO and  $Mg(NO_3)_2 \cdot 6H_2O$  were controlled to be 1:1.

Then, as received carbon fibers were cleared with refluxed acetone for 48 h to remove the polymer sizing and pollutants before deposition, denoted as desized CF. During the EPD process, the desized CF bundle was used as the working electrode (negative) while a perforated stainless steel pipe was used as the counter electrode. The parallel distance between the two electrodes was 1 cm, and the applied voltage was 160 V. Under the applied voltage, the positively charged GO sheets migrated toward the negative electrode and lied on the surface of carbon fibers. Also, influence of ultrasonic treatment on the deposition was studied. The GOdeposited carbon fiber prepared under ultrasonic treatment (EPD-U) was denoted as GO/CF-U while GO-deposited carbon fiber without ultrasonic was denoted as GO/CF. After that, the GOdeposited carbon fiber were cleaned by isopropyl alcohol and water alternately for 3 times, and then dried at room temperature for 24 h.

Lastly, GO/CF-U and GO/CF were annealed at 150 °C for 1 h, and the obtained samples were denoted as RGO/CF-U and RGO/CF, respectively. The parameters of each deposition technology are outlined in Table 1. The scheme of GO deposition is shown in Fig. 1 (a) and (b).

### 2.2.2. Characterizations of carbon fibers

Table 1

The morphologies of GO and the modified carbon fibers were observed by the scanning electron microscope (SEM) (200FEG, Quanta FEI Inc. the USA) at an accelerating voltage of 20 kV, gold sputtering was used to improve the conductivity. The microstructure of GO was investigated by the transmission electron microscopy (TEM) (Hitachi H-7650) operated at 200 kV. The thickness of the as-prepared GO was examined by atomic force microscopic

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(AFM) (Solver-P47H, NT-MDT, Russia) using tapping mode. X-ray photoelectron spectroscopy (XPS) (ESCALAB 220i-XL, VG, UK) was carried out to study the chemical state of carbon fibers using a monochromatic Al Ka source (1486.6 eV) at a base pressure of  $2 \times 10^{-9}$  mbar. The XPS was energy referenced to the C1s peak of graphite at 284.6 eV. The XPS Peak version 4.1 program was used for data analysis. Dynamic contact angle was measured using a dynamic contact angle meter and tensiometer (DCAT21, Data-Physics Instruments, Germany). Deionized water  $(\gamma_d^d = 21.8 \text{ mN m}^{-1}, \gamma = 72.8 \text{ mN m}^{-1})$  and diiodomethane  $(\gamma^{d} = 50.8 \text{ mN m}^{-1}, \gamma = 50.8 \text{ mN m}^{-1}, 99\%$  purity, Alfa Aesar, USA) were used as test liquids [24]. The dispersive and polar components can be determined by solving the following equation:

$$\gamma_{\rm I}(1 + \cos\theta) = 2\left(\gamma_{\rm I}^{\rm p}\gamma_{\rm f}^{\rm p}\right)^{1/2} + 2\left(\gamma_{\rm I}^{\rm d}\gamma_{\rm f}^{\rm d}\right)^{1/2} \tag{1}$$

Where  $\gamma_i$ ,  $\gamma_i^d$  and  $\gamma_i^p$  are the surface tension of the test liquid, its dispersive and polar components, respectively.

Monofilament tensile tests were conducted on a universal testing machine (Instron 5566, USA) according to the ASTM D3379-75 [25] with a load cell of 50 N. Firstly, filaments were glued on a paper frame and the paper frame was held by the clamps of testing machine. The paper frame was cut before the mechanical testing, shown as Fig. 1(c). And then, mechanical testing started and the load-extension curves were collected. The testing speed was 10 mm min<sup>-1</sup> and the gauge length is 20 mm. Lastly, the data from load-extension curves were normalized by the linear density of carbon fiber bundle to give specific stress strain curves, as well the tensile strength. A total of 100 data points were collected and the results were analyzed by a Weibull statistical method [26].

IFSS was adopted to quantify the interfacial property between carbon fiber and epoxy by the interfacial evaluation equipment (FA620, Japan). Epoxy resin (WSR618) and methyl tetrahyelroph-thalic anhydride hardener were mixed at the weight ratio of 100:32 to prepare microdroplets. The microdroplets were cured cured following a curing process: 90 °C for 2 h, 120 °C for 2 h and 150 °C for 4 h. The IFSS was calculated according to equation (2).

$$IFSS = \frac{F}{\pi dl}$$
(2)

Where F is the maximum load recorded, d is the carbon fiber diameter, and l is the embedded length. The final IFSS of each sample was averaged from the data of 50 successful measurements.

### 3. Results and discussion

### 3.1. The characterizations of GO sheets and GO suspension

SEM and TEM were used to determine the structure of GO sheets, show as Fig. 2(a) and (b), respectively. It can be seen that GO sheets appear thin and flat wrinkled structure. The thickness of the GO sheets was tested by using AFM and the result was shown as Fig. 2(c). The thickness of the as-prepared GO flakes is  $1.14 \pm 0.25$  nm, which indicates that the as-prepared GO sheets are

Samples	$C_{GO} (mg mL^{-1})$	Voltage (V cm <sup>-1</sup> )	Time (min)	Ultrasonic	Annealing (150 °C)
1. GO/CF	0.1	160	1	No	No
2. GO/CF-U	0.1	160	1	Yes	No
3. RGO/CF	0.1	160	1	No	Yes
4. RGO/CF-U	0.1	160	1	Yes	Yes



Fig. 1. The scheme of (a) deposition of graphene oxide onto carbon fiber surfaces, (b) influence of ultrasonic treatment on the deposition of GO. In case of EPD-U, GO sheets were uniformly scattered and adsorbed on carbon fiber surface. By contrast, GO sheets reagglomerated (or restacking together) and adsorbed on CF surface without ultrasonic treatment. (c) the tensile testing of sample.



Fig. 2. Morphology of GO sheets. (a) SEM image of GO, (b) TEM image of a GO film, and (c) AFM image of a GO sheet. The white line inset: the corresponding height profile of GO. (d) stable suspension of Mg<sup>2+</sup>-absorbed GO sheets.



Fig. 3. SEM images of (a) desized CF, (b) GO/CF-U, (c) GO/CF, (d) RGO/CF-U.



Fig. 4. XPS spectra of C1s peaks: (a) GO, (b) desized CF, (c) GO/CF-U and (d) RGO/CF-U.

Surface element	compositions	of the	samples.
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Samples	Element contents (%)		
	C (%)	O (%)	O/C
desized CF	87.37	12.63	0.1445
GO	69.46	30.54	0.4397
GO/CF-U	77.03	22.97	0.2982
RGO/CF-U	84.99	15.01	0.1766

composed of 2–3 layers of individual GO sheet, including oxygencontaining groups, such as epoxy and hydroxyl groups, on the GO surface [27]. The suspension of GO sheets in isopropyl alcohol is very good and shows no precipitates after 4 h, shown as Fig. 2 (d). In our understanding, the  $Mg^{2+}$  absorbed on GO sheets play an important role in the stability of suspension.

### 3.2. Surface morphologies of carbon fibers

The surface morphologies of carbon fibers are shown in Fig. 3. It can be seen that the surface of desized carbon fibers is smooth, shown as Fig. 3 (a). After deposition of GO sheets, the smooth surface of carbon fiber changed to be coarse. On one hand, the surface of GO/CF-U has a high GO density and uniform morphology (Fig. 3 (b)), which reveals the homogeneous distribution of GO sheets on the surface of GO/CF. On the other hand, GO sheets agglomerated (or restacking together) on the surface of carbon fiber when no ultrasonic treatment was applied (Fig. 3 (c)), which is attributed to the accelerating aggregate of the GO nanosheets

under the loaded voltage [28,29]. To enhance the interaction of carbon fiber and GO sheets, heat treatment at 150 °C was applied to the GO/CF-U fiber. As expected, the epoxy groups were opened and reacted with –COOH and –OH groups on the surface of carbon fiber, as shown in Fig. S1. Also, the GO sheets will be partly reduced into reduced GO (RGO). The thermal gravimetric curve of raw GO were shown as Fig. S2. Moreover, the layer of RGO sheets on the surface of RGO/CF-U shrank and cracked into a scale structure after heat treatment, shown as Fig. 3 (d). We believe this scale structure is beneficial to the improvement of interfacial property of carbon fiber/matrix composite.

### 3.3. Surface chemical elemental compositions of carbon fiber

XPS was performed to determine the surface element composition of carbon fiber and a quantitative analysis was carried out. The XPS curves were shown as Fig. 4 and the calculated results were summarized in Table 2. The peaks centered at around 284.6 and 532.2 eV are attributed to binding energy of C and O, respectively [30]. Compared with the desized carbon fiber, the fiber deposited with GO show a significant increase of oxygen content from 12.63% to 22.97%. This indicated that GO was deposited on the surface of carbon fiber. Moreover, the oxygen content decreased from 22.97% to 15.01% after thermal treatment at 150 °C. Meanwhile, the O/C element ratios decreased with heat treatment, which demonstrated that GO have been partly reduced to RGO.

By deconvolution of C1s region, the C1s spectra were fitted into five peaks in order to afford covalent bonding between the GOs/ RGOs and carbon fibers. The attributions of five peaks were shown as Fig. 4, including graphitic carbon (peak I, 284.6 eV), carbon in



Fig. 5. Surface properties and mechanical performance of Carbon fibers. (a) contact angles, (b) surface energy, (c) the stress-strain curves of different carbon fibers, (d) tensile strength and IFSS of the carbon fiber/epoxy composites.

Table 3	
Single fiber tensile	strength of the samples.

Samples	Number of samples	Weibull shape parameter (m)	Expectation (GPa)
As received CF	100	4.97	4.83
Desized CF	100	4.65	4.54
GO/CF	100	5.08	5.06
GO/CF-U	100	5.22	5.18
RGO/CF	100	5.81	5.76
RGO/CF-U	100	6.21	6.11

epoxy, phenolic, alcoholic groups (peak II, 286.1–286.3 eV) [31], carbonyl or quinone groups (peak III, 287.3–287.6 eV), carboxyl or ester groups (peak IV, 288.4–288.9 eV) and carbonate groups (peak V, 290.4–290.8 eV) [24]. As discussed above, the epoxy, hydroxyl and carboxyl groups on GO sheets and surface of carbon fiber were expected to react with each other to form a strong covalent binding. From Fig. 4(c), we can see that graphitic carbon (peak I) on the surface increased by 8.9% while reactive oxygenated groups II and IV decreased by 24.15% and 1.69%, respectively. It indicates that epoxy group of GO react with hydroxyl, carboxyl of carbon fibers.

### 3.4. Wettability of carbon fiber

Wettability of carbon fibers was investigated by using advancing dynamic contact angle [14]. The advancing contact angle ( $\theta$ ), the surface energy ( $\gamma$ ), dispersion component ( $\gamma^{d}$ ) and polar component ( $\gamma^{p}$ ) of desized CF, GO/CF-U and RGO/CF-U were shown in Fig. 5 (a) and (b). Obviously, contact angles of both water and diiodomethane decreased and the surface energy increased after

# deposition of GO sheets. Reasonably, the polarity of GO/CF-U became stronger after deposition of GO sheets, which contained many oxygen-based functional groups. After heat treatment, contact angles of carbon fiber increased and the surface energy decreased because of the reduction of GO sheets and decreased polarity. It means that oxygen-based functional groups of GO/CF-U have been partially reduced during the thermal annealing process. In addition, the increased dispersion component, caused by the increased roughness, also contributes to the increase of surface energy [32].

### 3.5. Tensile strength

The tensile tests were carried out and the results were shown in Fig. 5 (c)–(d) and summarized in Table 3. It can be seen that the tensile strength of modified carbon fiber were greater than that of the desized CF. In our understanding, the tips of small GO sheets filled in the defects on the surface of carbon fibers and part of the active groups on the GO sheets reacted with the surface of defects



Fig. 6. The scheme of chemical reactions between GO sheets and carbon fiber. (a) the scheme of surface structure change between EPD and thermal treatment, (b) chemical reactions during thermal treatment, (c) AFM of GO sheets, GO sheets of around 70 nm were found in the suspension, (d) fracture morphology of RGO/CF-U.

under high voltage of 160 V, which decreased the stress concentration and increased the tensile strength, as shown in Fig. 6. Moreover, the rough surfaces formed by deposition provide extra resistance against the external loading. Finally, the addition of GO sheets caused a random dispersion of particles within the regions surrounding fiber surface, which offered a strengthening mechanism by bridging the surface microcracks [5]. We also noted that the tensile strength of GO/CF (5.06 GPa) was lower than that of GO/ CF-U (5.18 GPa), which could be attributed to the GO agglomeration and inhomogeneous dispersion in the interfacial region.

Interestingly, it is found that the tensile strength of RGO/CFs-U is increased to 6.11 GPa. We believe the reason for the improvement is that more active groups on small GO sheets that filled in the defects on the surface of carbon fibers reacted with the surface defects of carbon fiber under 150 °C. As a result, a part of the defects on the surface of carbon fiber were cured after thermal treatment and the tensile strength increased significantly.

### 3.6. Interfacial property testing of carbon fiber/epoxy composite

IFSS of carbon fiber/epoxy composites were shown in Fig. 5 (d). After EPD of GO sheets, the IFSS of composites increases from 46.8 MPa of desized carbon fiber composite to 53 MPa of GO/CF and 56.1 MPa for GO/CF-U, respectively. After thermal annealing, the IFSS of RGO/CF-U increased to 79.5 MPa, namely improvement of 69.9% to desized carbon fiber composites and improvement of 27.6% to RGO/CFs composites. In our understanding, three reasons for the improvement of IFSS. Firstly, the increase of active functional groups and the roughness caused by the introduction of GO or RGO into the interfacial region strengthen the interfacial interaction of carbon fiber and epoxy. Chen et al. [33] reported that welldispersed and homogeneous distribution of the GO sheets were highly effective in suppressing crack propagation in epoxy matrix. Secondly, the increased specific surface with deposition of GO make it consume more energy to pull carbon fiber from the resin matrix [34]. Lastly, as discussed above, the functional groups of carbon fiber surface, such as hydroxyl groups and carboxyl groups reacted with epoxy groups of GO and helped to form chemical combination between carbon fibers and GO sheets, which improved the IFSS of carbon fiber and GO sheets [35].

Fig. 7 depicts the surface morphology of carbon fibers debonding from the resin matrix. For the desized carbon fibers composites (Fig. 7 (a)–(b)), the surface is similarly neat before and after debonding, which indicates that the interface is easily de-bonded because of the weak van der Waals force between fiber and epoxy resin. On the other hand, many epoxy debris is still adhered on the carbon fiber after debonding of the GO/CF-U composites (Fig. 7 (c)), which implies that the interface between the GO/CF-U and epoxy become stronger than that of desized carbon fibers composites. And it is found that the stronger the interaction of GO and carbon fiber, the more residual epoxy fragments and microcracks on carbon fiber, show as Fig. 7 (d). It means that the mechanical interlocking between fiber and matrix becomes stronger and cohesive failure occurs in composites of RGO/CF-U and epoxy.

### 4. Conclusion

In this study, an efficient EPD was proposed to deposit GO sheets onto the surface of carbon fiber. The deposition was carried out in isopropyl alcohol under ultrasonic treatment. It is found that both the tensile strength of carbon fiber and the IFSS of composites were improved significantly. For RGO/CF-U, the tensile strength was enhanced by 34.6% and the IFSS of RGO/CF-U composites improved by 69.9%. We believe the small GO sheets filled in the defects on the surface of carbon fiber suppressed crack propagation on the carbon



**Fig. 7.** SEM images of the carbon fiber. (a) before debonding, (b), (c) and (d) are the images of desized CF, GO/CF-U and RGO/CF-U after debonding, respectively.

fiber. Meanwhile, the chemical combination between RGO and carbon fibers, and increased surface roughness are responsible for the enhancement of IFSS in the RGO/CF composites. Moreover, this technology is very simple and 1 min is enough to finish the deposition. We believe this simple and time-saving method can be applied in versatile and scalable fabrication of high-performance carbon fiber, as well excellent carbon fiber composites.

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### Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.compscitech.2016.07.009.

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