



# Enhancement of interfacial adhesion in UHMWPE fiber/HDPE composites by electrophoretic deposition of graphene oxide on UHMWPE fibers

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In contrast to the conventional methods of improving interface and performances of UHMWPE fiber composites through fibre surface modification, this paper has reported a novel approach to deposit graphene oxide (GO) to increase the fiber/matrix interfacial shear strength (IFSS) of ultra high molecular weight polyethylene fibers (UHMWPE fiber) reinforced high density polyethylene (HDPE) composites. To validate our argument, GO has been synthesized and deposited over UHMWPE fiber through electrophoretic deposition. Tuned voltage lead to different thickness of deposited GO steadily increasing with the electric field up to 10 V/cm. Coated fibers have been aligned in a mold and an HDPE matrix has been used to create a single-fiber microcomposite. This latter has resulted to be much higher than the ILSS thus proving the efficiency of the new GO coating method here proposed for producing advanced graphene based composites. The failure of the composite at the GO/matrix rather than at the GO/UHMWPE fiber interface has been also confirmed by scanning electron microscopy observation of the fracture surfaces of microcomposites.

**Keywords:** IFSS, Graphene oxide, UHMWPE fiber, Electrophoretic deposition, HDPE

## 1 Introduction

Thermoplastic composite materials, due to their shorter processing cycle and higher reusability than thermoset composites, have constantly captured wide attention over the past years<sup>1</sup>. For thermoplastics, HDPE is widely used in the automotive industry, aerospace and instrument housings because of its excellent mechanical properties<sup>2,3</sup>. Thus, in order to obtain better mechanical properties to replace the role of metal or thermoset composites in industrial applications, it is a good choice to manufacture UHMWPE fiber reinforced HDPE composites.

There are amorphous regions in plant fiber polymers, and there are pores and voids, which provide conditions for fiber breakage and cracking. When the shock wave generated by the high-pressure or high-pressure release caused by cavitation or the alternating pressure change caused by the mechanical motion acts on the fiber, stress and strain concentration occur at the original defect of the fiber, and sub-critical expansion of the fatigue crack occurs, resulting in microcrystalline dislocation. The specific surface area increases, the crystallinity decreases, and the amorphous region increases. For non-defective materials, under the action of ultrasonic waves,

microscopic slippage occurs on the surface of the fiber, which forms a source of fatigue, resulting in a decrease in elastic modulus. The surface of the fiber is corroded, which exposes more reaction centers and enhances chemical activity. However, the fabrication of these coatings is a complex and costly process, and the oxidation resistance of these coatings, such as carbon and boron nitride, is poor<sup>4,6</sup>.

Efforts to improve the interfacial adhesion of UHMWPE flexible printed circuits (FPCs) have been mainly devoted to modification of the UHMWPE fiber surface through plasma treatment<sup>7,8</sup>, corona discharge<sup>5</sup>, UV induced grafting<sup>9,10</sup>, chemical oxidation or coating treatment<sup>11,12</sup>. In particular, the coating treatment is distinct from the other modification techniques in that it is easy to operate, does not require special equipment and can effectively improve the load transfer<sup>13-15</sup>. Graphene oxide and carbon nanotubes have been reported as coating materials to improve the interfacial strength of FPCs<sup>16</sup>. In a previous study, we reported the use of polypyrrole (PPy) to enhance the adhesion between UHMWPE fibers and epoxy<sup>17</sup>. The improvement was attributed to mechanical force of roughening surface and ionic bonding between the UHMWPE fiber and PPy coating. However, coating fiber interactions at a molecular level remain insufficient. Graphene, being a superlative nanomaterial,

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has been considered to be a promising and exciting research area because of its outstanding ideal properties including electron mobility at room temperature, thermal conductivity and mechanical properties, with a Young's modulus of 1 TPa and a record-breaking strength of 130 GPa.

In order to better exert the excellent mechanical properties of the UHMWPE fiber, we need to modify the surface to change the surface properties of the fiber, improve the bonding effect between the UHMWPE fiber and the resin, and finally optimize the interfacial bonding properties of the composite. Researchers usually use argon plasma<sup>3</sup>, oxygen plasma<sup>18</sup> and ammonia plasma<sup>19</sup> to process and optimize them by chemical or physical means. Although the wettability of the UHMWPE fiber after treatment, the oxygen atom content on the fiber surface, the number of oxygen-containing polar functional groups, and the surface roughness of the fiber are all improved, these methods have great limitations. Chemical treatment can significantly modify the inter laminar shear strength between UHMWPE fiber and resin, but there is a widespread problem of environmental pollution, and UHMWPE fiber has different degrees of damage. Therefore, in view of environmental protection issues and process cost factors, it is urgent to develop a new method that is environmentally friendly and can take into account mechanical properties to modify UHMWPE fiber.

This current work was aimed to assess the interfacial shear strength between an HDPE matrix and UHMWPE fibers coated with electrophoretically deposited graphene oxide. Delamination of GO was performed with optimized normal force to calculate the shear strength of the GO/UHMWPE fiber interface.

## 2 Experimental Section

### 2.1 Materials and Samples Preparation

Graphite powder, sodium nitrate, potassium permanganate, sulfuric acid and hydrogen peroxide were purchased from Sigma Aldrich while hydrochloric acid was from Codec Chemical Co. Ltd. The UHMWPE fiber was Dyneema SK60 (DSM Co., Netherlands) with a fibre diameter range of 12-21 mm. Injection moulding grade HDPE type Eraclene MP90 (Melt Flow Rate at 190 °C/2.16 kg of 7g/10 min and density of 0.96 g/cm<sup>3</sup>) from Eni Polimeri Europa (Mantova, Italy) was used as matrix. Graphene oxide was synthesized using an approach similar to Hummer's method<sup>20</sup>. A stable suspension is

the key for uniform deposition of graphene on UHMWPE fibers. Initially, graphite oxide powder was added in water with a concentration level of 1mg/ml and the dispersion was subjected to bath-sonication for 1 h. Since UHMWPE fibers are non-conductive materials, two copper plates were used as electrodes in the EPD process. The UHMWPE fibers were placed near the anode since GO display negative potential due to functionalities attached during the oxidation reaction. EPD was carried out at various applied voltages up to 10 V/cm with a constant deposition time of 5 min and electrodes gap of 2 cm. The coated samples were dried in a vacuum oven at 40 °C for 12 h.

### 2.2. Testing Methods

The fiber surface morphology was observed by a FEI Nova Nano 450 scanning electron microscope. Thickness (z-direction) and roughness of GO coatings on UHMWPE fiber were measured by AFM (tip radius around 15 nm) with a NT-MDT solver P47h device operated in intermittent contact mode (tapping mode).

XPS investigations were performed on a Kratos AXIS Ultra X-ray photoelectron spectrometer. The fiber surfaces were analyzed with a monochromatic Al K $\alpha$  X-ray source, operating at 1 keV and an emission current of 0.6  $\mu$ A. The C 1s peak of each fiber sample was analyzed by a peak synthesis procedure, which was estimated by a computer simulation.

Instron 4465 universal electronic tensile machine is used. A sample of at least five ISO 527<sup>21</sup> type specimens were prepared and the tests were carried out at a crosshead speed of 10 mm/min up to 1% axial deformation.

## 3 Results and Discussion

### 3.1 Characterization of fiber

#### 3.1.1 SEM

The SEM images of UHMWPE fiber, 1wt% graphene oxide filled UHMWPE fiber, and 3wt% graphene oxide filled UHMWPE fiber are shown in Fig. 1 to observe differences in morphological microstructure of those fibers. The surface of untreated UHMWPE fiber is smooth with a number of grooves along the fibre (Fig. 1a). The grooves on the surfaces of treated UHMWPE fiber (Fig. 1b) are slightly deeper, which may be due to GO deposition. The surface of 3wt% graphene oxide filled UHMWPE fiber was wrapped by grafting polymerization of graphene oxide. The grafted particles were evenly

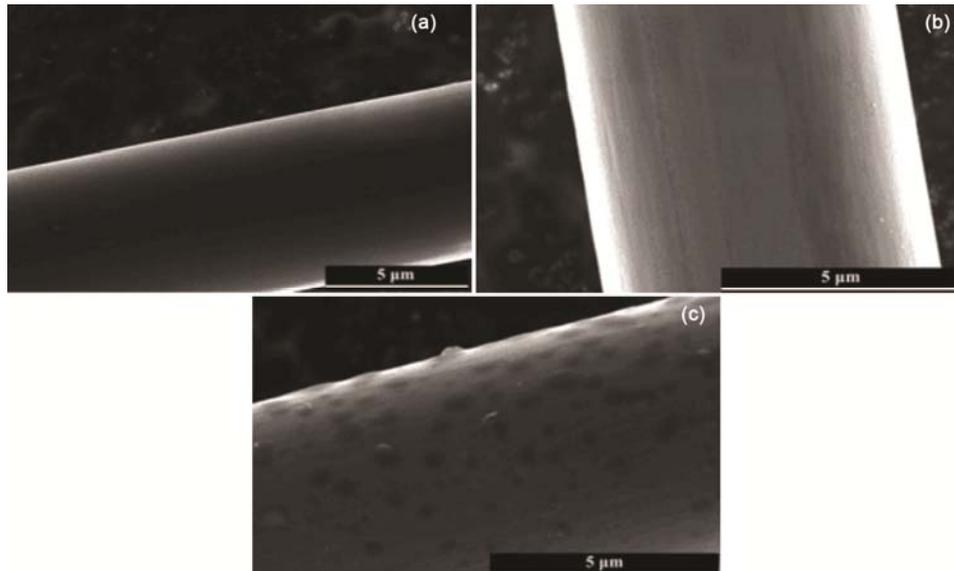


Fig. 1 — SEM images of (a) UHMWPE fiber, (b) 1wt% graphene oxide filled UHMWPE fiber and (c) 3wt% graphene oxide filled UHMWPE fiber.

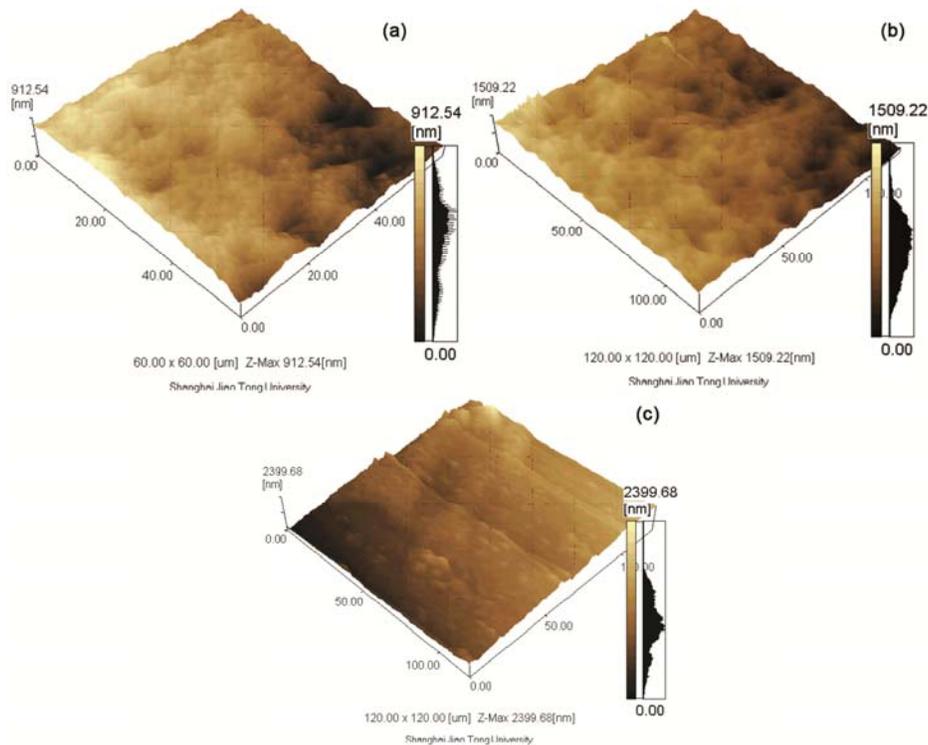


Fig. 2 — AFM images of (a) UHMWPE fiber, (b) 1wt% graphene oxide filled UHMWPE fiber and (c) 3wt% graphene oxide filled UHMWPE fiber.

distributed on the fiber surface and increased the fiber roughness effectively.

### 3.1.2 AFM

Atomic force microscope (AFM) can be used to observe the surface morphology of fibers effectively

at the nanoscale as well as quantify the surface roughness of the fiber. As it is shown in Fig. 2, the surface of UHMWPE fiber is not smooth in the scale of micrometers because of the existence of sizing agents. By analyzing the root mean square roughness

(Rq) and the arithmetic average roughness (Ra) over a  $2\mu\text{m} \times 2\mu\text{m}$  scanning area, we found that the Rq value increased. The roughness of 1wt% graphene oxide filled UHMWPE fiber decreased after electrophoretic deposition of graphene oxide, while still improved compared with the roughness of UHMWPE fiber. This is because that the graphene oxide coating was not evenly grafted on the surface of fiber but formed into some regular fluctuations instead, causing the decrease of roughness, although electrophoretic deposition of graphene oxide filled in the gullies formed by the former electrochemical process.

### 3.1.3 XPS Analysis

In order to detect the surface chemical composition and changes of CFs, XPS studies were performed. Figure 3 shows main peaks of the C1s for the carbon fibers samples with different modification. Little change was observed in the main peak of C1s spectra at 284.6 eV for the untreated and treated fibers.

High resolution C1s (280–295 eV) and O1s (525–540 eV) scans were collected in all samples. Then, by using an XPS curve-fitting software, the C1s scan was deconvoluted into five peaks to identify the type and number of functional groups on the fiber surface in detail. The C1s-deconvoluted

peaks, composed of C-C ( $\text{sp}^2$  carbon), C-O-C, C-OH (hydroxyls), C=O (carbonyls), and COOH (carboxylic acids) groups which are located at 284.5, 285.5, 286.2, 287.4, and 288.9 eV, respectively are shown in Fig. 3. As mentioned earlier, the oxygen functional groups on the fiber surface are the most important factor promoting strong chemical adhesion between the fiber and HDPE. In Fig. 3, the C-C peak area is the largest in all cases as compared to other peaks.

Table 1 shows that the proportions of the chemical elements of the fiber surface change significantly after the graphene oxide deposition. The C1s content related to  $\text{sp}^2$  bonding is reduced from 55.3% to 45.2% and the content of C-O increases from 20.8% to 24.0%, demonstrating that carbon bonds were transformed into C-O bonds *via* the surface treatment. The content of O and N in the surface of UHMWPE fiber after graphene oxide deposition surface treatment with different concentrations was greatly improved. The oxygen concentration and nitrogen concentration on the surface of the UHMWPE fiber vary with the change in the graphene oxide deposition concentration. When the GO concentration is 3wt%, the oxygen concentration and the nitrogen concentration on the surface of the fiber reach a

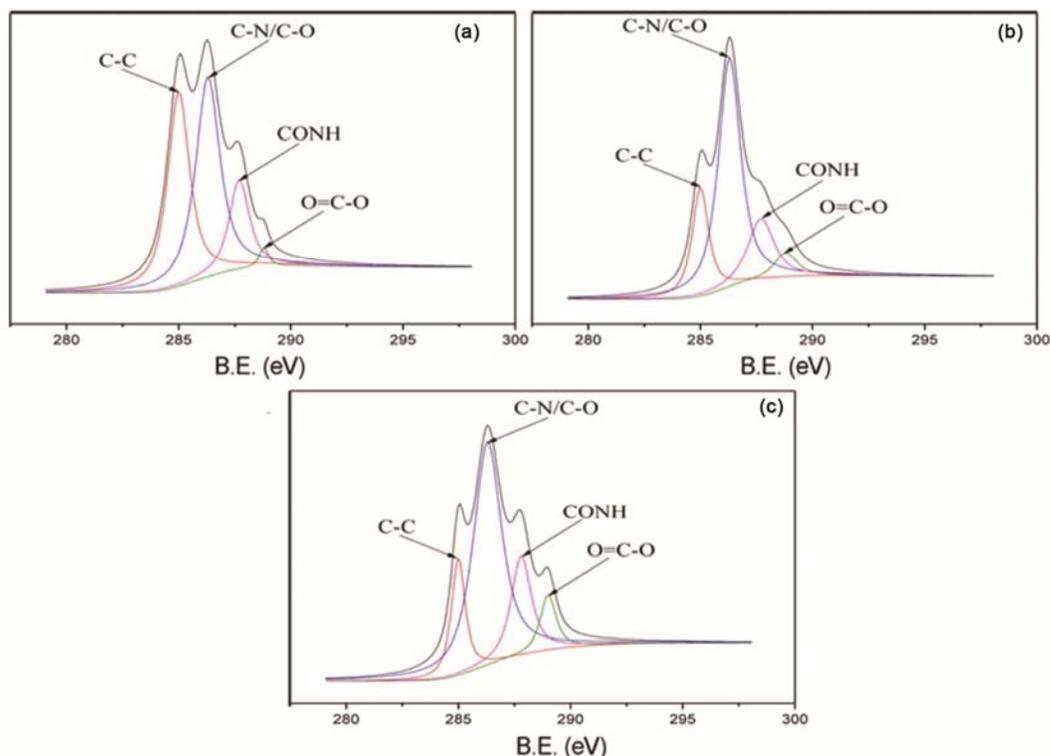


Fig. 3 — C1s XPS spectra of UHMWPE fiber surface before and after graphene oxide deposition (a) Untreated, (b) 1wt% graphene oxide and (c) 3wt% graphene oxide.

Table 1 — The proportions of the chemical elements of the fiber surface.

Sample	Chemical composition (%)					Atomic ratio (%)		
	C1s	O1s	N1s	S2p	Si2p	O/C	N/C	(O+N)/C
Untreated	71.11	14.00	6.52	4.01	4.36	19.69	9.17	28.86
1wt% graphene oxide	63.18	20.88	7.56	4.06	4.32	33.05	11.97	45.02
2wt% graphene oxide	62.45	22.56	7.98	4.07	4.31	35.67	12.45	47.35
3wt% graphene oxide	60.09	23.19	8.33	4.08	4.29	38.59	13.86	52.45
4wt% graphene oxide	58.97	25.97	8.45	4.11	4.26	39.65	14.54	53.16
5wt% graphene oxide	57.85	26.13	8.68	4.13	4.17	39.97	14.69	54.32

maximum. This indicates that the GO concentration has a great influence on the content of surface functional groups of UHMWPE fibers. When the GO content is low, the organic active groups adsorbed to the surface of the UHMWPE fiber are less, the surface activity of the UHMWPE fiber is not improved, and it is not sufficient to form an effective chemical bond with the C, O and N elements on the surface of the UHMWPE fiber. When the UHMWPE fiber is combined with the HDPE, the interface bonding zone is a small amount of chemical bonding. Although the interface bonding of the composite material is improved to some extent, the effect is not satisfactory, and the fiber and the HDPE resin are directly in contact at the interface. Part of the weak point of the composite material, the interface damage first occurs under the action of external force, resulting in the performance of the composite material.

Table 2 and Fig. 3 present the values of bonding energy in the functional groups containing carbon (such as -C-C-, -C-N-/C-O-, -CONH-, and -O=C-OH), which were 285.0, 286.3, 287.8, and 289.0 eV, respectively. When the GO content is suitable, an effective adhesive interface layer can be formed on the surface of the UHMWPE fiber, the strong chemical bonding is effective to improve the interfacial adhesion between the UHMWPE fiber and the resin matrix. Under the action of external force, the chemical bonds together play the role of transmitting the load, thereby improving the mechanical properties of the composite.

### 3.2 Wettability Improvements

Figure 4 illustrates that the water absorption time of the untreated UHMWPE fiber >400 s. The absorption time reduces after the graphene oxide deposition. The time drops with 1wt% graphene oxide deposition, and the time almost approaches zero after 3wt% graphene oxide deposition. These results can be explained by the increase in surface roughness of

Table 2 — The content of surface functional groups.

Sample	-C-C-	-C-N-/		
		-CONH-	-O=C-OH-C-O-	
Untreated	38.58	43.54	16.28	1.60
1wt% graphene oxide	19.96	55.78	17.83	6.43
2wt% graphene oxide	14.97	58.62	18.38	8.03
3wt% graphene oxide	13.98	59.45	18.78	9.23
4wt% graphene oxide	13.23	59.78	18.99	9.87
5wt% graphene oxide	13.11	59.95	19.31	10.12

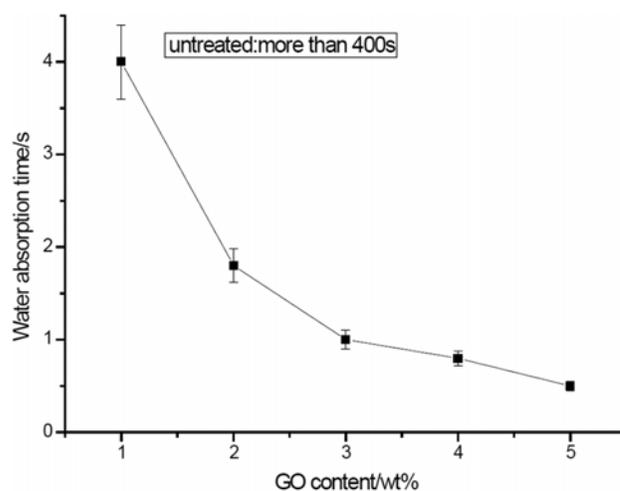


Fig. 4 — Effect of graphene oxide deposition content on water absorption time of UHMWPE fiber.

UHMWPE fiber by graphene oxide deposition, as evidenced by FESEM images, and Wenzel and Cassie theories<sup>15</sup>. The studies confirmed that the water absorption of natural fiber composites depends on the reinforced fiber amount, immersion temperature, fiber orientation, exposed area, and hydrophilic potential of the natural fiber. In our study, all the parameters were kept constant except the surface treatment, which reduced the -OH polar bonds after the treatment. This confirmed that the decline in the water absorption potential is due to the difference in fiber surface treatments. The decrease in the water uptake for the GO treated fiber was due to the stronger fiber/matrix

Table 3 — Effect of breaking strength of UHMWPE fiber before and after graphene oxide deposition.

Sample	Number of specimen	Breaking strength (Mean)	Standard deviation	P value
untreated	30	3.42	0.17	
1wt% graphene oxide	30	3.32	0.19	0.487
2wt% graphene oxide	30	3.30	0.16	0.402
3wt% graphene oxide	30	3.45	0.19	0.401
4wt% graphene oxide	30	3.41	0.18	0.403
5wt% graphene oxide	30	3.36	0.15	0.402

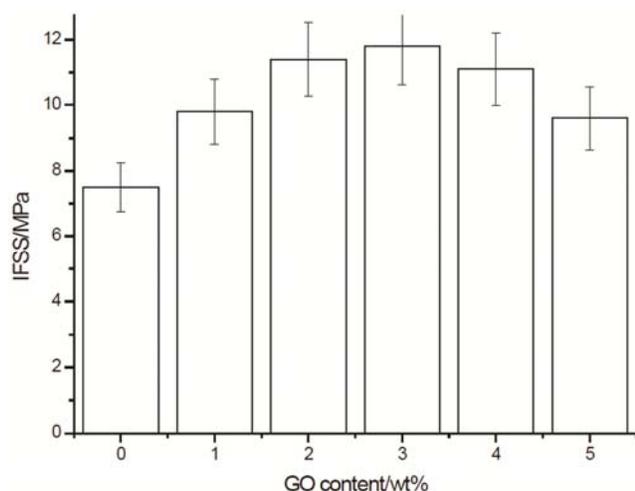


Fig. 5 — Effect of graphene oxide deposition time on IFSS value of UHMWPE fiber.

interface, which reduced the available polar  $-OH$  groups in the system.

### 3.3 Adhesion of UHMWPE Fiber

Figure 5 shows that the interfacial shear strength (IFSS) of the UHMWPE fiber increases after the graphene oxide deposition. Results of statistical analysis in IFSS showed that there is a significant difference in graphene oxide deposition. The low IFSS for the 5wt% GO sample might be due to the fact that the tested composites were deformation of the matrix induced by the fiber swelling at the fiber exit locations could be much severe in both axial and radial directions. The radial direction swelling of the fiber could likely result in creep of the matrix which enlarged the hole hosting the fiber. After the graphene oxide deposition, the number of the polar groups on the fiber surface is large, which indicates that the chemical adhesion between the fiber and resin has enhanced. The improvement can be ascribed to the enhancement of mechanical interlocking effect caused by GO with high specific surface area into the resin matrix and the good wettability with resin matrix resulted from fiber with abundant hydroxyl groups.

This is consistent with other nanoparticles enhancements method, such as sonication and dip coating methods.

As Table 3 shows, a short graphene oxide deposition has minor effects on the breaking strength of the UHMWPE fiber; the breaking strengths after 1wt% and 3wt% graphene oxide deposition are reduced by 2.92 % and 3.51 %, respectively. This result is obtained because the graphene oxide deposition at room temperature is limited to a small range of depth (5-100 nm), which does not affect the basic properties of the fiber within a short time period. However, a long-time graphene oxide deposition may damage such properties<sup>17</sup>.

## 4 Conclusions

GO deposition was used in this study to modify the UHMWPE fibers. Correspondingly, this process successfully improved the UHMWPE fiber surface wettability and IFSS. After the graphene oxide deposition, the polar groups created at the UHMWPE fiber surface, such as  $-C-O-$ ,  $-CONH-$ , and  $-O=C-OH$  groups, were analyzed by XPS and showed prominent increases compared with those of the untreated sample. After 3wt% graphene oxide deposition, the oxygen-containing polar groups reached the highest levels in this study.

With the graphene oxide deposition conditions at 40 Pa, 100 W, and 3wt%, the breaking strength of the UHMWPE fiber dropped by 3.51 %, IFSS value reached the peak value of 11.87 MPa. However, over 3wt% graphene oxide deposition, the polar groups on the fiber surface began to diminish and the IFSS value began to drop. Therefore, an optimum graphene oxide deposition content was determined.

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