SURFACE MODIFICATION OF FIBRES WITH GRAPHENE OXIDE FOR INTERFACE IMPROVEMENT IN COMPOSITES

Lei Zeng[1], Xuqing Liu[1], Xiaogang Chen[1] and Constantinos Soutis [1, 2]

[1]School of Material, University of Manchester, Manchester M13 9PL, UK
Email: lei.zeng-2@manchester.ac.uk; xuqing.liu@manchester.ac.uk;
xiaogang.chen@manchester.ac.uk
[2]Aerospace Research Institute, University of Manchester, UK
Email: Constantinos.soutis@manchester.ac.uk

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Abstract
A novel biomimetic surface modification method for fibres and the improvement on adhesion with epoxy resin was demonstrated. Inspired by the composition of adhesive proteins in mussels, the thin layer of poly(dopamine) (PDA) was self-polymerized onto the surface of carbon and aramid fibres. The graphene oxide (GO) was then grafted on the surface of PDA-coated fibres. The XPS results indicated successfully grafting of GO on the PDA-coated carbon and aramid fibres. The SEM observation showed the uniform coating of PDA and GO on the surface of fibres. The modification could increase the roughness of fibre surface. The single fibre tensile test and microbond test were carried out to evaluate the mechanical properties of the modified fibres. The interfacial shear strength of GO-PDA-fibres composites was significantly improved. Also, the bulk structure of fibres was protected by PDA and GO modification, and this increased the tensile strength of single fibre.

1. Introduction

Fibre reinforced composites have been widely used in aerospace, automobile, and military industries, due to their high specific strength, modulus, lightweight and flexible design. Particularly, carbon and aramid fibres are ideal reinforcements for high-performance composites as they contains high mechanical properties, chemical stability and low density [1, 2].

The surfaces of both carbon and aramid fibres are smooth and chemically inert which lead to less strong interface with the matrix. It has been reported that weak bonding can lead to low load transfer efficiency between the fibre and resin in a fibre composite [3]. To enhance the interfacial adhesion strength of fibre-reinforced composites, efforts were mainly made to modify fibre surface using plasma treatment, γ-ray irradiation, ultrasonic treatment, chemical grafting and etching [4-6]. However, these techniques request multistep procedures and are associated to the use of high cost instrument. In addition, these surface treatments are limited with strict reaction condition and in some case the use of toxic materials. Due to the damage caused to the fibre surface, fibre strength reduction is inevitable.

This paper aims to improve the interfacial adhesion between fibres and epoxy resin based on the use of a novel method for fibre surface treatment at ambient temperature. A biopolymer, polydopamine (PDA), is applied to form a coating layer on the surface of fibre via pH-induced oxidative self-polymerization, introducing functional groups for bonding enhancing between the fibre and resin to improve the physical properties of the composites [7, 8]. Then, graphene oxide (GO) is to be grafted onto the polydopamine-treated fibre to enhance the mechanical property of the fibre and to improve

the interfacial bonding between fibre and resin. As a 2D material, GO has high aspect ratio with flexible structure, and it also has extraordinary mechanical properties and superior thermal and electrical conductivity. Graphene oxide is chemically more active with the fibre and resin polymers than graphene, because of the epoxide and hydroxyl groups within the GO sheets and carbonyl and carboxyl at the edges of the GO sheets. Moreover, the chemical structure of GO provide the potential of $\pi - \pi$ bonding. Evaluations of the coated fibre are to be tested for strength and for interface adhesion with the epoxy resin.

2. Experiment details

2.1. Materials

The carbon fibres used in this research were type A-42 from AKSACA (USA) and the aramid fibres were type 248 from Bluestar (China). Both fibres were rinsed by acetone for 24h to remove surface sizing. Dopamine hydrochloride, epoxy (AY103) and hardener (HY951) were purchased from Sigma-Aldrich® (UK). The Tris(hydoxymethy)aminomethane (Tris) was purchased from Alfa Aesar Company (USA). The Hydrochloric acid solution was purchased from Fluka Analytical (UK) and used as received. Graphene oxide water dispersion (TM-01LI-06) was purchased from Institute of Coal Chemistry, Chinese Academy of Sciences (China).

2.2 Surface functionalization of fibres

Both carbon and aramid fibres were treated by the same method. Dopamine solution (2 mg/mL) was prepared by dissolving dopamine in Tris-HCl buffer solution (1.2 mg/mL) and the pH was controlled as 8.5. When dopamine was self-oxidising, the fibre bundles were immersed in the solution at ambient temperature for 24h to prepare the PDA-fibre. For the GO-PDA-fibre, after mixing dopamine with Tris-HCl buffer solution, fibre bundles were immersed and 0.1 mg/mL GO solution was added into the mixture. The pH was controlled as 8.5. After 24h, fibres were taken out of the solution and rinsed by distilled water, and then dried in oven at 60˚C.

2.3 Characterization of fibres

The morphology of untreated and treated fibres was studied by a Scanning Electron Microscopy SEM (Ultra-55 Scanning Electron Microscope, ZEISS, Germany). The carbon and aramid fibre samples were sputter-coated with gold before observation.
The chemical composition and functional groups on untreated and treated fibres were characterised by X-ray Photoelectron Spectroscopy XPS (Kratos Axis Ultra Hybrid, Shimadzu, Japan) equipped with a monochromatic source of Al Kα, base pressure below 5×10^{-8} mbar, spot area of 300 μm × 700 μm. The binding energy peaks were calibrated with C1s at 284.8 eV as reference.

2.4 Mechanical property testing of composites

A microbond test was used for the purpose of quantitatively identifying the interfacial properties between aramid fibres and resin matrix. To prepare the microbond test specimen, one fibre was randomly chosen from the fibre bundles. Then dropped the matrix, the mixture of epoxy resin (AY103) and hardener (HY951), on the surface of single fibre by using the point of a needle. Cured the specimen at room temperature for 24h. The specimen was pulled out from two blades (the gap between two blades was the fibre diameter), the matrix droplet was blocked by the blades. The interfacial shear strength (IFSS) between a single fibre and matrix is given by Eq. (1):

$$IFSS = \frac{F}{\pi d_f L_e}$$
(1)

where F is the failure tensile load, d_f is the fibre diameter and L_e is the embedded length in the resin. 50 data were collected and average IFSS was calculated for each sample.

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The single fibre tensile test was conducted on Instron 1122 with a 5N load cell at a constant speed of 1 mm min^{-1}. 10 specimens of each type of fibres were tested.

3. Results and discussion

3.1 Chemical structure of fibre surface

The chemical compositions of fibre surfaces were studied by X-ray photoelectron spectroscopy (XPS). The fitting was done after a liner background subtraction on the fitting interval and the results were showed in **Figure 1**. The carbon fibre results of the ratio for functional groups were presented in Table 1. For untreated carbon fibre, the C1s spectrum was peak fitted into seven fitting curves with peaks at 283.4, 284.8, 286.0, 286.7, 288.1, 289.1 and 291.5 eV, which are attributed to C-H, C-C/C=C, C-O, C-O-C=O, C=O, C(O)OH and $\pi - \pi^*$, respectively [9, 10]. The C1s spectrum of PDA treated carbon fibre was also fitted into seven curves (**Figure 1** (b)), and no new peaks emerged after PDA treatment. However, as seen from the Table 1, the $\pi - \pi^*$ bonding increased from 0.36% to 0.62% by comparing the untreated carbon fibre with the PDA treated carbon fibre, which indicated the PDA was bonded with carbon fibres through $\pi - \pi$ stacking. The $\pi - \pi$ stacking is a kind of van der Waals force relating to the molecules' π-electron backbone system, to form a stable hybrid structure [11]. For GO-PDA treated-carbon fibre, its XPS C1s core-level spectrum, shown in **Figure 1** (c) displays seven peak components with binding energies at about 283.4, 284.8, 285.9, 286.7, 288.0, 289.3 and 291.2 eV respectively, associating to the same function groups as the untreated carbon fibre. Compared to the untreated carbon fibre, the $\pi - \pi^*$ bonding of GO-PDA treated-carbon fibre significantly increased from 0.36% to 2.41%.

Table 1. Results of the fitting of C1s core level spectra of untreated-, PDA- and GO-PDA-carbon fibre.

	The ratio for functional groups [%]						
	C-H	C-C/C=C	C-O	C-O-C=O	C=O	COOH	$\pi - \pi^*$
Untreated carbon	11.89	64.29	5.37	12.50	2.14	3.36	0.36
PDA-carbon	0.65	58.36	15.94	17.32	2.55	4.56	0.62
GO-PDA-carbon	0.23	57.92	15.21	15.76	4.15	4.31	2.41

While for untreated aramid fibre, three peaks were exhibited in **Figure 1** (d), indicating C=C/C-C in aromatic rings (284.6 eV), C-N group (286.4 eV) and C=O group (288.8 eV), respectively. The PDA treated aramid fibre, three new peaks emerged as shown in **Figure 1** (e), representing the existence of O-C=O (289.1 eV), C-O (286.5 eV) and $\pi - \pi^*$ (290.5 eV). These three new peaks demonstrate the successful formation of PDA layer on the surface of aramid fibres. As shown in Table 2, the ratio for oxygen-containing groups increase from 6.35% to 17.50% while the ratio for C=C/C-C group decreases from 78.91% to 55.14% after the PDA treatment. This is mainly attributed to the fact that the intramolecular bonding (hydrogen bonding) in aramid fibre is destructed which activates the originally inert fibre surface. For GO-PDA treated-aramid fibre, its XPS C1s core-level spectrum, shown in **Figure 1** (f) displays six peak components with binding energies at about 284.6, 288.8, 286.3, 285.3, 287.4, and 290.1 eV respectively, associating to the sp^2-hybridized carbon, O-C=O, C-O, C-N, C=O and shake-up satellite ($\pi - \pi^*$) peak accordingly. Compared with the PDA treated aramid fibre, the ratio for C=O group increases from 3.37% to 4.16%. The increasing number of C=O group indicates potential hydrogen-bonding interaction with GO and PDA. The $\pi - \pi^*$ bonding also increases from 0.15% to 0.58%. The aramid fibres are consist of aromatic molecules, which are proven effective for intermolecular $\pi - \pi$ stacking through self-assembly processing [12, 13]. The strong $\pi - \pi$ stacking between the graphene oxide surface and the aromatic molecules usually makes the surface stacking quite stable against rinsing or other solution processing. It became evident that the GO-PDA

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treatment increased the surface activation of fibres and thus increasing their interfacial adhesion strength.

Table 2. Results of the fitting of C1s core level spectra of untreated-, PDA- and GO-PDA-aramid fibre.

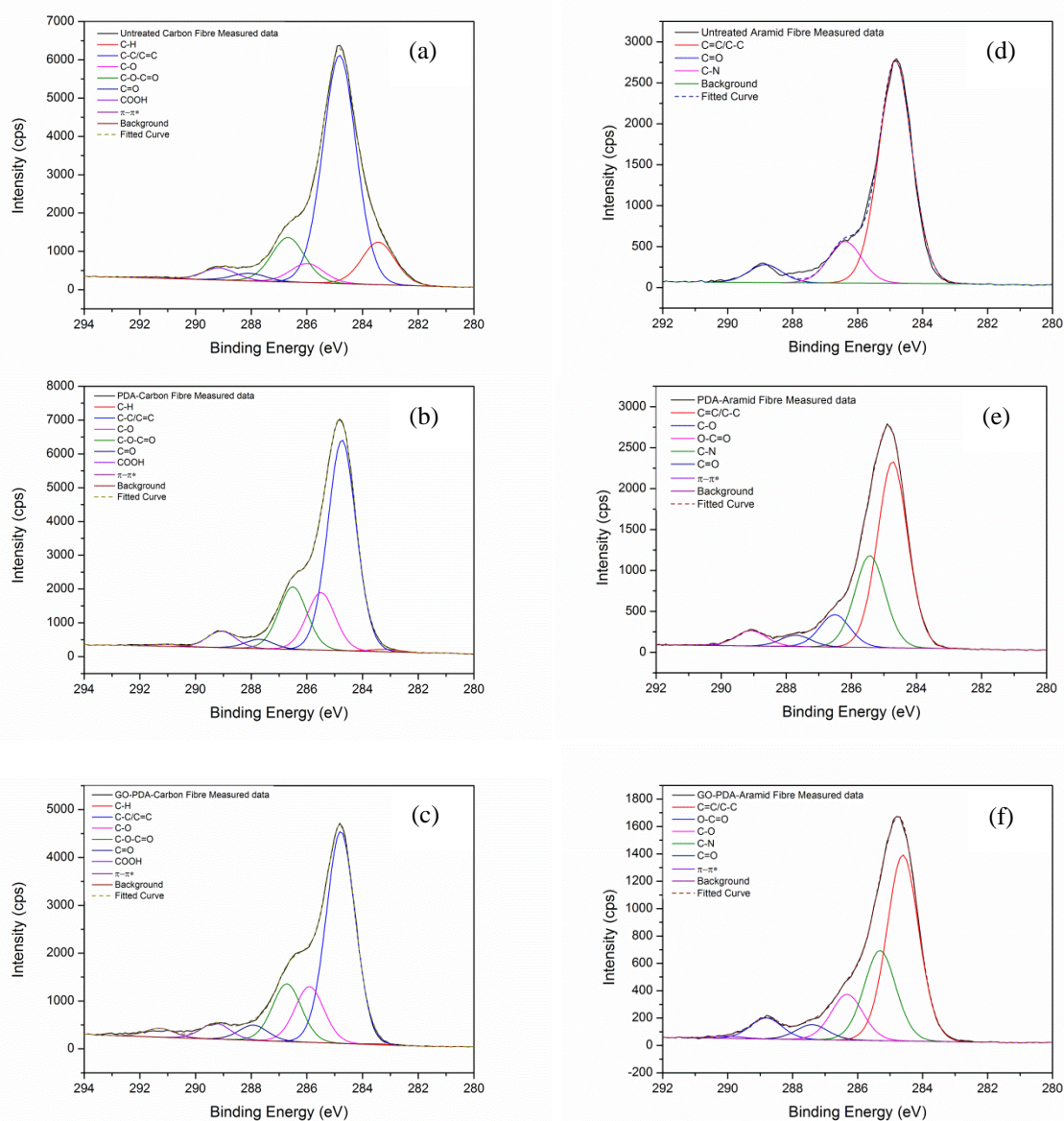|	The ratio for functional groups [%]					
	C=C/C-C	O-C=O	C=O	C-O	C-N	$\pi - \pi^*$
Untreated aramid	78.91	-	6.35	-	14.74	-
PDA-aramid	55.14	4.53	3.37	9.60	27.21	0.15
GO-PDA-aramid	51.67	5.84	4.16	12.70	25.05	0.58

Figure 1. XPS spectra of C1s of (a) untreated carbon fibre, (b) PDA-carbon fibre and (c) GO-PDA-carbon fibre, (d) untreated aramid fibre, (e) PDA-treated aramid fibre and (f) GO-PDA-treated aramid fibre.

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3.2 Surface topography of fibres

The surface morphology of fibres before and after the treatment was studied using SEM. It can be seen in Figure 2 (a) and (b) that both pristine carbon and aramid fibres display a clean and smooth surface. After modification by polydopamine, a homogeneous PDA layer was successfully coated onto the fibre surface. The PDA-fibres showed an uneven surface with micropits, as shown in Figure 2 (c) and (d). Figure 2 (e) and (f) indicated that, the roughness of fibre surfaces was further increased by depositing GO onto the PDA coated fibres. The typical thin paper-like wrinkled graphene oxide morphology was observed on both types of fibre surfaces. The SEM images demonstrated uniform deposition of PDA and GO on fibres, and both enhanced the roughness of the fibre surfaces.
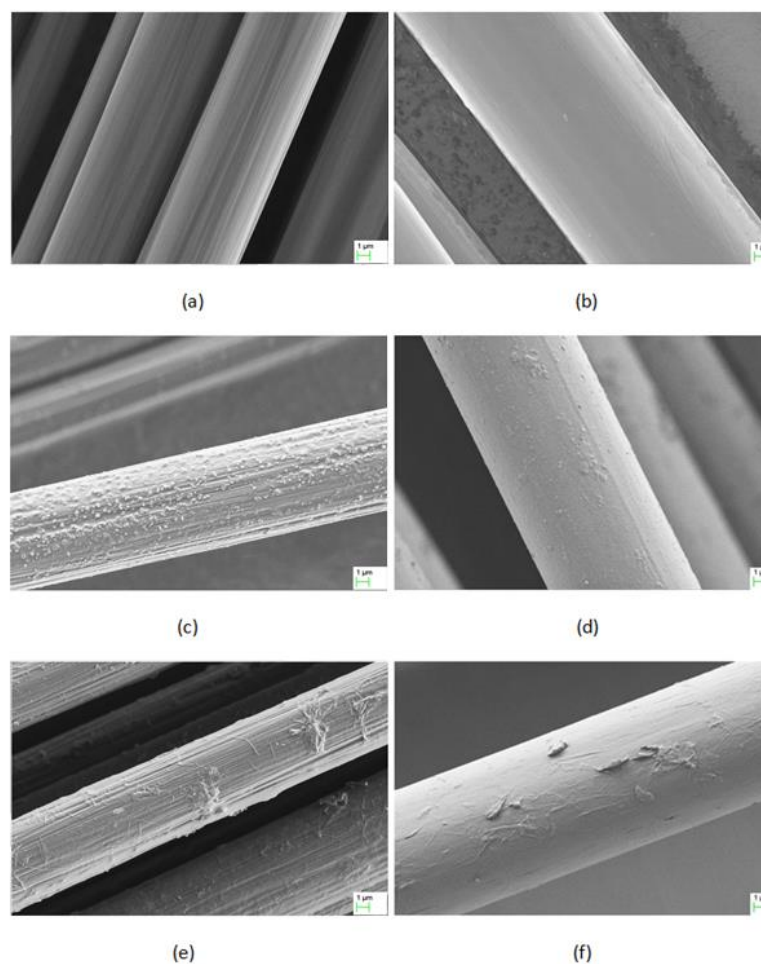

Figure 2. SEM images of (a) untreated carbon fibres; (b) untreated aramid fibres; (c) PDA treated carbon fibres; (d) PDA treated aramid fibres; (e) GO and PDA treated carbon fibres; (f) GO and PDA treated aramid fibres.

3.3 The fibre-resin interfacial shear strength analysis

The interfacial shear strength (IFSS) between fibre and resin was investigated by pulling a fibre out of resin droplet through a knife-edge and the results are shown in Figure 3. Compared with the untreated carbon fibre composites, the interfacial shear strength for the PDA treated-carbon composites

increased from 10.9 MPa to 14.7 MPa, representing a 35% increase, and for the GO-PDA-treated carbon composites, the IFSS was increased by 41% compared to that of untreated carbon fibre composites (Figure 3 (a)). While for aramid fibres, compared with the untreated aramid fibre composites, the IFSS for the PDA-aramid composites increased by 121%, and for the GO-PDA-aramid composites, the IFSS was increased by 210% compared to that of untreated aramid fibre composites as shown in Figure 3 (b). The IFSS increase can be attributed to the increased roughness of the fibre surface caused by PDA treatment and GO-PDA treatment. In addition, the successful grafting of GO introduced chemical groups which can also enhance the surface reactivity and polarity. The results revealed that the modification applied to the fibre surface by polydopamine and graphene oxide effectively enhances the interfacial property of both carbon and aramid fibre/epoxy composites.
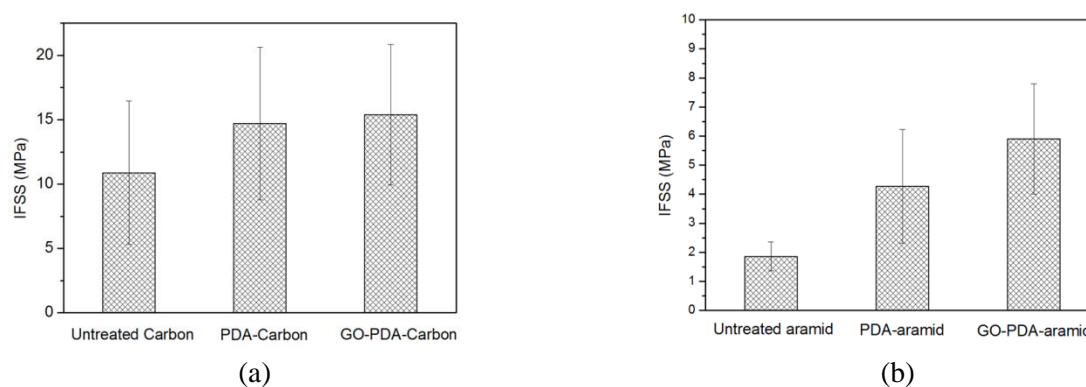

(a)	(b)

Figure 3. Interfacial shear strength between single (a) carbon (b) aramid fibre and resin.

3.4 Tensile strength of fibres

The single fibre tensile test was conducted to investigate the tensile strength of unmodified and modified fibres. As shown in Figure 4 (a), the single fibre tensile strength of untreated carbon fibre was 1987.1 MPa. For the PDA treated-carbon fibre, the tensile strength of single fibre was increase to 2595.5 MPa, representing a 30% increase by comparing with untreated carbon fibre. The single fibre tensile strength of GO-PDA treated-carbon fibre was increased to 3198.2 MPa, which is 61% higher than the unmodified carbon fibre. The ultra-thin coating protected the fibre surface and filled the groves of the ordinary carbon fibre, which improve the tensile strength by reducing the stress concentration of the fibre. In terms of the aramid fibre (Figure 4 (b)), the single fibre tensile strength of untreated aramid fibre was 2099.2 MPa. For the aramid fibre with PDA deposition, the tensile strength of single fibre was increased to 2470.9 MPa. After adding GO onto the PDA deposited fibre surface the single fibre tensile strength became 2603.4 MPa, which is 24% higher than the unmodified aramid fibre. This method modified the fibre surface by coating an ultra-thin layer without etching or damaging the bulk structure of the fibre. In addition, for the GO-PDA-fibres, the GO itself has superior mechanical properties, which also contribute the tensile strength improvement.
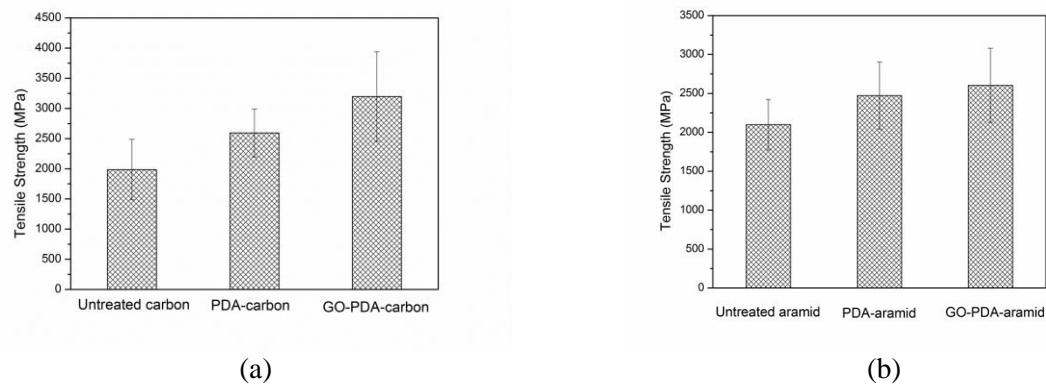
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(a)   (b)

Figure 4. Single fibre tensile strength of unmodified and modified (a) carbon (b) aramid fibres.

4. Conclusion

In this study, the GO and bioinspired PDA were used to functionalize carbon and aramid fibres, aiming to improve the interfacial adhesion between fibre and matrix. SEM and XPS confirmed that the fibres were successfully coated by GO and PDA. XPS demonstrated that more polar functional groups were introduced onto fibre after treatment, which could affect the fibre surface energy. Besides, the higher content of oxygen-containing groups would increase the polarity and reactivity of fibre and supply more reactive sites for interfacial bonding, which result in an improvement of the interfacial shear strength between fibre and matrix. The SEM observation displayed uniform coating of PDA and GO on the surface of fibre and the modification of GO increased the roughness of fibre surface. As a result, the interfacial shear strength of GO-PDA-fibre composites was significantly improved, and the surface modification has led to tensile strength increase of the fibre.

This study provides a novel method for surface modification of chemically inert high-performance fibres, which is believed to be beneficial for interface improvement for composites. Furthermore, the polydopamine and graphene oxide grafting will lead to the feasible application of high-performance fibres in the composites industry, aerospace and ballistic protection area.

Acknowledgement

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