



# Layer-by-layer grafting CNTs onto carbon fibers surface for enhancing the interfacial properties of epoxy resin composites



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## ABSTRACT

An effective method for bonding carbon nanotubes (CNTs) onto carbon fibers (CFs) surface *via* layer-by-layer (LBL) grafting method is reported here. The CNTs have been chemically grafted as confirmed by X-ray photoelectron spectroscopy (XPS). Scanning electron microscopy (SEM) indicates that this LBL method can increase the dispersion quality of the CNTs on CF surface. The polarity, wettability and roughness of the CFs have been significantly increased after the CNTs modifying. The interfacial shear strength (IFSS) and impact strength test suggest that the hierarchical structure can result in a remarkable improvement for the interfacial properties. The results also indicate that this LBL method is a promising technique to modify CFs with the high interfacial performance.

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## 1. Introduction

On account of their extraordinary strength-to-weight ratios and mechanical properties, the carbon fibers (CFs) reinforced high-performance composites have made a huge impact on many structural applications [1–3]. Generally, the performance of interface is pivotal for the mechanical behavior of composites. Excellent interphase can transfer the load from resin to the fibers to reduce the stress concentration and enhance the interfacial performance of composites [4,5]. Thus, modifying the CFs to obtain a preeminent interphase is critical to control the interfacial performance of composites.

CNTs have been regarded as ideal reinforcing materials to significantly enhance the overall performance of fiber reinforced

composites [6–9]. Over the past few decades, CNTs have been attached to the CFs and endow a better interfacial performance to the epoxy resin composites [10–12]. Some researches indicate that the interfacial reinforcing mechanisms of CNT grafted fiber/epoxy composites can be mainly ascribed to three aspects: (i) the Van der Waals interaction among CNTs; (ii) chemical reaction of CNTs with CFs as well as the matrix, and (iii) mechanical interlocking between CNTs and the resin [13–15]. Namely, CNTs could provide both intralaminar and interlaminar reinforcement. This combination of properties makes CNTs the potentially ideal candidates for preparing high-performance composites.

Plenty of studies have been carried out to deposit CNTs to the fiber surface *via* sizing, electrophoretic deposition (EPD), chemical vapor deposition (CVD) and chemical grafting [16–18]. Among them, CVD method is popular owing to the high density of CNTs formed on fiber surface. However, the predeposited catalyst, together with the high temperature in the depositing process generally result in a significant degradation of the CFs' properties, which restricts the application of this method. Although EPD and

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sizing methods are relatively easy to apply, these methods limit the reinforcing strength due to the weak physical adsorption between the CFs and CNTs. Generally, compared to these methods, chemical grafting has proven to be an effective method to obtain the controlled and active structure on the CF surface. In recent years, grafting CNTs onto the CFs surface *via* coupling agents has made great progress in enhancing the interfacial properties. For example, Zhao et al. attached CNTs to the CFs with the link of polyhedral oligomeric silsesquioxane (POSS) and the IFSS was increased by 105% [13]. Wu et al. reported that using 3-aminopropyl-triethoxysilane as coupling agent gave an increase of 31.12% for the impact properties of CF composites [19]. However, it should be noted that conventional coupling agents such as hexamethylenediamine, and 1,3-propodiamine only have two reactive groups in each molecule and always lead a low grafting density of CNTs [18,20]. Large molecules such as poly(amido amine) (PAMAM), POSS and other dendrimers can provide more reactive groups, however, some of them are too expensive and bring about the steric hindrance which are caused by molecular structure [12]. On the other hand, Alimardani et al. have verified that better interfacial properties of composites can be acquired if CNTs are uniformly dispersed onto the CF surface [21]. However, strong Van der Waals attraction among CNTs can cause serious self-aggregation which makes it hard to obtain good dispersion of CNTs [22,23].

Layer-by-layer (LBL) is an effective method to obtain homogeneously distributed CNTs and has already been employed to prepare CNT films on substrates [24–27]. It is performed by depositing two interactive materials alternately onto a substrate surface. The LBL technique possesses the advantage of non-complicated instruments needed and the controllable process, and the phase segregation between dissimilar materials can be avoided [28–30]. Moreover, it is independent of the size or shape of the substrate, and thus can be realized on the substrates with different shapes [31]. For example, Shchukin et al. have deposited polyelectrolyte onto silica nanoparticle substrate [32]. This method also has been applied to modify CNTs by covalent assembly and polymerization [24–26]. However, general protocols for the modification of CF surface are still lacking.

In this research, a synthesis approach by grafting CNTs onto CFs *via* LBL method is presented. The LBL grafting process is conducted by alternately grafting melamine and carboxylic acid-functionalized CNTs onto CFs surface. Melamine is hired as the coupling agent in consideration of its low cost and higher amino density since melamine can result in high chemical bonding at the interface for enhancing the interfacial performance efficiently [33]. Meanwhile, extending such technology to modify CF surface could provide a promising approach to tailor the composites with desired interfacial properties.

## 2. Materials and methods

### 2.1. Materials

Carbon fibers (PAN-based with the diameter of 6–7  $\mu\text{m}$ ) were obtained from Sino Steel Jilin Carbon Co., China. Epoxy resin (E-51) was supplied by China National Blue Star (Group) Co., Ltd. 4,4'-Methylenebis (2-ethylbenzenamine) (H-256, Hubei Jusheng Technology Co., Ltd.) was used as the curing agent. The CNTs (diameter 10–20 nm, length 1–2  $\mu\text{m}$ ) were purchased from Shenzhen Nanotech Port Co., Ltd. The *N*-[(dimethylamino)-1H-1,2,3-triazolo [4,5,6]-pyridin-1-ylmethylene]-*N*-methylmethanaminium hexafluoro-*oro*-phosphate *N*-oxide (HATU) was supplied by GL Biochem Ltd. All other chemicals were supplied by Tianjin Bodi Organic Chemicals Co. Ltd.

### 2.2. Fabrication of oxidized CNT

2.0 g CNTs were added into 160 mL mixture of  $\text{HNO}_3/\text{H}_2\text{SO}_4$  (1/3, v/v) at 70 °C for 6 h. After diluting with deionized water, the mixture was filtered and the oxidized CNTs were collected. The obtained CNTs were then washed continually with deionized water till to neutral and dried at 60 °C for 24 h. The obtained CNTs were denoted as OCNTs.

### 2.3. Grafting CNT onto CFs by LBL approach

The raw CFs were firstly immersed into acetone and treated with Soxhlet extraction for 8 h to remove the sizing agent on CF surface, the obtained fibers were untreated CF. Subsequently, the CFs were put into the  $\text{AgNO}_3/\text{K}_2\text{S}_2\text{O}_8$  solution at 70 °C for 1 h following by washing with ethanol and drying, the obtained CFs were denoted as CF-COOH. Thereafter, the CF-COOH was tied to a glass frame and placed into the melamine/THF solution, then the ultrasonical addition of HATU was performed and stirred at 55 °C for 4 h to induce plenty of amino groups onto the CF surface, denoted as CF@M. After washing by THF and drying, the CF@M was mixed with OCNTs in DMF and HATU was added into the above solvent under ultrasonication. The mixture was stirred at 90 °C for 4 h to obtain CF@MC1. This cycle procedure of melamine treatment followed by OCNTs grafting was repeated twice to obtain the products of CF@MC2 and CF@MC3. During the grafting processes, HATU was used as the condensing agent to complete the reaction of the carboxyl groups on CF-COOH and OCNT surface with the amino groups of melamine. The overall reaction is shown in Fig. 1.

### 2.4. Preparation of CF/epoxy resin composites

The compression molding method was used to prepare the composites. Briefly, the CFs at each step were impregnated with epoxy resin with a content of  $35 \pm 1.5$  mass% and then put them into the mould. Subsequently, the mould was heated to 90 °C for 2 h under 5 MPa, to 120 °C for 2 h and 150 °C for 3 h under 10 MPa, respectively. The dimension of the composite specimens was 6.5 mm in width and 2 mm in thickness.

### 2.5. Characterization

The groups on CFs surface were analyzed by XPS (ESCALAB 220i-XL, VG, UK). The surface morphologies and the fractured surfaces of the CFs and the composites were observed on SEM (Quanta 200FEG, Hitachi Instrument, Inc. Japan). The contact angle between CFs and the test liquids (deionized water and diiodomethane) was measured by dynamic contact angle meter and tensiometer (DCAT21, Data Physics Instruments, Germany). The result of each sample was the average of 20 valid data.

The interfacial property of the composites was quantified by IFSS using the interfacial evaluation equipment (Tohei Sangyo Co. Ltd., Japan). The microdroplets were prepared by mixing the epoxy resin and curing agent in a weight ratio of 100:32. The IFSS can be calculated from Eq. (1):

$$IFSS = \frac{F}{\pi dl} \quad (1)$$

where  $F$  is the maximum load recorded,  $d$  is the carbon fiber diameter, and  $l$  is the embedded length. The final value was averaged from the 50 valid data for each sample. TEM (transmission electron microscopy, Hitachi H-7650, Japan) was used to investigate the interfacial sections of the composites.

The impact strength was tested on the impact test system

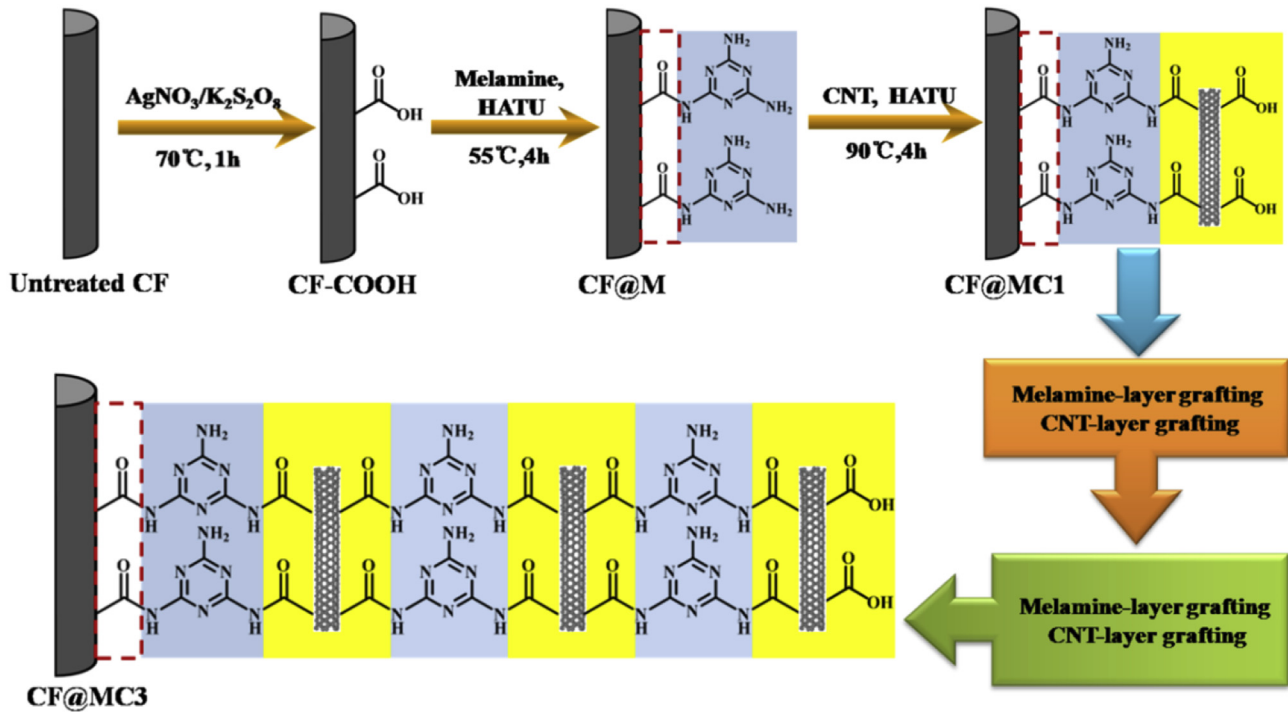


Fig. 1. Schematic illustration of layer-by-layer grafting CNTs onto CF surface.

(9250HV, Instron, USA) with the 40 mm impact span and 3 kg drop weight. The samples were cut into the specimens with the size of 55 mm × 6.5 mm × 2 mm. Each data was the average of 5 specimens.

The tensile strength of CFs was tested on a universal testing machine (5500R, Instron, USA) according to ASTM D3379-75. The testing speed was 10 mm · min<sup>-1</sup> and the gauge length was 200 mm for all samples. 50 data were collected and the result of each sample was analyzed using Weibull statistical method.

### 3. Results and discussion

#### 3.1. Chemical characterization of CFs surface

The modified CFs at each reaction step are evaluated by XPS to analyze the chemical surface compositions. In Fig. 2, the C1s XPS spectra are peak fitted for estimating the functional groups on the fiber surface. According to Fig. 2a, the main peak C1 at 284.4 eV is assigned to Csp<sup>2</sup> and Csp<sup>3</sup> in the CF structure, the peak at 285.6 eV (peak C2) can be attributed to C-C bonding of amorphous carbon, and the peak around 286.3eV (peak C3) represents the C-O bond resulting from the CF purification process. After being modified with melamine (Fig. 2b), the C1s peak shows three new peaks. The two peaks at 285.8 eV and 287.6 eV are assigned to C-N and C=N bond of melamine, respectively [34]. The chemical bonding between melamine and CF-COOH is confirmed by the presence of amide group (NH-CO) peak around 288.0 eV. With respect to the ones after CNT functionalization (Fig. 2c–e), a new peak located at 288.9 eV has shown up which is assigned to -COOH of the carboxyl functionalized CNTs, indicating the presence of CNTs [35]. The content ratios of NH-CO and -COOH are shown in Fig. 2f. For untreated CF, the ratio is zero due to no amide group on the CF surface. After LBL grafting CNTs, the ratio increases obviously to 0.75 for CF@MC1 and then shows a decreasing trend. This can be mainly attributed to the increased content of -COOH that is higher than

that of NH-CO with increasing the amount of grafted OCNTs, indicating that the density of CNTs is enhanced remarkably on the surface of CFs after LBL grafting. The XPS results confirm the reaction on the CFs surface, indicating the successful growth of hierarchical architecture on the surface of CFs.

#### 3.2. CF surface microstructures

Fig. 3 shows the SEM images of CF surface morphology before and after functionalization. Initially, a smooth and neat surface of untreated CF is presented in Fig. 3a and some grooves are distributed on the CF surface. Fig. 3b–d presents the microstructure of the CFs grafting with CNTs. For CF@MC1, small amount of CNTs have been grafted on the CFs, the CNTs are distributed well on the fiber surface and form a hierarchical network. With respect to CF@MC2, it is noted that higher density CNTs are obtained and a thin layer of CNTs is observed on the CF surface. For CF@MC3, the morphology reveals the mats of fine CNTs, which form a random, dense interconnected network with full surface coverage and nearly no visible agglomerates. This may attribute to the abundant chemical bonds between melamine and CNTs, which can prevent the CNTs from agglomerating. It can be presumed that LBL grafting of CNTs can effectively enhance the interfacial properties due to the increasing reactive points as well as the improved mechanical interlocking caused by increased density and dispersion quality of CNTs on CFs surface.

#### 3.3. Contact angle measurements

The contact angle and the surface energy are studied and summarized in Fig. 4 to evaluate the wettability of the untreated and modified CFs. According to Fig. 4a, the contact angle significantly decreases from 77.4° to 48.3° with water and 52.6° to 35.5° with diiodomethane when the untreated CF and CF@M are compared. For CF@MC1–3, the decrease of contact angles is more

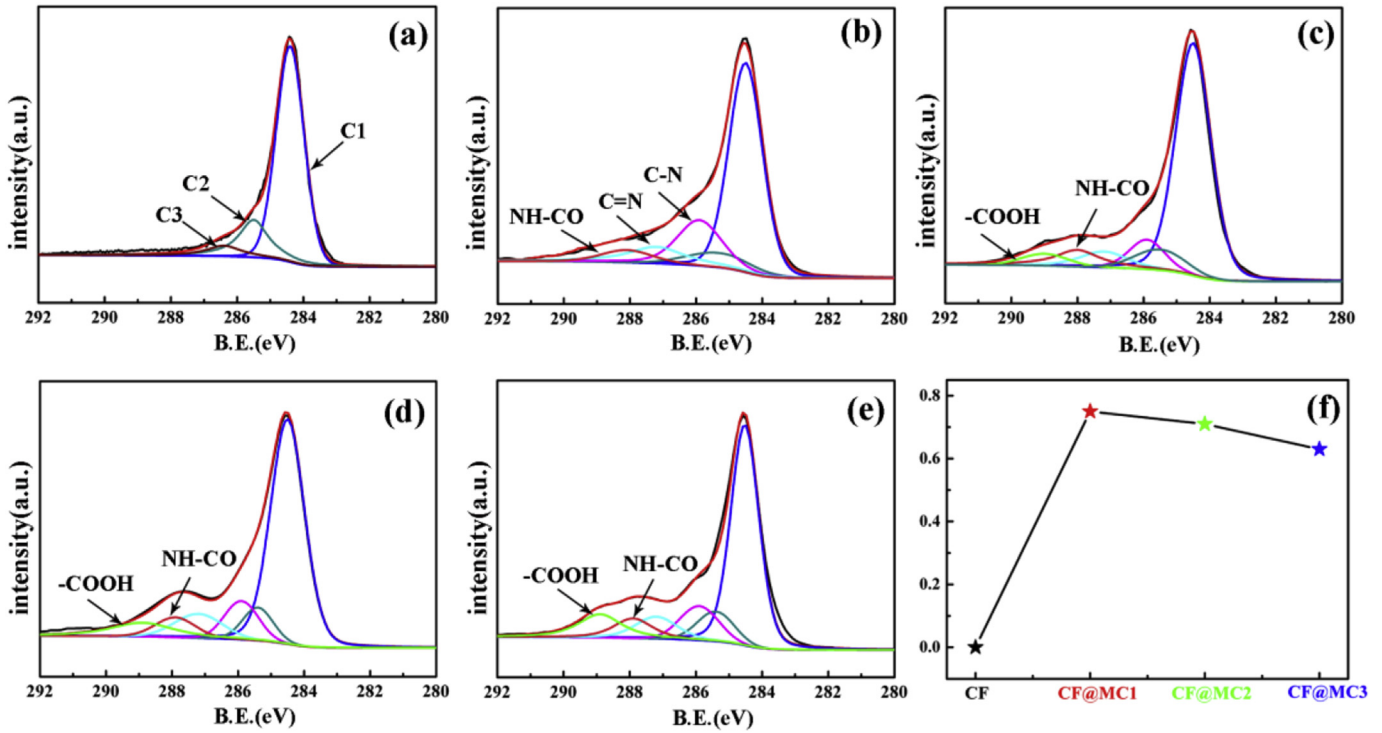


Fig. 2. XPS curve fitting for C1s peak: (a) untreated CF, (b) CF@M, (c–e) CF@MC1–3 and (f) the content ratios of -NH-CO/-COOH for CFs.

remarkable, indicating the improved wettability of the CNTs modified CFs which can be ascribed to the increase of chemical groups and surface roughness on CFs.

The fiber surface energy ( $\gamma_f$ ) reflects the ability of interfacial adhesion between CF and epoxy resin. It is typically determined by the sum of dispersive ( $\gamma_f^d$ ) and polar component ( $\gamma_f^p$ ) based on the double fluid method, which can be calculated by solving Eqs. (1) and (2) [36]:

$$\gamma_l(1 + \cos\theta) = 2(\gamma_l^p \gamma_f^p)^{1/2} + 2(\gamma_l^d \gamma_f^d)^{1/2} \quad (1)$$

$$\gamma_f = \gamma_f^p + \gamma_f^d \quad (2)$$

In Fig. 4b, the surface energy increases from  $38.9 \text{ mN}\cdot\text{m}^{-1}$  for untreated CFs to  $59.7 \text{ mN}\cdot\text{m}^{-1}$  for CF@MC1 and it is more pronounced with the layer of CNTs increasing. Meanwhile, the polar and dispersive component also show the same rising tendency. The increased polar groups arising from the grafted CNTs and melamine mainly contribute to the increased polar component. The increasing of dispersion component can be contributed to the increased roughness caused by the increasing density of CNTs on the CF surface. The higher density of CNTs makes it easy to form a higher density of physical bonds and mechanical interlocking on fiber surface, which is beneficial for enhancing the interfacial properties. The surface energy increased with increasing the treatment circle, indicating the improved wettability of the CFs, which can further enhance the adhesion at the interface of the composites.

#### 3.4. IFSS test of carbon fiber composites

Fig. 5 shows the IFSS test of the CF/epoxy composites. Fig. 5a and b is the images of resin droplet before and after de-bonding. The

IFSS values are shown in Fig. 5c. For CF@M, the IFSS value is 63.4 MPa, with an enhancement of 30.5% compared to that of untreated CFs. After being modified by LBL grafting CNTs, the IFSS value of CF@MC1 is improved by 35.2% and 77.2% than that of CF@M and untreated CF, respectively, confirming the strong influence of grafting CNTs on the interfacial properties. For CF@MC2/epoxy composites, the IFSS value is 105.8 MPa, increased by 117.7% and much higher than previous researches in which the IFSS was increased by 30.8%–109.3% in comparison with that of untreated CF [37–40]. This remarkable increase can be attributed to two aspects. Firstly, the detachment of CNTs from CF needs relatively high strength because of the strong chemical bonding between CFs and CNTs. On the other hand, the interlocking between CFs and matrix can enhance the infiltration of CNTs into the matrix when the liquid matrix wraps onto CFs, and the epoxy monomer inter-diffuses through the CNT-grafted network and interacts chemically with the carboxyl groups of the CNTs and the amine groups of unreacted melamine. Thus, larger strength is needed to pull the CNTs out of the resin. Moreover, the increased surface roughness caused by LBL coverage of CNTs may further improve interfacial strength. However, the IFSS of CF@MC3 presents a slight decrease from 105.8 MPa for CF@MC2 to 98.8 MPa because of the “over-coverage” of the CNTs. Excessive CNTs could induce a local stress concentration and decrease the energy dissipation. Besides, the narrow gap among CNTs can restrict the afflux of resin to the CF surface and result in a poor interfacial adhesion between CFs and epoxy resin [12,40,41]. Therefore, the interfacial defect may occur within CNTs due to weak Vander Waals interaction among CNTs and make the IFSS value reduced.

To further analyze the mechanism for the enhancement of IFSS, the de-bonding morphologies of CFs are performed on SEM. In Fig. 6a, the de-bonded surface of untreated CF is almost neat, which means that the de-bonding can take place in the interface due to the weak interfacial adhesion as discussed above. In the case of

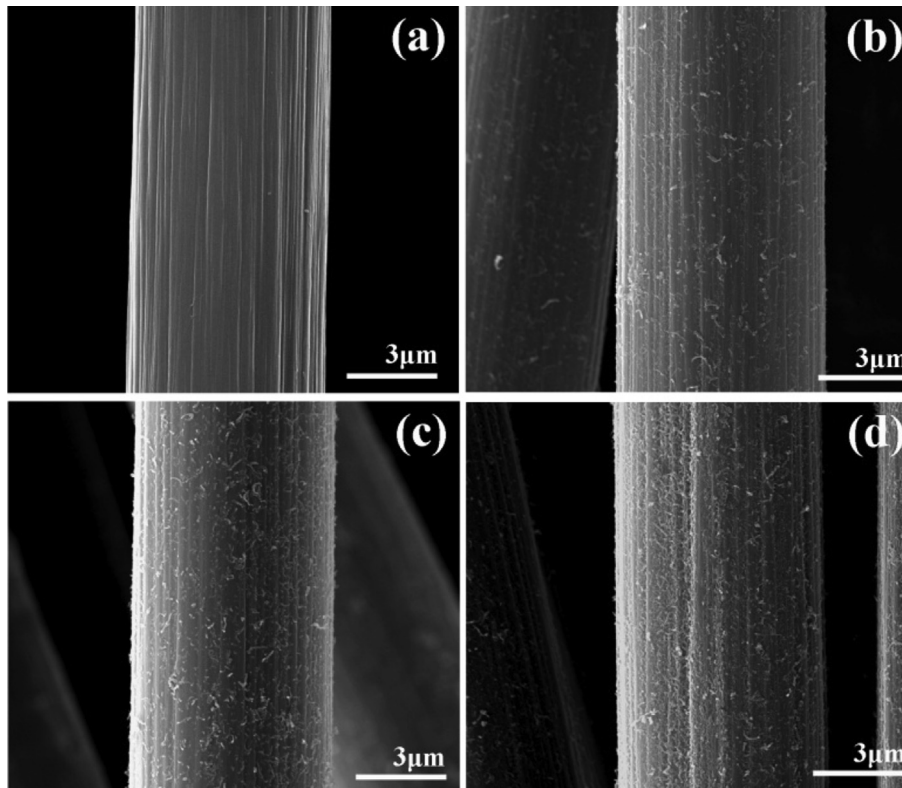


Fig. 3. SEM images for the CFs: (a) untreated CF, (b) CF@MC1, (c) CF@MC2 and (d) CF@MC3.

CF@MC1-3 (Fig. 6b–d), the images reveal that the amount of the resin remaining on CF surface is consistent with the changing tendency of the IFSS values, indicating that the formation of strong adhesion in the interface and the de-bonding may occur not only in the interface but also within the epoxy resin.

The microstructure of the composites is also investigated by TEM to deeper explore the composite interfacial status and the images are shown in Fig. 6e–h. In Fig. 6e, there's nearly no resin bonded with the untreated CF, indicating poor interfacial property. For CF@MC1 (Fig. 6f), an obvious resin layer existed on the CF surface, indicating that the interfacial properties have been improved after modifying the CNTs. However, the distribution of resin is non-uniform and even to be de-bonded. The microstructures of CF@MC2 and CF@MC3 composites presented in Fig. 6g–h

are all thicker, more homogeneous and compact resin layer is observed on the CF surface than that of CF@MC1 due to the improved interfacial adhesion derived from LBL grafting of the CNTs as discussed above. Besides, the CF@MC3 bond thinner resin than that of CF@MC2 resulting from the “overload” CNTs and this is also consistent with the IFSS and SEM results.

### 3.5. Impact property of CFs composites

Fig. 7a shows the impact results to evaluate the overall mechanical features of the CFs reinforced composites. For the reason of poor interfacial adhesion, the impact strength of composites reinforced with untreated CFs is the lowest. After LBL grafting CNTs, the strength of the composites reinforced with CF@MC1-3 presents

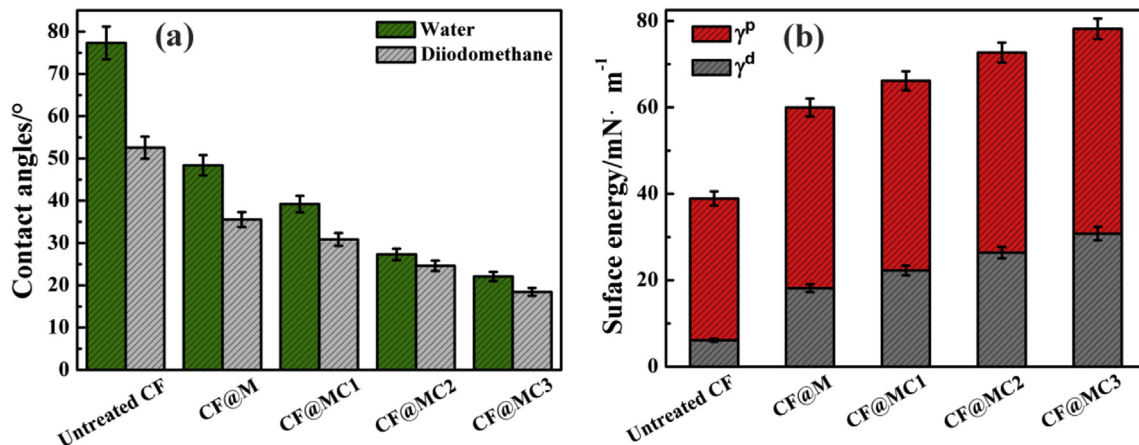


Fig. 4. Contact angles (a) and surface energy (b) for untreated CF and CF@MC1-3.

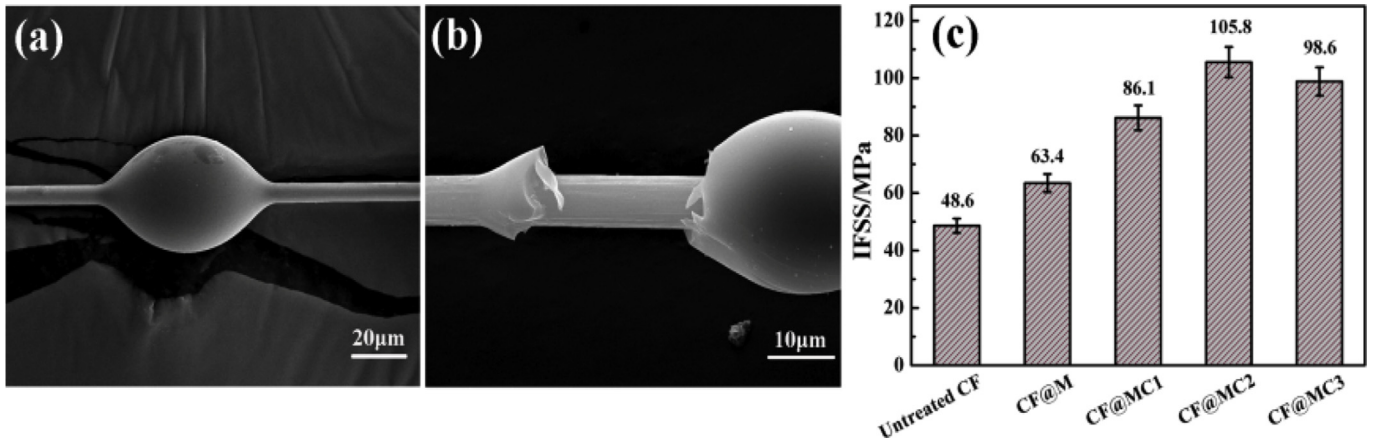


Fig. 5. SEM pictures of micro-droplet. (a) Before de-bonding, (b) After de-bonding and (c) IFSS of the carbon fiber/epoxy composites.

varying degree of increase in comparison to that of untreated CF, which is increased by 21.4%, 34.7% and 49.8%, respectively. This 49.8% increase caused by grafting the CNTs is more significant than previous results [42,43]. For example, Wu et al. grafted APS and CNTs onto the CFs and the impact strength was increased by 33.17% [44]. Moreover, these results can be confirmed directly by observing the impact fracture surfaces of composites, as shown in Fig. 7b–e. In Fig. 7b, the untreated CFs have been pulled out from the matrix and the surface is bare in some area. In the case of CF@MC1 (Fig. 7c), the composite shows a flat fracture surface, implying an improved interfacial adhesion but some small cracks still can be observed. For the composite sample derived from CF@MC2, as shown in Fig. 7d, the interfacial adhesion is improved obviously and the fracture surface is flatter. In Fig. 7e, the breakage surface of CF@MC3 composites presents a strong adhesion. The fragments of fibers and resin are uniformly dispersed on the fracture. This may be because a network structure has been built in the interphase during the impacting process, thus the nearby resin and fiber can be broken into pieces when suffering the impact [45,46].

Fig. 8 depicts the schematic of the impact test model to directly disclose the impact properties of the CF reinforced composites. For untreated CF (Fig. 8a), the crack tips can directly contact the fiber surface due to poor adhesion in the interface. As a result, the composites can crack easily under a low impact. For CF@MC1–3 (Fig. 8b–d), the CNTs on the CFs surface could release the stress concentration and make the direction of the cracks turn to the interphase [47]. Additionally, the increasing number of CNTs on CF could induce more cracks to consume more energy, which makes the impact strength of composites increased.

### 3.6. Tensile strength test of single fiber

Single fiber tensile test is performed to evaluate the inherent mechanical property of CFs and the results are presented in Fig. 9. For CF@MC1–3, the tensile strength has been improved compared with that of untreated CFs (3.82 GPa). It is also noted that a slight increase of the tensile strength is detected for the CNTs modified CFs, which can be ascribed to that more and more CNTs are grafted

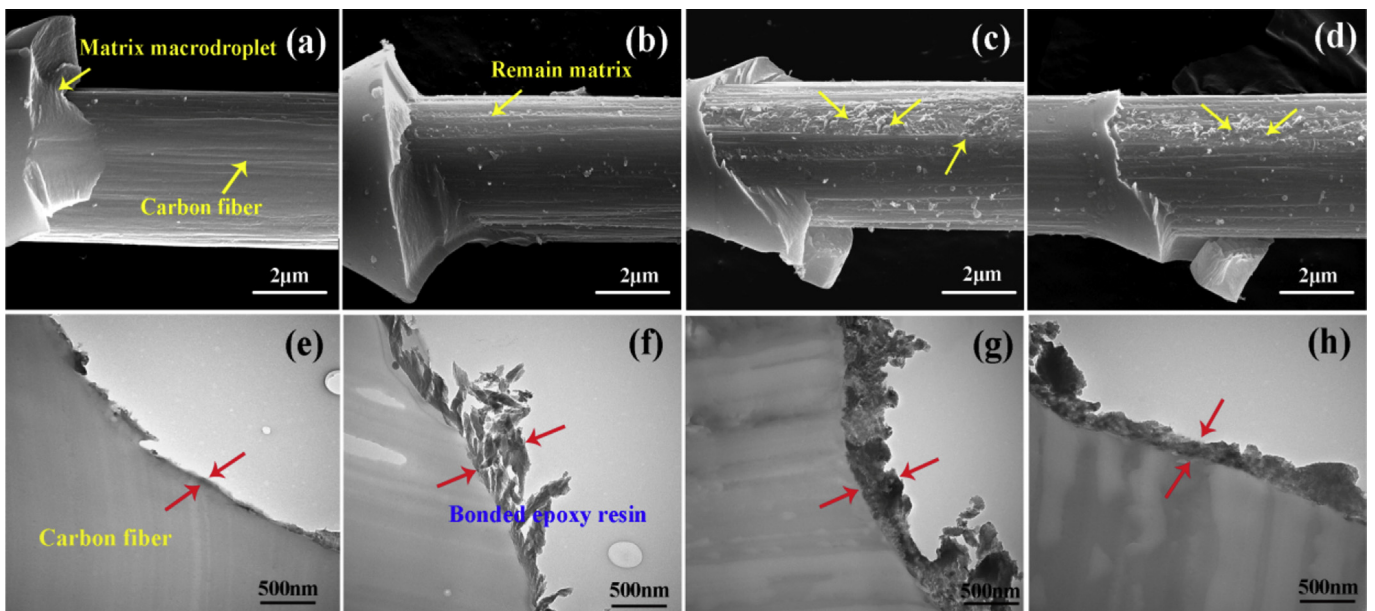


Fig. 6. SEM pictures after de-bonding and TEM interface microstructures of single CFs epoxy composites: (a) and (e) untreated CFs, (b) and (f) CF@MC1, (c) and (g) CF@MC2, (d) and (h) CF@MC3.

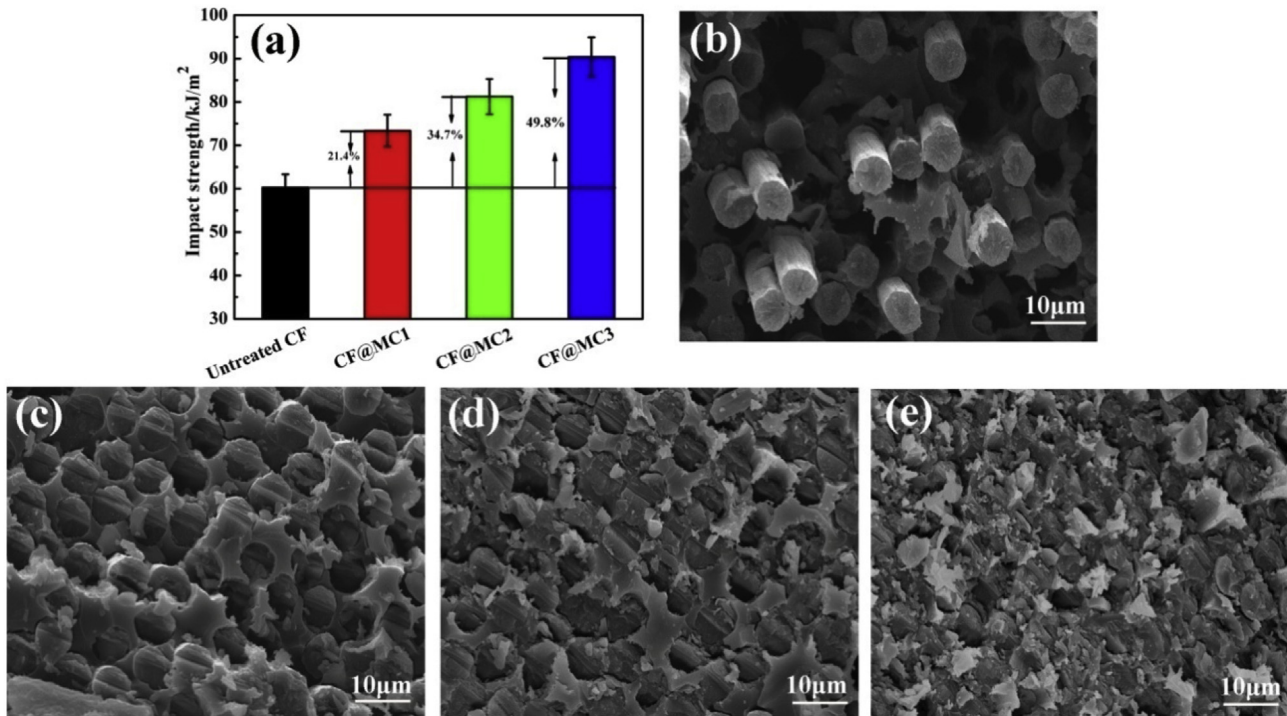


Fig. 7. Impact test of composites (a) and SEM micrographs of fracture (b) untreated CF, (c–e) CF@MC1–3.

to the CFs with the treatment repeated and the CNT layer acts as a shelter to prevent the introduction of damages to the fiber surface during the modified process. Single fiber tensile testing implies that the inherent graphitic structure of CFs are still maintained and the process of LBL grafting even can enhance the tensile strength of CFs.

#### 4. Conclusion

The layer-by-layer covalent depositing of CNTs onto the fiber surface for CFs/epoxy resin application is demonstrated. The CNTs are uniformly distributed onto CF with full surface coverage. The

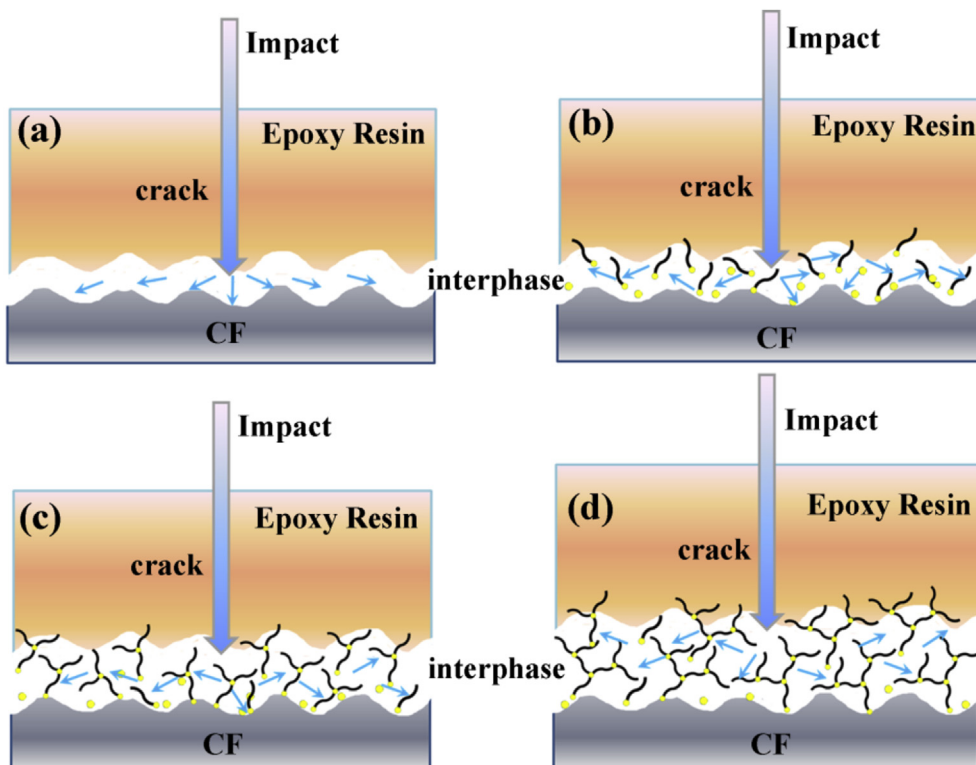


Fig. 8. Schematic of impact test of composites reinforced with (a) untreated CFs, (b–d) CF@MC1–3.

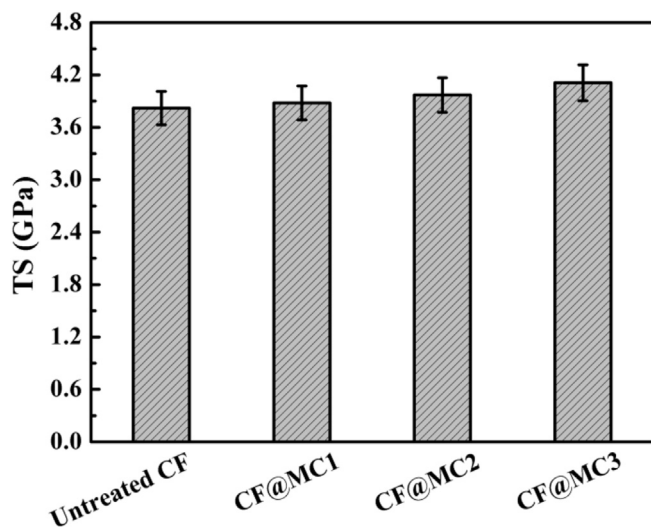


Fig. 9. Tensile strength of CFs, including untreated CF and CF@MC1–3.

presence of CNTs improves the interfacial properties and mechanical interlocking between CFs and epoxy matrix effectively. It is found that CF@MC2 composites achieve the highest IFSS, which is improved by 117.7%. The impact strength of CF@MC3 reinforced composites is increased by 49.8%. Besides, the LBL method would not bring any reduction of tensile strength according to the tensile test. The study reveals that this facile and flexible process will provide great potential for the manufacture of high-performance CF/epoxy composites without harming the in-plane properties of CFs.

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