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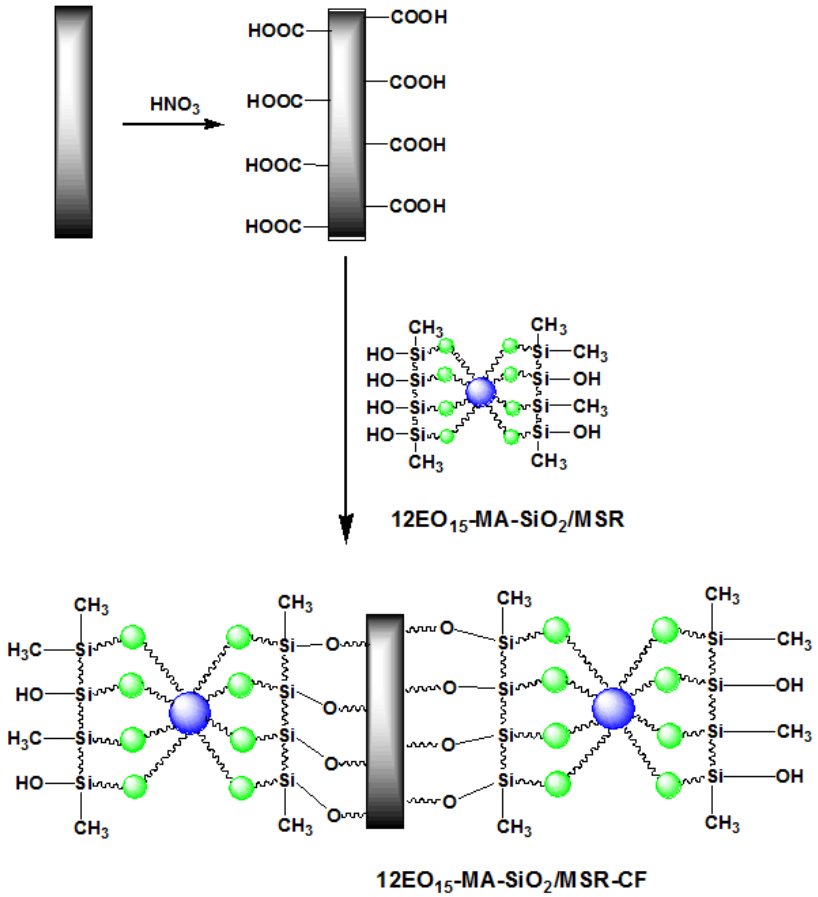

# Interfacially reinforced carbon fiber composites by grafting modified methylsilicone resin

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**Abstract:**

Modified methylsilicone resin ($12EO_{15}$-MA-$SiO_2$/MSR) containing nano-silica grafted hyperbranched polymer ($12EO_{15}$-MA-$SiO_2$) was grafted successfully onto carbon fibers (CFs) surface to enhance the interfacial properties of carbon fiber/methylsilicone resin composites. Fourier transform infrared (FTIR) and X-ray photoelectron spectroscopy (XPS) confirmed the chemical bonding nature between $12EO_{15}$-MA-$SiO_2$/MSR and CFs. Scanning electron microscopy (SEM) and interfacial shear strength (IFSS) indicated that the surface morphology and interfacial properties of carbon fibers were highly dependent on the concentration of $12EO_{15}$-MA-$SiO_2$ and $12EO_{15}$-MA-$SiO_2$/MSR. The results showed that the optimal condition was that the concentration of $12EO_{15}$-MA-$SiO_2$/MSR was 1%, in which containing 6%-$12EO_{15}$-MA-$SiO_2$. Furthermore, significant enhancement of interfacial shear strength was achieved in the composites after modified methylsilicone resin introduced on the fiber. In addition, the tensile strength of the carbon fibers remained stable after the grafted treatment. Thus, it is a facile and effective interface design strategy to develop multifunctional fibers with desirable properties in industry applications.

**Keywords**:

A: Carbon fibers; A: Methylsilicone resin; A: Nano-silica B: Interfacial properties;

## 1. Introduction

Carbon fibers (CFs) are widely used as reinforcements for advanced composites, due to its excellent mechanical properties, heat and oxidation resistance, light weight, relative flexibility, environmental stabilities and high corrosion resistance [1-5], which make carbon fiber fabrics ideal reinforcing materials in the advanced composite fields, such as marine, aerospace and automobile industries [6, 7]. However, the potential of CF reinforced composites has not yet been fully exploited due to the chemically inert surface and low surface energy of the fiber, which make it difficult to exhibit desired interfacial adhesion with matrix resin and negatively affects the mechanical properties of CFs/polymer composites [8]. Hence, numerous methods concerning surface treatment such as electrochemical method, plasma treatment, high-energy irradiation and oxidation method have been developed to activate the fiber surface and thus improve the interfacial adhesion of the resulting composites [9-13]. As one of the silicon-containing compounds, methylsilicone resins have exhibited various attractive properties, such as unusual heat resistance, good electric insulation and excellent weather resistance, allowed these types of resins to be used as an advanced composites matrices, adhesives, electronic encapsulation and coatings, adhesives [14-18]. However, applications of CFs/methylsilicone resins composites are restricted owing to the poor interfacial adhesion between the fibers and matrix resin.

Interfacial adhesion of composites depends largely on interfacial structures and interfacial interactions [19]. Therefore, efforts to increase greatly the interfacial strength and to work out the factors in influencing the interfacial properties of

composites are important and urgent targets. The surface silanization of carbon fibers (CFs) was developed to improve the interfacial adhesion of carbon fiber reinforced polyurethane (PU) composites [20]. Melamine was used as a coupling agent to functionalize the carbon fiber surface to improve the interfacial properties of CF reinforced epoxy composites [21]. Furthermore, polyhedral oligomeric silsesquioxane (POSS) modified onto the CFs surface were studied [22-24]. However, the interfacial performance of CF reinforced composites need to be further improved. Several researchers have also made effort on the chemical grafting of functional nanofillers aiming to enhance the interfacial properties, such as grafting carbon nanotubes (CNTs) onto CFs based on different bridging agents by realizing chemical bonding between CFs and CNTs. For example, Li et al. [25] have reported a facile method of grafting CNTs onto CFs by 1,3-propodiamine as the coupling agent. Wu et al. [26, 27] grafted carbon nanotubes onto carbon fibers to enhance the interfacial strength of CFs reinforced methylphenylsilicone resin composites. Recently, some studies also have reported that the branched polymer was grafted onto the CFs surface resulting in a high chemical bonding at the interface and improving the interfacial properties of composites [28, 29].

In this paper, methylsilicone resin modified by nano-silica grafted hyperbranched polymer was grated onto the surface of CFs to enhance the interfacial properties of carbon fiber composites. The CFs composites with different concentration of nano-silica grafted hyperbranched polymer and modified methylsilicone resin were observed and the optimal concentration condition was confirmed. Meanwhile, the

interfacial shear strength and tensile strength of carbon fiber composites were also discussed. Combining the advantages of methylsilicone resin, nano-silica grafted hyperbranched polymer and carbon fibers may be a promising and attractive alternative to preparing high performance polymer composites. The schematic illustration of $12EO_{15}$-MA-$SiO_2$/MSR-CF preparation was depicted in Fig. 1.

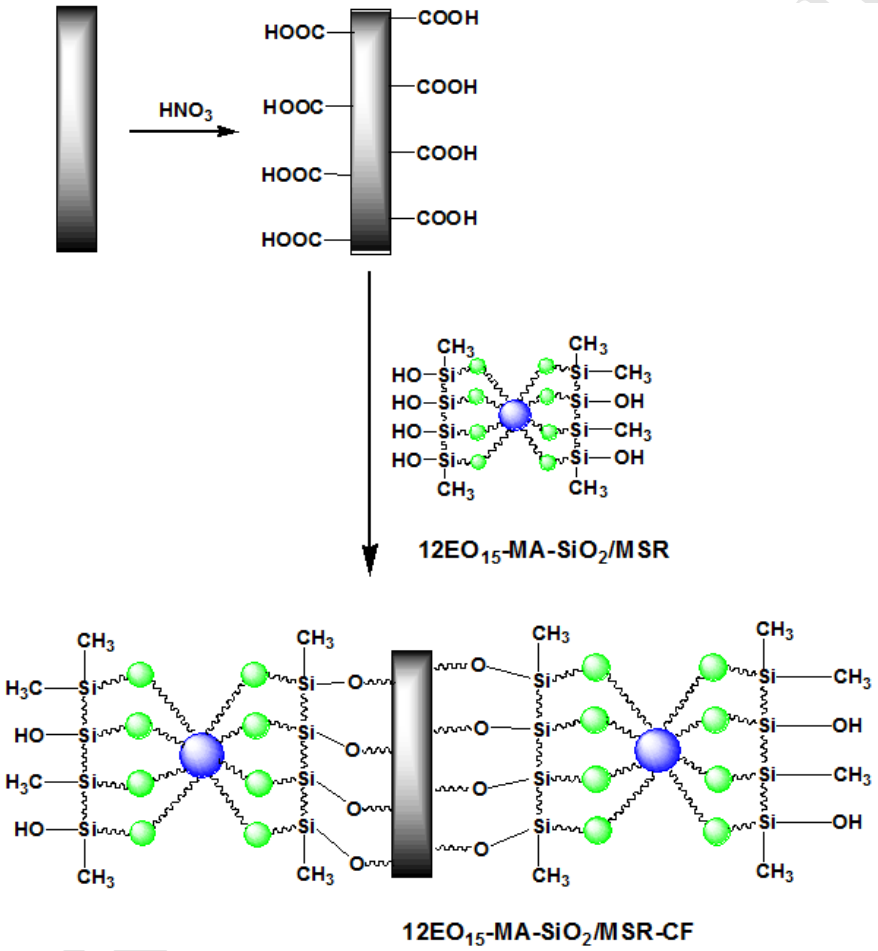


Fig.1. Schematic of the grafting procedure of $12EO_{15}$-MA-$SiO_2$/MSR-CF.

## 2. Experimental

### 2.1 Materials

(3-Aminopropyl)triethoxysilane (KH550) was supplied by Jiangsu Chenguang Silane Co., Ltd (China). Methyltriethoxysilane and dimethyldiethoxylsilane were purchased from Qufu Chenguang Chemical Co., Ltd, (China). Ethyl silicate (TEOS)

and anhydrous ethanol were provided from Sigma-Aldrich. (15)Ethoxylated trimethylolpropane triacrylate ($EO_{15}$-TMPTA) was purchased from Tianjin Tianjiao Chemical Co., Ltd, (China). Laurylamine (LA) and methylacrylate (MA) were supplied by Tianjin Tianli Chemical Reagent Co., Ltd. (China). All solvents were purchased from Tianjin Kermel Chemical Reagent Co., Ltd (China), and used without further purification.

**2.2 Preparation of hyperbranched polymer ($12EO_{15}$-MA)**

Initially, $EO_{15}$-TMPTA (0.05 mol, 47.80 g) and LA (0.075 mol, 13.90 g) were added into a 250 mL three neck round bottom flask equipped with a mechanical stirrer. The reaction mixture stirred at room temperature for 48 h under a seal condition. Then the reaction mixture was poured into 80 mL anhydrous ethanol and refluxed at 60 $^{o}$C for 36 h under nitrogen atmosphere. After that, the pale yellow viscous liquid product ($12EO_{15}$) was isolated by distillation at 78 $^{o}$C under nitrogen atmosphere.

Then, $12EO_{15}$ (10 g), methacrylate (3 g) and anhydrous ethanol (40 mL) were added into a three neck round bottom flask equipped with a mechanical stirrer and refluxing condenser. The reaction mixture was refluxed at 78 $^{o}$C for 8 h under nitrogen atmosphere. The deep yellow viscous liquid product ($12EO_{15}$-MA) was obtained after distillation.

**2.3 Preparation of nano-silica grafted hyperbranched polymer ($12EO_{15}$-MA-$SiO_2$) and modified methylsilicone resin ($12EO_{15}$-MA-$SiO_2$/MSR)**

Nano-silica grafted hyperbranched polymer ($12EO_{15}$-MA-$SiO_2$) was prepared via the Michael addition reaction from $12EO_{15}$-MA and the nano-silica particles.

Methylsilicone resin (MSR) was prepared via the hydrolysis reaction of methyltriethoxysilane and dimethyldiethoxylsilane. Methyltriethoxysilane and dimethyldiethoxylsilane with the molar ratio of 7:3 were charged into a three-necked, round-bottom flask with magnetic stirring and reflux condenser. Anhydrous ethanol was poured into the mixture. The system was heated at 60 $^{o}$C and then hydrochloric acid solution (10%, diluted by Ultrapure water) was slowly added dropwise through the constant-pressure funnel. After that, ammonium hydroxide was added into the mixture to adjust the pH value to 7. The transparent viscous liquid (MSR) was obtained after dried. $12EO_{15}$-MA-$SiO_2$/MSR containing various concentration $12EO_{15}$-MA-$SiO_2$ were obtained by blending method.

**2.4 Preparation of modified methylsilicone resin grafted carbon fibers ($12EO_{15}$-MA-$SiO_2$/MSR-CF)**

The CFs were extracted with supercritical acetone and oxidized in nitric acid at 60 $^{o}$C for 2 h. Next, the carboxy functionalized CFs (COOH-CFs) were obtained after washed several times with deionized water until the pH of the wash water was neutral, and then dried under vacuum. The COOH-CFs were put into the uniform mixture solution of the $12EO_{15}$-MA-$SiO_2$/MSR and anhydrous ethanol, which was stirred at 60 $^{o}$C for 30 min. Then the reaction was carried out at 78 $^{o}$C for 10 h. The $12EO_{15}$-MA-$SiO_2$/MSR-CFs was obtained after being washed with deionized water and dried. Besides, the $12EO_{15}$-MA-$SiO_2$/MSR was directly coated on functional carbon fiber as a contrast experiment.

**2.5 Characterization**

The surface morphologies of carbon fibers, nano-silica and $12EO_{15}$-MA-$SiO_2$/MSR were measured by high-resolution scanning electron microscopy (SEM). The samples were adhered to an SEM mount with conductive adhesive and coated with a thin gold layer by sputter prior to capture a clear image of the treated surface.

The surface functional groups of the samples ($12EO_{15}$-MA-$SiO_2$, $SiO_2$. $12EO_{15}$-MA-$SiO_2$/MSR, $12EO_{15}$-MA-$SiO_2$/MSR-CF) were analyzed by FTIR spectrophotometer (Nicolet, Nexus670, USA) over the range from 400 to 4000 $cm^{-1}$, the resolution of the wavenumber was 2 $cm^{-1}$.

X-Ray Photoelectron Spectroscopy (XPS) Analysis experiment was conducted to study the chemical composition of methylsilicone resin. The XPS analysis of the samples was performed with a VG electron spectrometer with a resolution of 0.3–0.5 eV from a monochromated aluminum anode X-ray source with Karadiation (1486.6 eV) (ESCALAB Mk II, made in UK).

Single fiber tensile tests were performed (YG004N, Nantong Hongda Experiment Instruments, Co. Ltd., China) to investigate the mechanical properties. According to the China Standard GB/T14337-2008，the tensile rate was 10 mm $min^{-1}$, the gauge length was 10 mm.

Single fiber pull-out test was performed to evaluate the interfacial shear strength between fibers and resin matrix. Methylsilicone resin (MSR) was prepared microdroplets, and the microdroplets were cured at 60 $^{o}$C/1 h, 80 $^{o}$C/ 1 h, 100 $^{o}$C/1 h, 130 $^{o}$C/2 h, 160 $^{o}$C/2 h, 200 $^{o}$C/2 h and 250 $^{o}$C/ 2 h.

Thermal gravimetric analyses (TGA, NETZSCH STA 449C, Germany) were used to evaluated the modified methylsilicone resins at a heating rate of 10 $^{o}$C min$^{-1}$ under nitrogen atmosphere.

A dynamic contact angle analysis system (DCAT21, Data Physics Instruments, Germany) was carried out to test the surface free energy and contact angle of a bundle of fibers with a length of 48 μm.

## 3. Results and discussion

### 3.1. Surface structure analysis of functionalized CFs (12EO$_{15}$-MA-SiO$_2$/SAR-CF)

The FTIR spectra of untreated-CF, COOH-CF and 12EO$_{15}$-MA-SiO$_2$/MSR-CF were presented in Fig. 2. (The characterization data of 12EO$_{15}$-MA-SiO$_2$ and 12EO$_{15}$-MA-SiO$_2$/MSR are shown in supporting information Fig. S1 and S4). For the untreated CF, in addition to the bonds of carbon dioxide in the air some organic groups can be observed. The absorption peak around 3400 cm$^{-1}$ attributes to O–H stretching vibration of the absorbed water on fiber surface [21, 30]. The bands around 1084 cm$^{-1}$ and 1615 cm$^{-1}$ are assigned to the C–C and C=C stretching vibration, respectively [23, 24]. For COOH-CF, carboxylic acid groups (–COOH) exhibits a broad band at 3435 cm$^{-1}$ which is attributed to the hydroxyl stretching vibration. The new absorption peak around 1700 cm$^{-1}$ corresponds to the stretching of carbonyl group generated by the oxidized. For 12EO$_{15}$-MA-SiO$_2$/MSR, the bonds in the range of 2962–2853 cm$^{-1}$ are assigned to the C–H stretching of methyl and methylene. The strong bands centered at 1105 cm$^{-1}$ correspond to Si–O–Si stretching vibrations [31]. The absorption peak at 1733 cm$^{-1}$, belonging to the C=O stretching. In addition, the

absorption band located at 1270 $cm^{-1}$ and 1025 $cm^{-1}$ corresponds to the asymmetric and symmetric stretching vibrations of C–O–C, respectively. Besides, there is no absorption band related to the vibration of hydroxyl (O–H) absorption, indicating that the reaction is completed. The results indicated that the $12EO_{15}$-MA-$SiO_2$/MSR was grafted to the carbon fiber successfully.

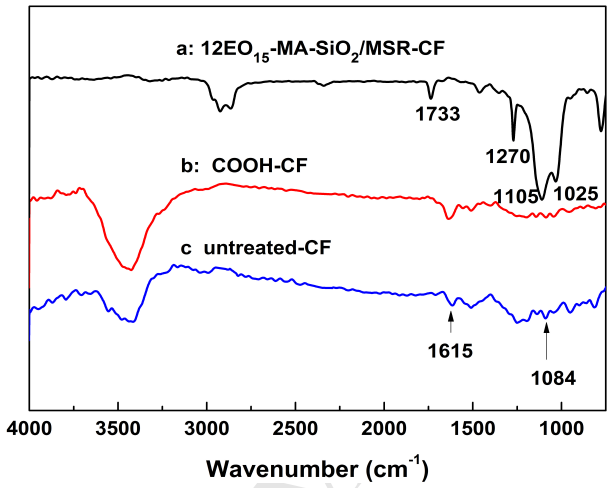


Fig. 2. FTIR spectra CFs of a) untreated-CF, b) COOH-CF and c)$12EO_{15}$-MA-$SiO_2$/MSR-CF.

The $Si_{2p}$ XPS was further carried out to detect the specific contents of various functional groups, as shown in Fig. 3. The results were summarized in Table 1. The $Si_{2p}$ spectrum of $12EO_{15}$-MA-$SiO_2$/MSR was composed of 89.18% Si–O–Si, 7.63% Si–OH and 3.19% Si–O–C. Compared with the original MSR, the Si–O–Si content increased and the Si–OH content decreased significantly from 12.13 to 7.63%. In addition, significant silicon elements of Si–O–C were observed, which indicated that the $12EO_{15}$-MA-$SiO_2$/MSR molecular structure had been successfully grafted on the carbon fiber surface. This is also consistent with the FTIR result shown in Fig. 2.

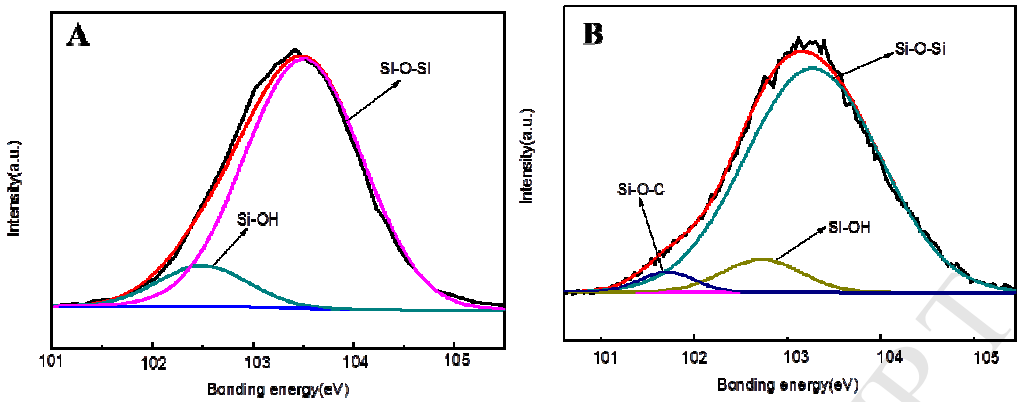


Fig. 3. $Si_{2p}$ XPS spectra of (A) original MSR and (B) $12EO_{15}$-MA-$SiO_2$/MSR-CF.

Table 1. XPS spectra for $Si_{2p}$ peak of original MSR and $12EO_{15}$-MA-$SiO_2$/MSR-CF.

| | $Si_{2p}$ | Energy (eV) | Area | Percentage composition(%) |
|---|---|---|---|---|
| Original MSR | Si–O–Si | 102.6 | 29918.73 | 87.87 |
| | Si–OH | 103.5 | 3748.735 | 12.13 |
| $12EO_{15}$-MA-Si $O_2$/MSR-CF | Si–O–Si | 103.5 | 21996.19 | 89.18 |
| | Si–OH | 102.6 | 1882.249 | 7.63 |
| | Si–O–C | 101.6 | 786.7727 | 3.19 |

### 3.2. Surface morphology of carbon fibers

The surface morphology of carbon fibers were characterized by SEM. Fig. 4 showed the SEM images of untreated and oxidized CFs. Remarkable differences of the surface between the untreated and oxidized CFs can be observed. As shown in Fig. 4A, the untreated CF surface is relatively neat and smooth. Compared with the untreated CF, the fiber surface becomes rougher due to oxidation and corrosion effect of nitric acid and a few narrow grooves distribute along the longitudinal direction of the fiber.

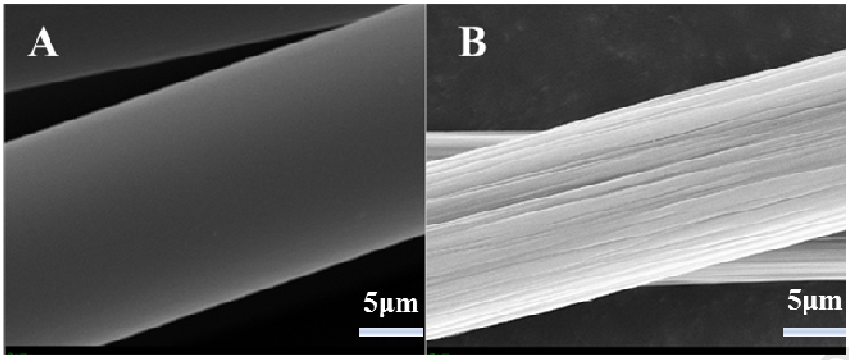


Fig. 4. SEM images of CFs (A) untreated-CF and (B) COOH-CF.

Besides, the SEM also verified the effect of the concentration of $12EO_{15}$-MA-$SiO_2$ and $12EO_{15}$-MA-$SiO_2$/MSR on the surface morphology's changes for the carbon fibers, and the results are depicted in Fig. 5. Table S3 shows the different compound content of these material systems. The virgin carbon fiber with smooth surface is observed (Fig. 4). Fig. 5A-C shows the surface particles of CFs increase with the increased concentration of $12EO_{15}$-MA-$SiO_2$, and the surface particles presents an uneven dispersion with obvious segregation. $12EO_{15}$-MA-$SiO_2$/MSR-CF with 1% $12EO_{15}$-MA-$SiO_2$/MSR is shown in Fig. 5D-F, the surfaces particles of modified CFs in which has 6% $12EO_{15}$-MA-$SiO_2$ presents a better dispersion quality. It can be presumed that $12EO_{15}$-MA-$SiO_2$ presents a good dispersion in MSR without visible aggregation. Besides, the proportion of $12EO_{15}$-MA and $SiO_2$ also influence the preparation of the $12EO_{15}$-MA-$SiO_2$, which may further influence the dispersion of $12EO_{15}$-MA-$SiO_2$/MSR on the surfaces of CFs. The dispersion of $SiO_2$ reached an optimal condition when the mass ratio of $12EO_{15}$-MA to $SiO_2$ is 1:1 (Fig. S5). However, as the concentration of $12EO_{15}$-MA-$SiO_2$/MSR increases, the surface particles of carbon fiber present varying degrees of aggregation. As shown in Fig. 5G-L, when the concentration of

$12EO_{15}$-MA-$SiO_2$/MSR reach 1.5% and 2%, the dispersion quality of surfaces particles are inferior to the one that reach 1%. In general, the optimal condition is that the concentration of $12EO_{15}$-MA-$SiO_2$/MSR is 1%, which contains 6%-$12EO_{15}$-MA-$SiO_2$.

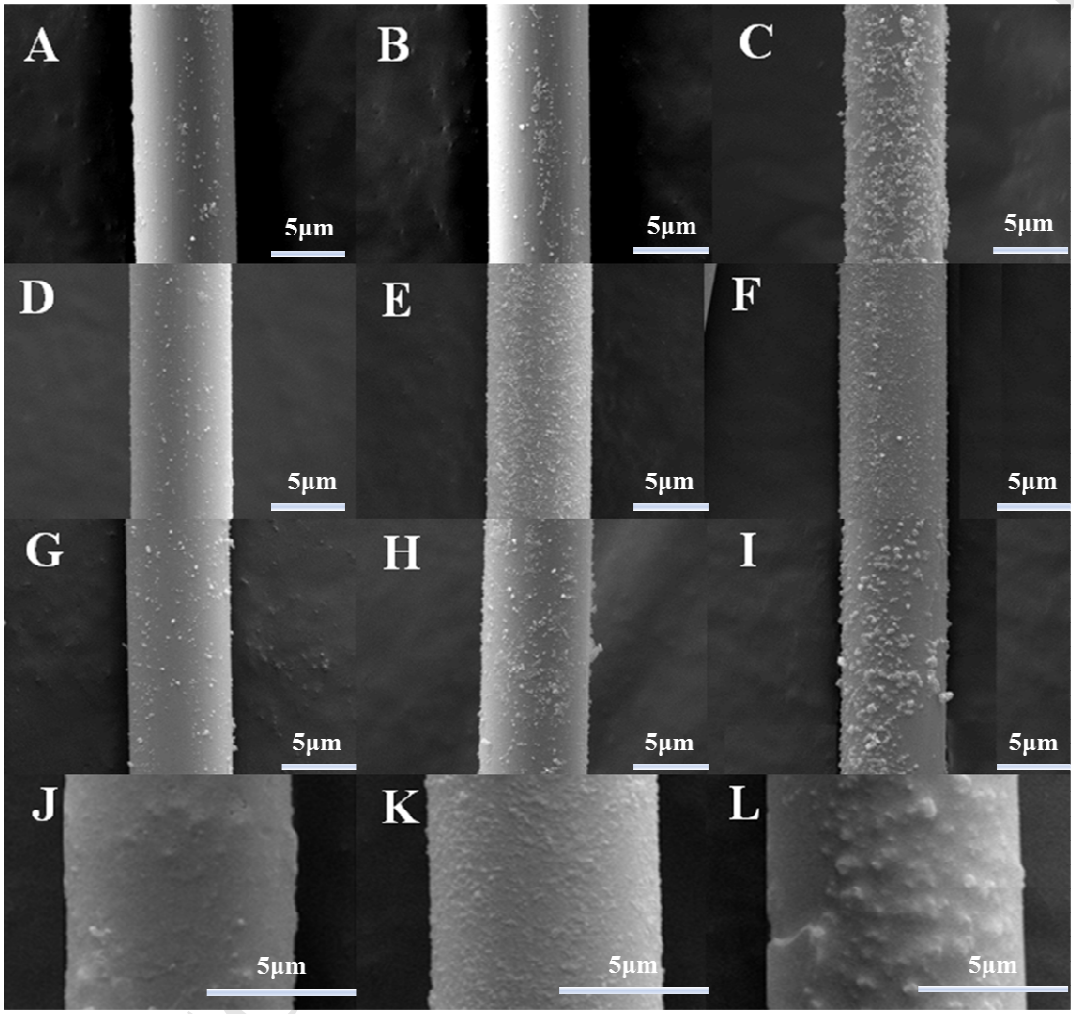


Fig. 5. SEM images of $12EO_{15}$-MA-$SiO_2$/MSR-CF with different concentration of $12EO_{15}$-MA-$SiO_2$ and $12EO_{15}$-MA-$SiO_2$/MSR.

### 3.3. Interfacial properties testing of composites

Pull-out method is one of the most common and popular techniques to measure the interfacial bonding strength between fibers and matrix [32]. The IFSS results of the composites reinforced by the untreated, oxidation, $12EO_{15}$-MA-$SiO_2$/MSR-coated

and -grafted carbon fibers are depicted in Fig. 6. Clearly, it can be seen that grafting $12EO_{15}$-MA-$SiO_2$/MSR significantly increased the interfacial strength of the composites, which may be attributed mainly to an enhancement in chemical bonding, surface energy and mechanical interlocking between CFs and matrix [33, 34]. The IFSS increases from 68.8 to 97.9 MPa by grafting $12EO_{15}$-MA-$SiO_2$/MSR, enlarges at 42.3% in comparison with that of untreated-CF. The $12EO_{15}$-MA-$SiO_2$/MSR-coated CFs affords an IFSS value of 76.8 MPa, which is significantly lower than that of the $12EO_{15}$-MA-$SiO_2$/MSR-grafted CFs. The IFSS of $12EO_{15}$-MA-$SiO_2$/MSR-grafted carbon fiber composites are much higher than that of previous researches [21, 22, 35, 36], and are similar to those of carbon fiber/epoxy composites modified with graphene oxide, in which the IFSS results of SCF-GO0 and SCF-GO10 fibers are 72.0 and 97.9 MPa, respectively [37] and carbon fiber/epoxy resin composites modified branched polyethyleneimine [29]. According to literature [38], stronger interactions are helpful for transferring external stress from matrix to CFs fillers, and then improve the mechanical properties of the composites.

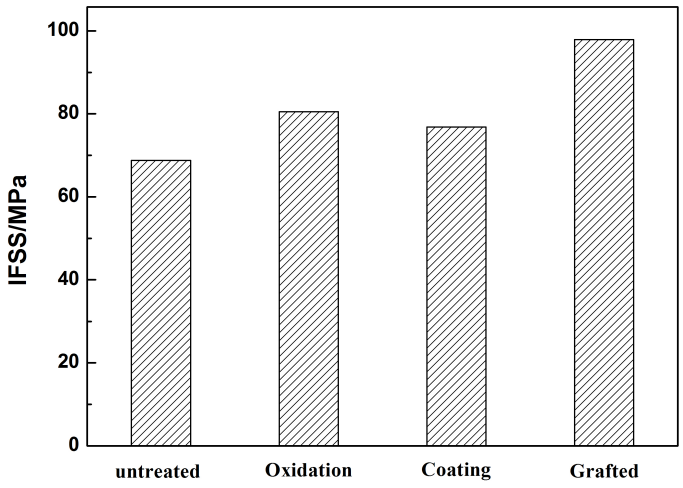


Fig. 6. IFSS of untreated-CF, COOH-CF, $12EO_{15}$-MA-$SiO_2$/MSR (0.5 wt%) coated carbon

fibers and $12EO_{15}$-MA-$SiO_2$/MSR (0.5 wt%) grafted carbon fibers.

Fig. 7 shows the effect of $12EO_{15}$-MA-$SiO_2$ and $12EO_{15}$-MA-$SiO_2$/MSR concentration on the interfacial strength of the composites. Table S3 shows different compound content of these material systems. It is found that the IFSS of 1%-$12EO_{15}$-MA-$SiO_2$/MSR-CF which contains 6%-$12EO_{15}$-MA-$SiO_2$ is the highest, yielding IFSS of 107.8 MPa. The result is consistent with the previous SEM. Besides, comparing the IFSS values of $12EO_{15}$-MA-$SiO_2$/MSR-CF based on the optimal condition, the others have lower IFSS. This might be related to the relative lower content of $12EO_{15}$-MA-$SiO_2$, poor dispersity of $12EO_{15}$-MA-$SiO_2$ and the weaker strength of chemical bonding between CFs and $12EO_{15}$-MA-$SiO_2$/MSR.

The enhancement of interfacial adhesion between $12EO_{15}$-MA-$SiO_2$/MSR and CF may be attributed to two aspects: on the one hand, $12EO_{15}$-MA-$SiO_2$ disperses uniformly onto the surface of methylsilicone resin are beneficial to prevent undesired agglomeration of $12EO_{15}$-MA-$SiO_2$, improving the dispersion of $12EO_{15}$-MA-$SiO_2$ in MSR. On the other hand, the abundant hydroxyl groups on the surface of $12EO_{15}$-MA-$SiO_2$/SAR are expected to form chemical bonding with the abundant carboxyl groups of carbon fibers. Consequently, the quality of interface between $12EO_{15}$-MA-$SiO_2$/SAR and carbon fibers is improved significantly.

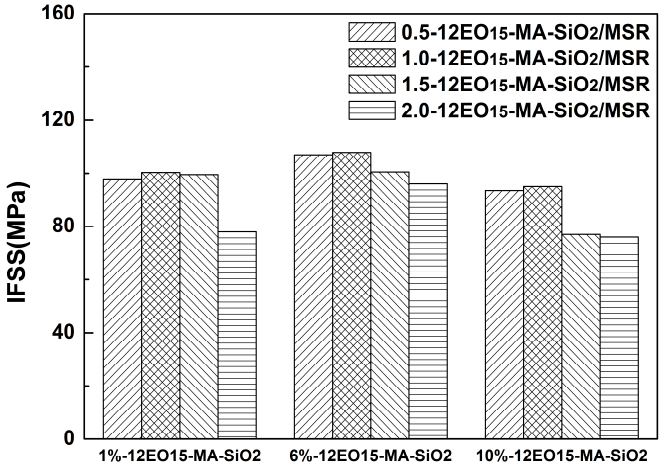


Fig. 7. IFSS of $12EO_{15}$-MA-$SiO_2$/MSR grafted carbon fibers with various content (different compound content is shown in Table S3).

### 3.4. Tensile strength of single carbon fiber

Single fiber tensile strength is usually performed to assess the influence of the grafting modification on the tensile strength of the fiber [34]. As shown in Fig. 8, compared with the strength of the untreated-CF (4.89 GPa), comparable fiber tensile strength is observed for the CFs grafted with $12EO_{15}$-MA-$SiO_2$/MSR (4.65 GPa), which imply that the tensile strength of CFs remain stable after the grafted treatment. Oxidation and grafting treatment will unavoidably introduce defects on the surface of fibers, which could decrease the fiber strength [39, 40]. The tensile strength of COOH-CF decreased 34.5 % comparing to the untreated carbon fiber. However, the tensile strength of the $12EO_{15}$-MA-$SiO_2$/MSR grafted carbon fibers increased 23.3 % comparing to the $12EO_{15}$-MA-$SiO_2$/MSR coated carbon fibers. Therefore, the characterizations highlight the successful introduction of new chemical species to the surface.

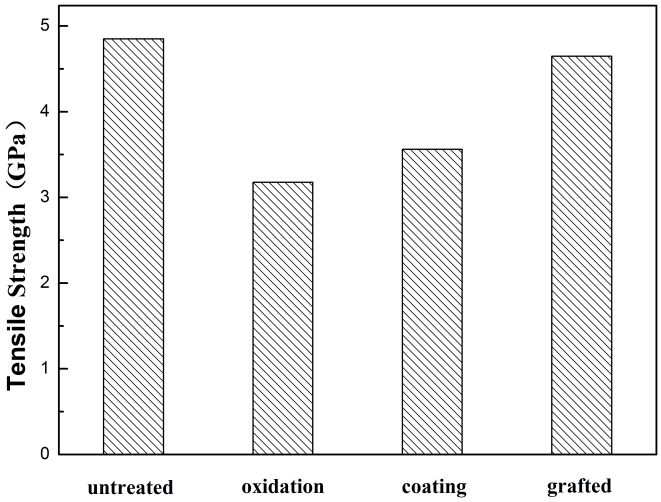


Fig. 8. Tensile strength of untreated-CF, COOH-CF, $12EO_{15}$-MA-$SiO_2$/MSR (0.5 wt%) coated carbon fibers and $12EO_{15}$-MA-$SiO_2$/MSR (0.5 wt%) grafted carbon fibers.

## 4. Conclusion

In summary, we have reported an efficient technique to enhance the interfacial properties of the carbon fiber/methylsilicone resin composites by grafting $12EO_{15}$-MA-$SiO_2$/MSR on CFs. The results indicate that the interfacial shear strength between CFs and $12EO_{15}$-MA-$SiO_2$/MSR depend on the concentration of $12EO_{15}$-MA-$SiO_2$ and $12EO_{15}$-MA-$SiO_2$/MSR. The optimal condition is that the concentration of $12EO_{15}$-MA-$SiO_2$/MSR is 1%, which contains 6%-$12EO_{15}$-MA-$SiO_2$. At the optimal condition, the interfacial shear strength of $12EO_{15}$-MA-$SiO_2$/MSR-CF is 107.8 MPa, which has significant enhancement compared with that of untreated CF. Based on these findings, it can be concluded that this work provides a facile and effective method to improve the interfacial properties of carbon fiber/methylsilicone resin composites. Such an effective method of preparing $12EO_{15}$-MA-$SiO_2$/MSR-CF shows great commercial potential for improving the interfacial performance without harming the fiber tensile strength.

**Supporting Information**

Experimental details including the preparation of nano-silica and partial characterization data of nano-silica, hyperbranched polymer ($12EO_{15}$-MA), nano-silica grafted hyperbranched polymer ($12EO_{15}$-MA-$SiO_2$) and nano-silica grafted hyperbranched polymer modified methylsilicone resin ($12EO_{15}$-MA-$SiO_2$/MSR) and the thermal properties of $12EO_{15}$-MA-$SiO_2$/MSR, besides the dynamic contact angle analysis of CFs.

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