



Chemical grafting of nano-TiO₂ onto carbon fiber via thiol–ene click chemistry and its effect on the interfacial and mechanical properties of carbon fiber/epoxy composites

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ABSTRACT

The interface in carbon fiber (CF)-reinforced polymer composites plays an important role in determining the mechanical properties of composites. In order to improve the interfacial adhesion between the carbon fiber and resin matrix, we presented a facile and rapid method for grafting nano-sized titanium dioxide (nano-TiO₂) onto the CF surface by means of thiol–ene click chemistry under UV irradiation. Experimental results demonstrate that the chemical bonds are formed between the CF and nano-TiO₂. The introduction of nano-TiO₂ significantly enhances the surface energy of fiber and increases the wettability and mechanical interlocking between fiber and resin, resulting in a significant increase in the interfacial properties of composites. Compared to the raw CF/epoxy composites, the composites reinforced by the CF grafted with nano-TiO₂ show an improvement of 78% in the interfacial shear strength. Moreover, the results of the mechanical properties tests reveal that the flexural strength and tensile strength of composites increase by 32.3 and 39.6% after grafting with nano-TiO₂.

Introduction

The application of fiber-reinforced polymer composites (FRP) has dramatically increased in the aerospace, aviation, defense and automobile industries. Due to excellent mechanical properties and light weight, carbon fiber (CF) is regarded as an ideal candidate for improving the specific strength, specific stiffness and fatigue resistance of polymer

composites [1–4]. It is well known that the mechanical properties of composites are closely related to the load transfer in composites. Previous studies have pointed out that a strong interface offers effective load transfer from the matrix to the fiber, which is beneficial to reduce the stress concentrations and improve the mechanical properties of composites [5–8]. However, the weak interface between CF and polymer matrix due to the inert and nonpolar surface

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of CF is supposed to alter the method of load transfer in a way, resulting in the debonding, crack initiation and failure of composites [9–11].

As a result, a great deal of efforts has been put on the surface modification of CF to improve the interfacial properties of composites [12, 13]. In the work of Huang et al. [14], the hexamethylenetetramine (HMTA) was grafted onto the CF surface to improve the load transfer and interfacial properties through increasing fiber surface area and interfacial stiffness. Fan et al. [15] directly introduced the graphene oxide (GO) sheets dispersed in the fiber sizing onto the CF surface. The introduced GO sheets on the surface of CF increased the strength and toughness of interface because of the “crack healing” effect and the potential chemical reactions between GO sheets and resin. Compared to the commercial-sized fiber composites, the tensile strength of GO-modified carbon fiber composites increased by 34.2%. In addition, the modeling aspect of the interface behavior is an effective route for exploring the improvement of mechanical properties of composites, such as three-phase models and cohesive models [11, 16, 17].

At present, a promising way for surface modification of CF is to introduce nanoparticles (including nano-SiO₂, carbon nanotubes, graphene oxide and nano-TiO₂) onto CF surface [18–22]. The introduction of nanoparticles can increase the surface area and improve wettability. In addition, the nanoparticles on CF surface are useful in improving mechanical interlocking and local stiffening at the fiber/matrix interface. As a typical nanoparticle, nano-TiO₂ has been used in the modification of composites. As reported, a small amount of nano-TiO₂ can significantly increase the mechanical properties of composites. Furthermore, abundant hydroxyl groups on nano-TiO₂ surface provide potential sites for the grafting of TiO₂ onto CF when assisted with silane coupling agent [23, 24]. Thus, nano-TiO₂ is chosen to modify the surface of carbon fiber in this paper.

The introduction of nanoparticles can be achieved by many techniques, such as sol–gel method, vapor deposition, surface coating and chemical grafting [25–27]. But most of them are difficult to apply in application due to their high energy consumption, time-consuming, high cost and environmental pollution. Thus, it is necessary to design some rapid and convenient techniques to introduce nanoparticles onto CF surface. Recently, thiol–ene click chemistry has received much attention due to its high selectivity

and conversion, rapid reaction speed, environmental friendly and simple experimental condition, which has been applied in surface modification of inorganic substrates [28, 29]. Surface modification that utilizes the thiol–ene click reaction mainly includes “grafting to,” “grafting from” and a combination of “grafting to” and “grafting from” methods [30, 31]. In the “grafting to” method, the preformed polymers or inorganic materials are attached onto the substrate via thiol–ene coupling reactions at the substrate surface. Compared to other methods, this method is relatively easy. For the “grafting from” method, the surface of substrate usually contains initiators or residual thiols to induce grafting reactions. In the combination of “grafting to” and “grafting from” methods, a difunctional ene and a difunctional thiol are reacted on a thiol-terminated surface to form linear polymer attached to the substrate surface.

In this paper, to improve the interfacial properties of composites, nano-TiO₂ was grafted onto the carbon fiber surface via thiol–ene click chemistry. To our knowledge, there has been no report on the grafting of nano-TiO₂ onto CF by this technique. Through thiol–ene click chemistry, nano-TiO₂ can be grafted onto the carbon fiber by UV irradiation in a short time (< 1 h), and strong covalent bonds can be formed between nano-TiO₂ and carbon fiber. Therefore, thiol–ene click chemistry is a very promising technique to introduce nano-TiO₂ onto the surface of carbon fiber in a rapid and energy saving fashion. Fourier transform infrared (FT-IR), thermogravimetric analysis (TGA), X-ray photoelectron spectroscopy (XPS), scanning electron microscope (SEM) and dynamic contact angle analysis (DCAA) were carried out for the confirmation of the grafting of nano-TiO₂. The influence of grafting nano-TiO₂ on the interfacial and mechanical properties of epoxy (EP) based composites was also extensively investigated.

Experimental

Materials

Polyacrylonitrile-based carbon fibers used in this study were purchased from Toray Co., Ltd. Nano-TiO₂ was provided by Zhoushan Nano-materials Co., Ltd. Allyl glycidyl ether, (3-mercaptopropyl)trimethoxysilane (KH590) and 3-aminopropyltriethoxysilane (KH550) were purchased from

Aladdin Chemical Reagent Corporation and used as received. 2, 2-Dimethoxy-2-phenylacetophenone (DMPA) was obtained from Sigma-Aldrich. The E-51 epoxy resin consisting of diglycidyl ether of bisphenol A (DGEBA) with its harder (methyltetrahydrophthalic anhydride) was purchased from Fengguang Chemical Co., Ltd. All other reagents used in this work were purchased from commercial sources and used without further purification.

Preparation of vinyl TiO₂

The raw nano-TiO₂ was treated with a mixture of KH550 and toluene at 110 °C for 6 h under reflux. The reaction mixture was washed with toluene for four times to remove excess KH550 and dried under vacuum at 90 °C for 48 h, obtaining the amino-functionalized TiO₂ (TiO₂-KH550) [32]. Then, the resulted TiO₂-KH550 was immersed in allyl glycidyl ether solution (allyl glycidyl ether:ethanol = 1:5), and the mixture was stirred at 30 °C for 48 h. After that, the products were washed with excess ethanol for four times and dried in vacuum oven at 80 °C for 24 h to give vinyl groups-functionalized TiO₂ (vinyl TiO₂).

Immobilization of KH590 onto CF

As-received CF was first treated in 65% nitric acid at 80 °C for 2 h, followed by rinsing and drying to generate oxidized CF. The oxidized CF was then reacted with a solution with a mix ratio of 95:5 (ethanol:KH590) by volume at 70 °C for 6 h. The resulted products were washed with ethanol for several times to remove ungrafted KH590. After drying in vacuum oven at 60 °C for 24 h, the KH590-functionalized CF (CF-KH590) was obtained.

Grafting nano-TiO₂ onto CF surface via thiol-ene click chemistry

To obtain carbon fiber grafted with nano-TiO₂ (CF-TiO₂), the CF-KH590 and vinyl TiO₂ were dispersed into dimethylformamide (DMF) and sonicated at room temperature for 30 min. Then, the UV photoinitiator (DMPA) was placed into the mixture. The click reaction between CF and KH590 and vinyl TiO₂ was performed at room temperature for 30 min by irradiation with a 365-nm UV light. The as-prepared CF-TiO₂ was washed with DMF for four times to remove the ungrafted vinyl TiO₂ and residual

initiator, and dried under vacuum at 90 °C for 48 h. The process of grafting TiO₂ nanoparticles onto carbon fiber surface through thiol-ene click chemistry is illustrated in Fig. 1.

Preparation of composites

The carbon fiber-reinforced epoxy composite specimens for mechanical properties test were prepared by hand layup process, and fiber volume fraction was about 60%. The curing schedule was as follows: 4 MPa for 2 h at 80 °C, 8 MPa for 2 h at 120 °C and 8 MPa for 2 h at 150 °C. Furthermore, the specimens for the micro-bond test were prepared as follows: A mixture of epoxy and hardener was dropped onto a carbon fiber monofilament to form microdroplets, which were oven-cured at 120 °C for 2 h and 160 °C for 2 h in sequence [33]. The cured microdroplets were evaluated by a micro-bond evaluation instrument to obtain the IFSS of composites.

Characterization

A Fourier transform infrared (FT-IR) spectrometer (Shimadzu IR Prestige-21, Japan) was used to investigate the surface functional groups of the CF samples in the range of 500–4000 cm⁻¹. To evaluate the influence of nano-TiO₂ on the thermal behavior of CF and the grafting content of nano-TiO₂, thermogravimetric analysis (TGA) was performed on a thermogravimetric analyzer (TGAQ50, USA) in the range from room temperature to 1000 °C, with a heating rate of 10 °C/min in air. The surface chemical composition of sample was studied by X-ray photoelectron spectroscopy (XPS; Axis Ultra DLD, Japan). The scanning electron microscopy (SEM) was used to observe morphology of the CF samples as well as the fracture surface of composites on a FEI Nova Nano-SEM 450 instrument. All the specimens were sputter coated with gold layer before SEM observation. Dynamic contact angle measurement instrument (Data physics DCAT21, Germany) was used to explore the wetting performance of the carbon fiber, using the deionized water (surface energy (γ) = 72.8 mN/m, dispersive component (γ_d) = 22.1 mN/m, polar component (γ_p) = 50.7 - mN/m) and diiodomethane (γ = 50.8 mN/m, γ_d = 50.8 mN/m, γ_p = 0 mN/m) as the test liquids. The interfacial shear strength (IFSS) of composites was measured by the micro-bond test using a micro-

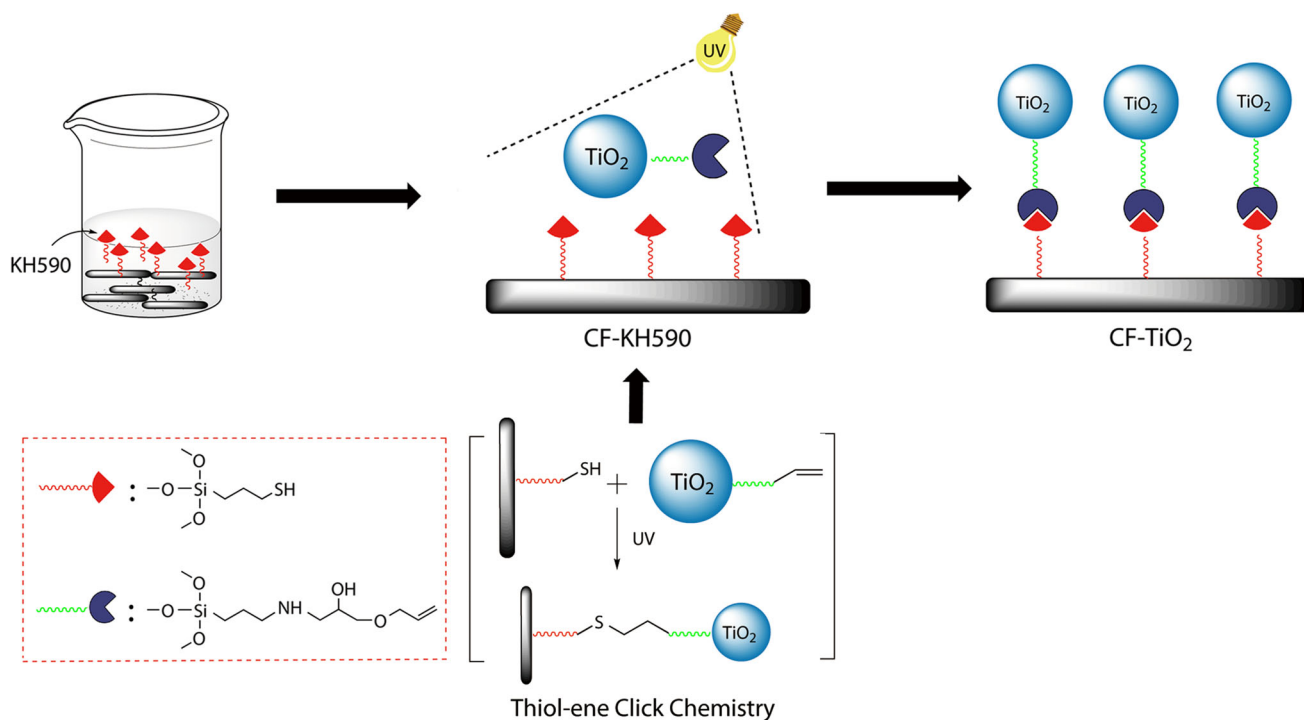


Figure 1 Synthetic route of CF-TiO₂.

bond evaluation instrument (FA620, Japan). At least 100 measurements were conducted for each fiber type. The mechanical test was performed on a universal testing machine (WD-1, China) following GB/T 1447-2005 for tensile properties and GB/T 1449-2005 for flexural properties. The tensile tests were performed at 5 mm/min cross-head speed using type I specimen. The flexural tests were carried out with a cross-head speed of 10 mm/min. More than five specimens were tested for each sample to obtain an average value.

Results and discussion

Characteristics of CF-TiO₂

The FT-IR spectrum of vinyl TiO₂ (Fig. 2a) shows several characteristic peaks at 2924, 810 and 1090 cm⁻¹, corresponding to C-H, C=C and Si-O vibrations, respectively. This result indicates that the vinyl groups were immobilized onto nano-TiO₂ via the grafting KH550. For the CF-KH590 (Fig. 2b), the characteristic peak of -SH groups (2554 cm⁻¹) resulting from KH590 appears in FT-IR curve. After the click reaction, the -SH absorbance peak almost disappears in FT-IR spectrum of CF-TiO₂ (Fig. 2c).

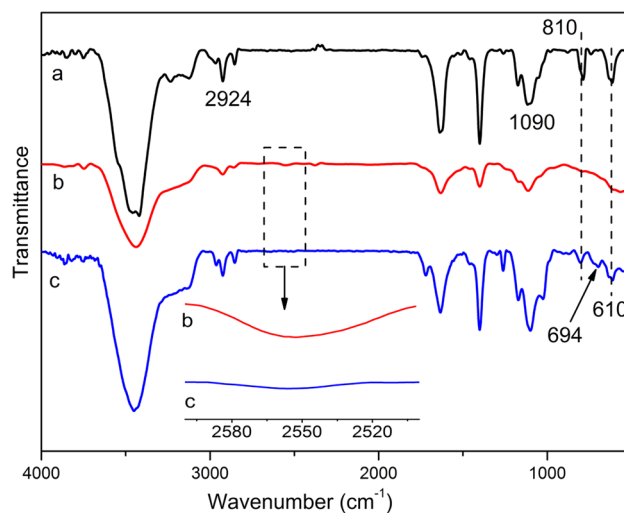


Figure 2 FT-IR spectra of a vinyl TiO₂; b CF-KH590; and c CF-TiO₂.

Moreover, the appearance of the vibration of C-S-C (694 cm⁻¹) and Ti-O (610 cm⁻¹) indicates that the nano-TiO₂ was covalently attached to the carbon fiber surface via the thiol-ene click reaction between vinyl groups in vinyl TiO₂ and -SH groups in CF-KH590 [34, 35].

The XPS was used to characterize the surface elemental composition of CF-TiO₂, and the results are

shown in Fig. 3. The peaks at 530.4, 457.2, 398.1, 283.2, 167.6, 151.9 and 101.1 eV are attributed to O1s, Ti2p, N1s, C1s, S2p, Si2s and Si2p, respectively. The content of elements on CF surface can be calculated by the area of each element. According to the XPS analysis, the atomic percent of Ti on CF-TiO₂ is about 2.05%. In addition, the S2p peak of CF-TiO₂ can be deconvoluted into two peaks with binding energy at 167.4 and 168.6 eV originating from C-S-C and C-S-H, respectively. This result further confirms that the covalent bonds are formed between CF and nano-TiO₂ via thiol-ene click reaction. Meanwhile, some of -SH groups on CF are still not reacted with vinyl groups.

The effect of the grafted nano-TiO₂ on the thermal behaviors of CF was investigated by TGA, and the TGA-DTG curves are shown in Fig. 4. It can be clearly seen that both raw CF and CF-TiO₂ have a weight loss of 1% below 250 °C, which may be due to the decomposition of physically adsorbed water and oxygen-containing groups on the fiber surface. The 5% weight loss temperature (T_5) and maximum degradation rate temperature (T_{max}) are used to investigate the thermal stability. As can be seen, T_5 and T_{max} of the raw CF are 530 and 703 °C, respectively. With the introduction of nano-TiO₂, T_5 and T_{max} of CF-TiO₂ significantly increase to 644 and 835 °C. These results indicate that the thermal stability of carbon fiber can be significantly enhanced with the grafting of nano-TiO₂. Two reasons can be given to explain this finding. First, the thermal stability of TiO₂ is much higher than that of CF. Second,

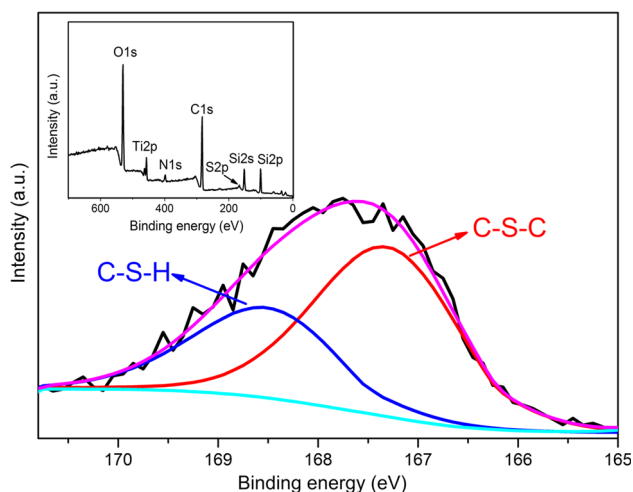


Figure 3 XPS survey spectra and S2p high-resolution spectra of CF-TiO₂.

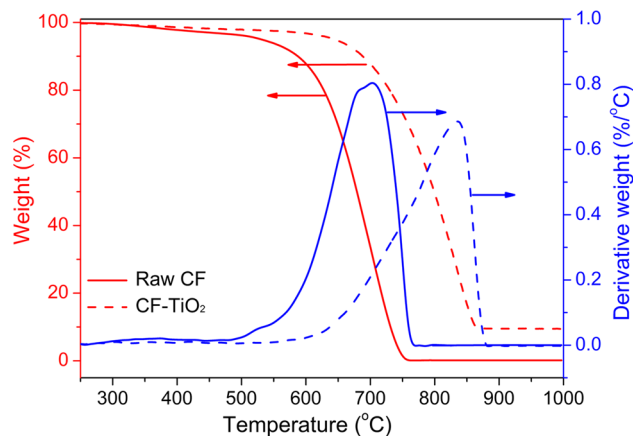


Figure 4 TGA-DTG curves of raw CF and CF-TiO₂.

strong bonding interactions are formed between TiO₂ and CF, as confirmed by FT-IR. This is in agreement with literature work [36]. According to TGA measurement, the grafting content of nano-TiO₂ on the carbon fiber is approximately 9%. The FT-IR, XPS and TGA results clearly demonstrate that nano-TiO₂ has been chemically grafted onto the carbon fiber surface via thiol-ene click chemistry.

The surface characteristics of raw CF and as-prepared CF-TiO₂ were investigated by SEM, and the results are illustrated in Fig. 5. As shown in Fig. 5a, the raw CF shows a relatively smooth surface with some shallow and narrow grooves along the axis direction, which are formed during the production process. This smooth and inert surface leads to a poor interfacial interaction between carbon fiber and resin matrix. Compared to the raw CF, the surface of CF-TiO₂ shows obvious changes. The carbon fiber is evenly covered by a large number of TiO₂ nanoparticles, as shown in Fig. 5b, c. So, the CF-TiO₂ presents a much rougher surface and possesses higher surface area. The increase in surface area may increase the contact point for interaction of fiber with resin matrix, resulting in the improvement of interfacial adhesion of composites. In addition, this rough surface can also increase the mechanical interlocking between carbon fiber and resin.

An analysis of surface energy was carried out on a dynamic contact angle measurement instrument to acquire the information about the surface activity of CF before and after grafting nano-TiO₂. Table 1 summarizes the contact angles, the surface energy (γ), dispersive component (γ_d) and polar component (γ_p) of different carbon fibers. As shown in Table 1, the contact angles of raw CF in deionized water (θ_w) and

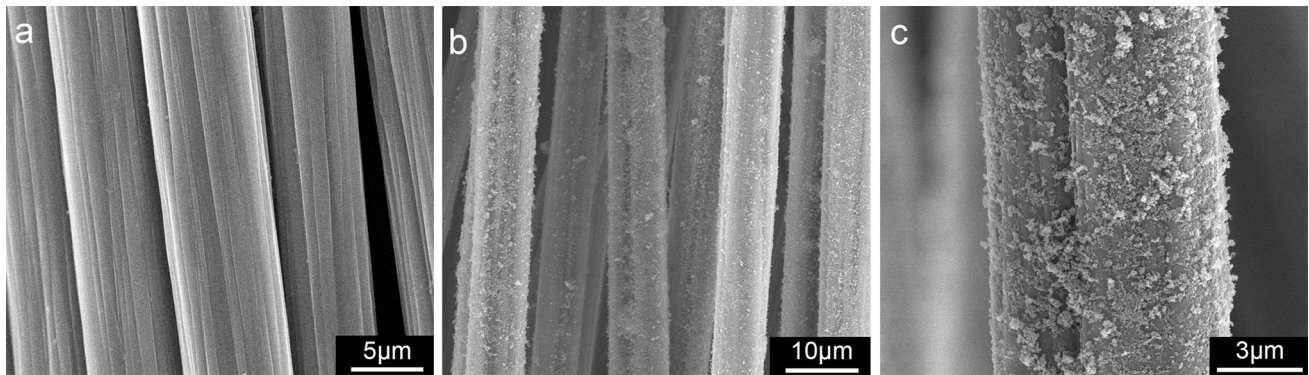


Figure 5 SEM images of **a** raw CF and **b**, **c** CF-TiO₂.

Table 1 Contact angles and surface energy of carbon fibers

Samples	Contact angle (°)		γ_d (mN/m)	γ_p (mN/m)	γ (mN/m)
	Deionized water	Diiodomethane			
Raw CF	68.87	89.43	12.95	20.96	33.91
Oxidized CF	64.75	87.34	13.91	23.34	37.25
CF-KH590	63.64	88.13	13.54	24.52	38.06
CF-TiO ₂	32.24	64.08	26.23	36.66	62.89

diiodomethane (θ_d) are about 68.87° and 89.43°, respectively. A slight decrease in contact angles is found after nitric acid treatment, and the θ_w and θ_d of oxidized CF decrease to 64.75° and 87.34°, respectively. Meanwhile, the contact angles of CF-KH590 do not show significant variation in comparison with the oxidized CF. After grafting nano-TiO₂ onto the CF surface, the θ_w and θ_d further decrease to 32.24° and 64.08°, respectively.

The surface energy (γ) generally consists of two components, dispersive component (γ_d) and polar component (γ_p), which can be determined by the contact angles measured in different liquid. As shown in Table 1, the surface energy of the raw CF is about 33.91 mN/m, with a dispersive component of 12.95 mN/m and a polar component of 20.96 mN/m. It is clearly found that the surface energy increases slightly for the oxidized CF and CF-KH590. However, the surface energy and its components show an obvious increase after grafting nano-TiO₂ onto carbon fiber surface. Compared to the raw CF, the γ_d , γ_p and γ of the CF-TiO₂ increase by 13.28, 15.70 and 28.98 mN/m, respectively. The increase in dispersive component is related to the increased CF surface roughness caused by grafting nano-TiO₂, while the increase in polar component can be interpreted from the high number of functional groups introducing on the CF surface [10, 37]. Therefore, CF-TiO₂ has the

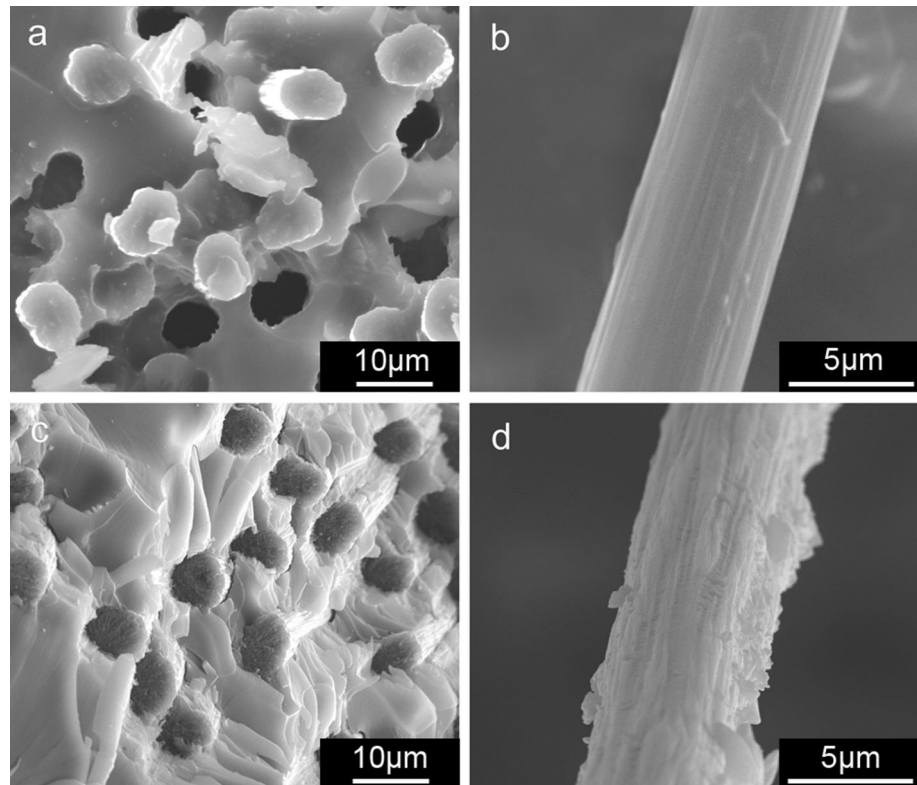
highest surface energy in comparison with raw CF, oxidized CF and CF-KH590. Generally, the increase in surface energy can improve the wettability of the reinforcement to resin matrix, which is beneficial to the improvement of interfacial properties of composites.

Mechanical properties of composites

As we know, the interfacial tests between CF and resin matrix provide a direct evidence for the effect of grafting modification on the mechanical properties of composites. The micro-bond test was used to evaluate the interfacial properties of composites, and the results are shown in Table 2. It can be clearly found that the raw CF/EP composites have the lowest IFSS (41 MPa) due to the poor interfacial interaction between the raw CF and resin matrix. After nitric acid treatment and silane functionalization, the IFSS of oxidized CF/EP composites and CF-KH590/EP composites increases by 9.8 and 17.1%, respectively, as compared with the raw CF/EP composites. These results might be related to the increase in functional groups on the carbon fiber surface. The IFSS of CF-TiO₂/EP composites is the highest (73 MPa), with an increase of 78% in comparison with the raw CF/epoxy composites.

Table 2 Mechanical properties of composites

Samples	IFSS (MPa)	Tensile strength (MPa)	Flexural strength (MPa)
Raw CF/EP	41	240	359
Oxidized CF/EP	45	226	349
CF-KH590/EP	48	241	361
CF-TiO ₂ /EP	73	335	475

Figure 6 Fractographs of **a**, **b** raw CF/EP composites and **c**, **d** CF-TiO₂/EP composites.

The increment in the IFSS of composites is mainly attributed to two factors. On the one hand, the introduction of nano-TiO₂ via thiol–ene click reaction can increase the asperity of the CF surface, resulting in the enhancement of frictional force between fiber and matrix. On the other hand, the significant increase in the surface energy and functional groups improves the wettability between CF and resin matrix and increases the molecular contact at composites interface [15, 21, 38]. The results are in agreement with previous reports for different fibers. Qian et al. [39] used nano-TiO₂ to modify the fiber surface and investigated the effect of treating conditions on the IFSS of composites. Under the optimized treatment condition, the IFSS of treated fiber/EP composites increases by about 56% compared to that of untreated fiber/EP composites. Hence, the grafting of nano-TiO₂ can effectively improve the interfacial

properties of composites, which finally results in the improvement of the IFSS.

The effect of grafting TiO₂ nanoparticles on the mechanical strength of composites was evaluated by examining the tensile strength and flexural strength. Table 2 illustrates the tensile and flexural strength results. As can be seen, the tensile strength and flexural strength for raw CF/EP composites are about 240 and 359 MPa, respectively. In addition, the tensile strength and flexural strength of oxidized CF/EP composites are 226 and 349 MPa, respectively. The decrease in mechanical properties may be attributed to surface damage of carbon fiber caused by nitric acid treatment. Compared to the oxidized CF/EP composites, the CF-KH590/EP composites show a slight increase in mechanical properties due to the introduction of silane coupling agent. After grafting nano-TiO₂ onto the surface of CF, the tensile strength

and flexural strength of CF-TiO₂/EP composites increase by 39.6 and 32.3%, respectively. These values are much higher than the reported ones, for example, 9.2% for tensile strength and 9.5% for flexural strength by Hui et al. [40], indicating that the introduction of nano-TiO₂ onto CF via click reaction can significantly enhance the mechanical properties.

Fracture morphologies of composites

To confirm the reason for enhancement in the mechanical properties, the fractographs of the composites reinforced by different carbon fibers were studied by SEM, as shown in Fig. 6. In the case of raw CF/EP composites (Fig. 6a, b), the raw CF is easily pulled out from the epoxy matrix and a number of holes are observed on the fracture surface. In addition, the pullout carbon fiber is almost clean and few adhering resins remain on the fiber surface. This indicates that the interface of raw CF/EP composites is easily debonded because of poor interfacial adhesion between the raw CF and epoxy resin. In the case of CF-TiO₂/EP composites (Fig. 6c, d), the holes are seldom found on the fractographs of CF-TiO₂/EP composites. Furthermore, the surface of pullout CF-TiO₂ is much rougher than that of raw CF and some of resins are attached on the fiber surface, meaning that the interface of CF-TiO₂/EP composites becomes so strong and stable that the failure is not just confined to the interface. Hence, as mentioned above, the mechanical properties of the CF-TiO₂/EP composites are improved because the external load can be effectively transferred from the resin matrix to the carbon fiber.

Conclusions

In order to modify the carbon fiber surface and improve the interfacial properties of composites, nano-TiO₂ was chemically grafted onto the carbon fiber surface via thiol–ene click chemistry. Experimental results demonstrate that TiO₂ nanoparticles are evenly grafted on the carbon fiber surface through covalent bonds, leading to the increase in the wettability and mechanical interlocking between carbon fiber and resin. Thus, the composite reinforced with CF-TiO₂ had the highest value of IFSS and the best mechanical properties. The presented chemical grafting modification of carbon fiber

through thiol–ene click chemistry, which involved rapid reaction speed and simple experimental condition, promises to be a practical and efficient method for the surface treatment of carbon fiber.

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