

Grafting Graphene Oxide Onto Carbon Fiber for Reinforcing Interfacial and Flexural Properties of CF/Epoxy Composites

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Abstract

Based on the grafting of HBP on the surface of carbon fiber, graphene oxide with excellent mechanical properties was grafted onto the surface of carbon fiber. The multi-structure reinforced fibers grafted with graphene showed an increase in IFSS and bending strength of 74.4% and 45.9% (HBP), respectively, compared to ungrafted carbon fibers. This is due to the multiple interfaces of the hyperbranched polymer and GO, which on the one hand increases the roughness of the fiber and on the other hand provides a large number of polar groups.

Keywords

Carbon fiber, graphene oxide, multiple structure.

1. Introduction

Recently, the researchers transferred the energy of the study to carbon fiber modification by grafting GO or CNTs onto CF surfaces [1-3] to improve the interfacial properties of composites [4,5]. This is because the separation of the matrix from the inorganic body requires excessive energy consumption. In addition, multi-scale reinforcements of graphene containing fibers and in the matrix or on the graphite surface can enhance the interface properties (eg, fatigue life) of the carbon fiber/epoxy composite. Graphene oxide (GO) has an oxygen functional group on its base surface and edges, and is a monolayer of graphite oxide, exhibiting excellent performance.

Graphene as a material with a planar structure, its performance is more superior than the general dimension of the material, and as a single-layer graphite, is widely used in many fields [6]. The addition of graphene oxide can, on the one hand, produce a better modification effect on the carbon fiber body; on the other hand, graphene itself can be used as a resin toughening agent [7,8], which can provide various enhancement effects. Graft graphene oxide is a very promising modification option. In addition, the “bridge”—hyperbranched polymer that acts as a multi-component structural reinforcement in the matrix or on the surface of the fiber, is also one of the boosts in the interfacial bonding performance. Graphene's micrometer size, high aspect ratio, and two-dimensional sheet geometry make it very effective when placed at the microfibre/matrix interface of composites when deflected by bending/shear cracks.[9]

In this paper, from the perspective of interface microstructure, the use of graphene oxide structure and performance advantages, the use of amino-terminated hyperbranched polymer as a connecting bridge [10], prepared CF-HBP-GO multi-structure reinforcement, and the main body of the fiber Performance and interface (HBP-GO) properties were characterized, and the interface enhancement mechanism of the reinforcement obtained by this method was analyzed. Firstly, the HBP hyperbranched macromolecular polymer is grafted on the carbon fiber surface, and the polar functional group at the end of the highly branched branch is used to graft the graphene oxide containing a polar group onto the surface of the carbon fiber, and the interface can be effectively increased. Mechanical engagement effect. Compared with traditional chemical grafting methods, the introduction of hyperbranched polymers and graphene oxides will improve the carbon fiber modification performance and improve the interface properties and mechanical properties.

2. Experiment

2.1 Materials

CF, is the production of Jilin Carbon Co., Ltd. with coating epoxy resin. The number of pores was 3K, the density was $1.76 \text{ g}\cdot\text{cm}^{-3}$, the average diameter was $6.44 \mu\text{m}$. Other reagents were purchased from Aladdin: γ -Aminopropyl-triethoxysilane (γ -APS) was used as coupling agent. The grafting monomer, 3,5-diaminobenzoic acid (DABA) was purified by recrystallization from water and dried in a vacuum at $80 \text{ }^\circ\text{C}$ for 12 h. Lithium chloride (LiCl) was dried at $230 \text{ }^\circ\text{C}$ overnight before use. Other solvents, like triphenyl phosphate (TPP), N-methyl-2-pyrrolidone (NMP), N,N-dimethylformamide (DMF), methanol, acetone and pyridine were analytical grade, provided by Sinopharm Chemical Reagent Co., Ltd, China, and were used without further purification. $\text{K}_2\text{S}_2\text{O}_8$ were purchased from Sigma Aldrich Chemicals. AgNO_3 were supplied by Sinopharm Chemical Reagent Co., Ltd.. Graphene oxide (Laboratory homemade)

2.2 Preparation of CF-HBP-GO and Its Composites

a) Carbon fiber treatment

First, the carbon fiber was subjected to acetone extraction treatment for 48 hours, oxidized at $60 \text{ }^\circ\text{C}$ for 4 hours, and the oxidized carbon fiber was immersed in a lithium aluminum hydride-tetrahydrofuran saturated solution for 2 hours for reduction treatment, and silylated with KH550. In one step, the amino-terminated hyperbranched polymer was grafted onto the fiber surface; HANO was used as a condensing agent to graft graphene oxide onto the carbon fiber surface (seen in Fig.1).

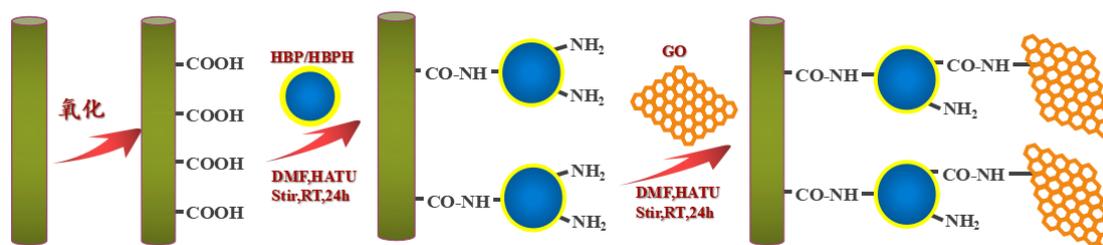


Fig.1. The schematic illustration of the formation of CF-HBP-GO

b) Preparation of composite materials

The resin system was uniformly mixed with a mass ratio of epoxy resin and curing agent of 100:32, and the resin content of the molded parts was controlled within the range of $35 \pm 1.5\%$. The resin-impregnated fibers were placed in a hot press after being placed in a mold preheated to $90 \text{ }^\circ\text{C}$. At $90 \text{ }^\circ\text{C}$, pressure was maintained for 2 hours, the state of the glue was observed, and the pressure was increased to 5 MPa when the gel was started. Raise the temperature to $120 \text{ }^\circ\text{C}$, keep warm for 2 hours, continue to raise the temperature to $150 \text{ }^\circ\text{C}$, continue to hold heat for 3 hours, then turn off the press, maintain pressure until the mold cools, and open the mold.

c) Characterization

X-ray electron spectroscopy, scanning electron microscopy, dynamic contact angle measurement and electronic tension machine were used to test the microstructure and wettability of the fiber and the interface strength and bending properties of the composite.

3. Results and Discussion

3.1 Surface Chemical Composition of CF-HBP-GO Multi-Structure Reinforcement

As can be seen in Figure 2, after the hyperbranched polymer is introduced into the surface of the fiber by means of chemical bonds, the nitrogen content increases to some extent. Because the carbon fibers after grafting HBP and HPBH contain a large amount of terminal amino groups and terminal hydroxyl groups respectively, on this basis, the prepared graphene oxide is grafted, and the element content of the multi-scale reinforcement is changed, and the fitting result by XPS is obtained. It can be concluded that in Table 1, the content of nitrogen is reduced, and the content of oxygen is greatly increased.

After many authoritative studies have confirmed that the graphene oxide has more functional groups, of which carbonyl and other oxygen are more important. The group, a large number of reactive groups that have not participated in the reaction after grafting can further participate in the chemical bonding and action during the curing of the epoxy resin. Because the end groups of the two hyperbranched polymers are different, the results of the grafted graphene are also different. Fig.2b shows that the amino groups on the surface of the carbon fibers after grafting HBP and GO reduce the number of amide bonds.

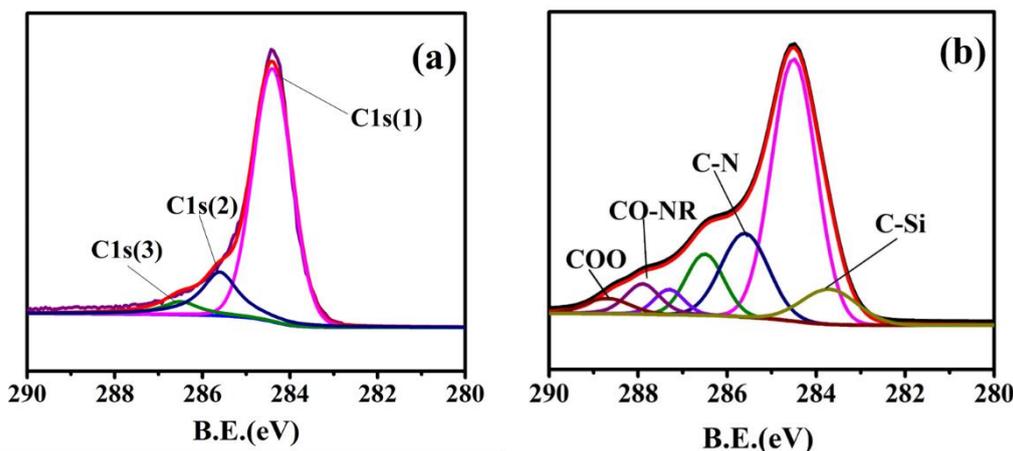


Fig.2. XPS peak fit curve of multi-structured carbon fibers grafted with GO

Table 1 Changes in surface element content of CF-HBP-GO

Samples	Element content (%)					N/C
	C	N	O	Si		
CF	95.57	1.11	3.32	--		0.0116
CF-COOH	88.34	1.67	9.99	--		0.0189
CF-OH	87.56	2.25	10.18	--		0.0257
CF-APS	75.35	2.39	17.89	4.37		0.0317
CF-HBP	75.90	3.76	16.12	4.21		0.0495
CF-HBP-GO	74.50	2.93	18.58	2.99		0.0393

3.2 Microstructure of CF-HBP/HBPH-GO Multistructure Reinforced Body

As shown in Fig. 3, the surface morphology of CF before and after GO treatment was observed using a field emission scanning electron microscope (FESEM). After GO modified carbon fiber, the surface morphology and the grafted hyperbranched polymer are quite different. You can see the distribution of the GO slice on the carbon fiber surface. The GO slice is spread on the surface. The grafted HBP is formed by the polymerization of small molecules, and the surface of CFs is relatively uniform. However, after GO was introduced, the CF surface morphology changed greatly, as shown in Figure d. We can see that different sizes of GO slices are connected to the CF surface, forming a new hierarchy. At the same time, due to the easy discrimination of the graphene structure, there is a layer of material between the fibers, which provides a direct evidence that the new interface is a multi-scale structure of CF-HBP-GO. Since the prepared GO sheet can not guarantee the uniformity of the size of the structure, and due to the presence of the small size effect, the observed GO distribution on the surface of the carbon fiber has non-uniformity. The introduction of graphene oxide significantly increases the roughness of the surface, which is beneficial to the mechanical locking of the epoxy resin compounding process. At the same time, the graphite oxide contains strong polar functional groups, which is beneficial to reduce the surface tension of the fibers and is also beneficial to the

resin. The infiltration spreads on it. The GO sheet was introduced to the surface of the carbon fiber. Based on the effect of changing the hyperbranched polymer, this may be complementary to improving the mechanical properties of the carbon fiber/epoxy composite.

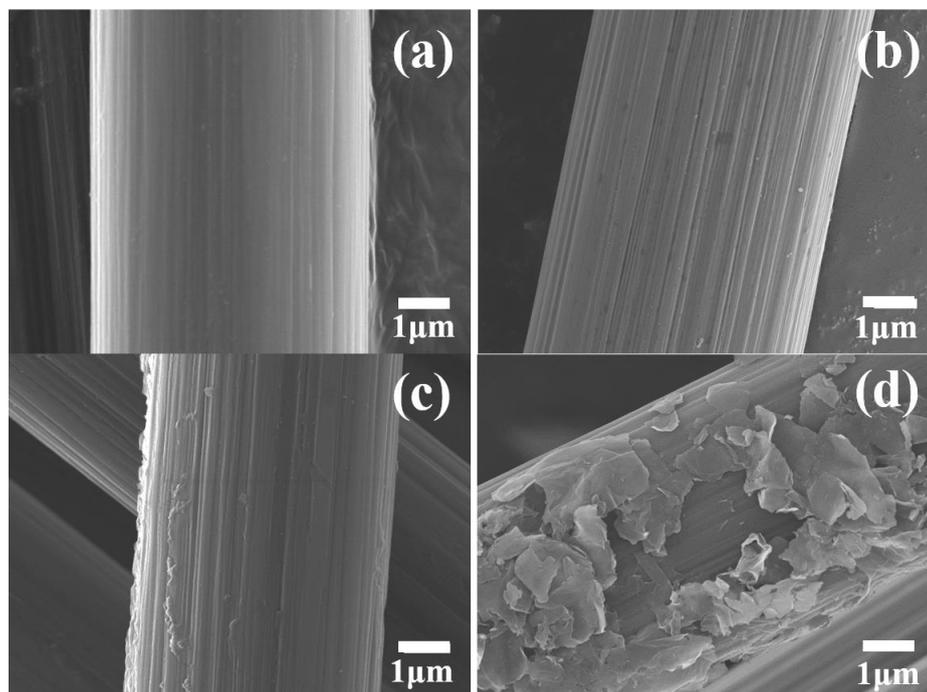


Fig. 3. Surface morphology of multi-component carbon fiber: (a) CF; (b) CF-COOH; (c) CF-HBP (d) CF-HBP-GO

3.3 Infiltration of CF-HBP -GO Multi-Structure Reinforcements

By measuring the contact angle, we can study the wettability between carbon fiber and resin. Usually, the untreated carbon fiber surface has no hydrophilicity, and after the modification, the contact angle formed when the melt flows is reduced. The increase of the surface energy of carbon fiber helps the resin matrix to spread on its surface, thus achieving a good infiltration and recombination between the two, and improving the interface properties of the composite material.

Before the grafting of GO, the contact angles of the surface-treated carbon fibers in water (polarity) and diiodomethane (non-polar) showed a decreasing trend, indicating that the wetting effect of the carbon fiber surface was improved. The carbon fibers with multi-structures formed after grafting onto GO sheets were mainly characterized, and the effects of graphene on the properties of carbon fibers were investigated. The decrease in contact angle and the increase in surface energy of the multi-component reinforcement appear as shown in Fig. 4. Compared with the CF-HBP binary reinforcement, the contact angle of the GO/carbon fiber in different polar solvents shows a difference in polarity. The contact angle in the solvent increases while the opposite change occurs in the polar solvent.

Through the change of the contact angle, the surface energy of the GO/carbon fiber can be obtained by combining the formula calculations. It can be seen from the comparison that the surface energy of the carbon fiber is increasing overall, but this is mainly due to the large amplitude of the dispersion component in the surface energy. increase. For the two components of surface energy, the impact is from different aspects. The factor that determines the change of the dispersion component is the smoothness of the fiber surface. After the carbon fiber grafted with graphene oxide, both the increase of the roughness and the increase of the specific surface area, so the increase of the dispersion component greatly reduces the surface tension of the fiber. Surface energy increases. After the GO is connected to the surface of the carbon fiber through the end group polymer, due to the lamellar structure of the graphene, a large amount of terminal functional groups are consumed in the grafting

reaction, and spreading on the surface of the fiber also causes the occurrence of the hyperbranched polymer and the solvent. isolation. Although functional groups on the surface of graphene oxide make up for this, the content of functional groups cannot be compared with the hyperbranched polymers with higher density of end groups. As a result, the distribution density of the surface active carbon groups in the carbon fiber is reduced, and the polar component of the multicomponent fiber is not increased. Compared with the untreated carbon fiber, the addition of GO flakes is also conducive to the improvement of the carbon fiber properties, and the roughness and the number of reactive groups are greatly increased.

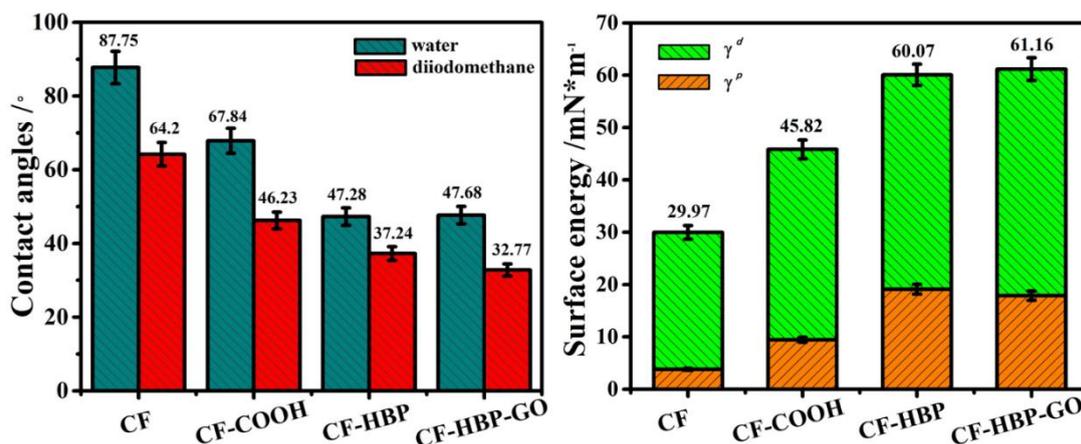


Fig. 4. Contact angle and surface energy analysis of CF-HBP-GO

3.4 Interface Properties of CF-HBP-GO/Epoxy Resin Composites

As shown in Fig. 5, it is clearly shown that the interfacial adhesion strength between the fiber and the matrix after GO modification is enhanced, and the IFSS value reaches 85.13 MPa. This may be due to changes in the chemical composition on the carbon fiber surface. The surface properties change as the amount of GO flakes with many oxygen-containing reactive functional groups increases. It can be seen that the resin matrix is more conducive to the adhesion of the fiber surface. In general, the chemical interaction between the fiber and the matrix has a great influence on the interfacial properties, which can lead to the enhancement of the interaction, the reduction of carbon fiber/epoxy resin interface defects and cracks, and the mechanical strengthening of the composite material. The GO plate has a unique two-dimensional (2D) structure, and mechanical interlocking between the fibers and the matrix also plays a key role in the mechanical properties of the carbon fiber/epoxy composite. Although chemical interactions at the GO interface may have little effect, they have a great influence on the mechanical interlocking between the fibers and the matrix. Aggregation of excess GO sheet in the interface region of the composite may affect the improvement of IFSS.

For multiple reinforcements, many substrates are left on the surface of the de-bonded CF, and de-bonding may occur in the matrix (Figure 6), which means that the interface between CF and epoxy is so strong that the interfacial shear strength becomes greater. Larger, the more epoxy is left on the CF surface. After the binary graft modification of HBP/HBPH and GO, the surface energy and wettability of the fiber increase, and part of the graphene oxide reacts with the functional group on the surface of the carbon fiber, and part of the graphene can be embedded in the resin, and the resin is bound to the resin during extraction. Fiber surface. In addition, due to the non-uniformity of GO on the surface of carbon fibers, the physical entanglement of the molecular chains of the hyperbranched polymer that is not involved in the grafting and the resin may require more energy to break the epoxy resin during the pull-out process. More resin retention can be observed. Thus, it was proved that the interface strength between the resin and the fiber is greatly improved, which is consistent with the result of IFSS.

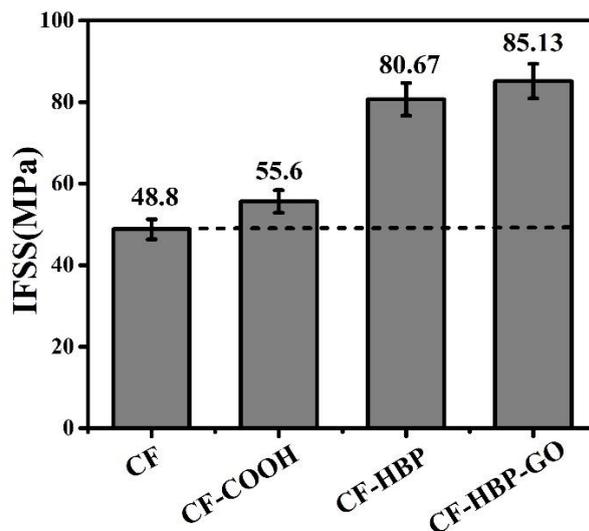


Fig. 5. Interfacial shear strength of multi-component carbon fiber composites

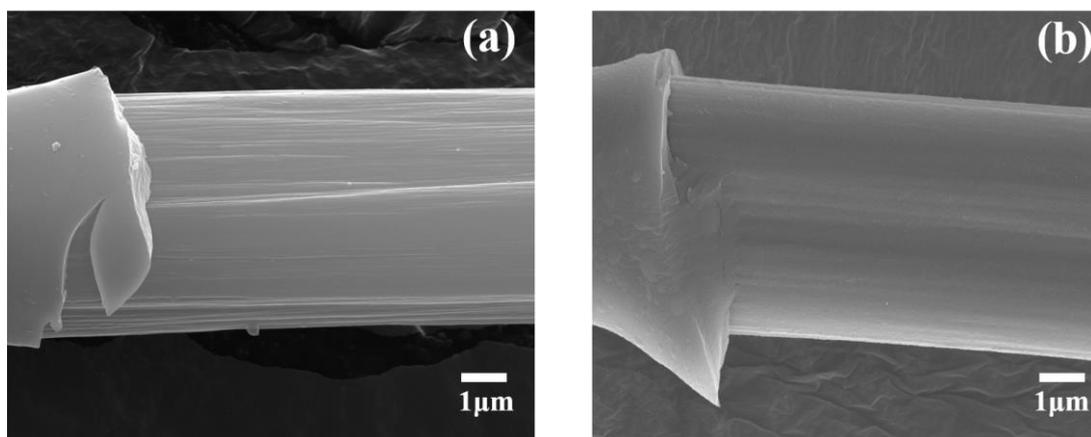


Fig. 6. Multi-structured carbon fiber grafted fracture morphology of grafted GO

3.5 Flexural Properties of CF-HBP-GO/Epoxy Resin Composites

Fig. 7 depicts the flexural strength and flexural modulus of CF/epoxy composites before and after grafting graphene oxide. The bending strength of the composites first appeared to be optimal with the grafting of GO, which was an increase of 45.9% compared to the untreated ones, and also a slight increase (38.2%) compared to the pure grafted hyperbranched polymers. At the same time, the same increasing trend can be seen in the flexural modulus of the composites, which are 101.6% and 71.9%, respectively. The improvement in composite bending properties is due to the enhancement of interfacial adhesion between CF and epoxy matrix caused by GO on CF. The enhanced interfacial adhesion allows for better load transfer from the epoxy matrix to the CF. The bending test results of the composite material show an upward trend, including bending strength and modulus.

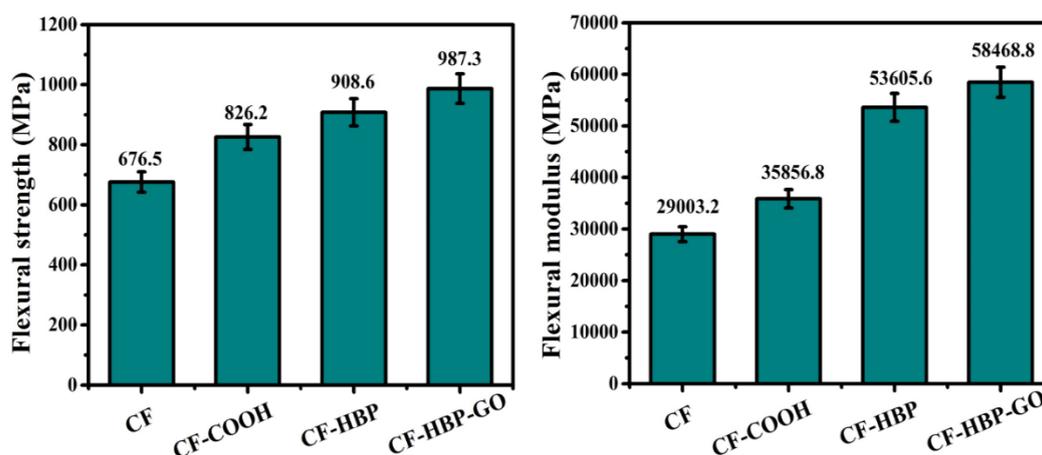


Fig.7. Change in flexural strength and flexural modulus of CF-HBP-GO composites

4. Conclusion

(1) Graphene oxide and carbon fibers with hyperbranched polymers are chemically grafted under the effect of the condensing agent HATU. It can be seen from the XPS results that after grafting graphene onto the CF surface, the carbon fiber surface is grafted with HBP and The functional group content and elemental content of HBPH change. The introduction of GO and hyperbranched molecules has significantly improved the carboxyl content, especially the change of oxygen.

(2) The multi-structured fibrous reinforcement surface topography shows that the grafting of graphene oxide on the fiber surface increases the degree of roughening, and the graphene oxide is attached to the surface of the carbon fiber or spreads or pleates to strengthen the two. Inter-machine interlocks.

(3) The surface polar component and dispersion component of carbon fibers after carbon nanofiber grafting are changed. The oxygen-containing group carried by graphene oxide can increase the polar component of the carbon fiber, and the increase in the dispersion component is a result of the increase in roughness caused by the graphene oxide.

(4) The interfacial bondability and flexural properties of the composites were tested using interface droplet debonding and three-point bending. The multi-scale reinforced fibers grafted with graphene showed a 74.4% and 45.9% increase in IFSS and flexural strength compared to ungrafted carbon fibers, respectively.

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