

## Research Article

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# The tribological properties study of carbon fabric/epoxy composites reinforced by nano-TiO<sub>2</sub> and MWNTs

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**Abstract:** A kind of carbon fabric/epoxy composite was successfully prepared with carbon fiber fabric as reinforced phase and epoxy resin as binder phase, then the nano-TiO<sub>2</sub> and a hybrid system of TiO<sub>2</sub>/MWNTs was added into the carbon fabric/epoxy composite matrix respectively to prepare a kind of nano-composite. The friction and wear properties of CF/EP composites under different load conditions have been studied in this article, during the study the effects of filler types and contents on the tribological properties were researched, at last the worn surfaces were investigated and the abrasion mechanism was discussed. The results showed that: whether filling the nano-TiO<sub>2</sub> alone or mixing the TiO<sub>2</sub>/MWNTs, it was able to achieve a good effect on decreasing friction and reducing wear, and the optimum addition ratio of the nano-TiO<sub>2</sub> particles was 3.0% , meanwhile 3.0% of nano-TiO<sub>2</sub> and 0.4% of MWNTs could cooperate with each other in their dimension, and could show a synergistic effect on modifying the tribological properties of CF/EP composites, the coefficient of friction of the modified composites decreased by 20% and the wear life increased by more than 140% compared with that of pristine composite materials, in the process of friction and wear, the wear form of the composites materials varied from brittle rupture to abrasive wear gradually.

**Keywords:** epoxy resin, carbon fabric, filling modification, friction and wear, synergistic effect

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## 1 Introduction

Polymer matrix composites are increasingly used in the field of mechanical friction because of their unique advantages of light weight, high strength, abrasion resistance, and resistance to load. The thermosetting polymer of epoxy resin (EP) exhibits an excellent adhesion due to the presence of epoxy groups in the structure that can interact with the active hydrogen groups on the surface of the metal material, and is often used as a protective coating that is applied to the surface of metal parts to improve their wear resistance. However, the simple epoxy resin is limited by its cross-linking structure of the three-dimensional network, and has a large brittleness. The peeling resistance and friction and wear properties are inferior to other materials such as polyether ether ketone, polytetrafluoroethylene, and nylon, which is difficult to satisfy increasingly stringent performance requirements for friction materials in real-world conditions. For this reason, people usually adopt the method of compounding epoxy resin with other materials in order to obtain better friction reduction effect [1–4].

Carbon fiber fabric/epoxy composite (CF/EP) is a new type of composite material developed in recent years. This kind of material uses carbon fiber fabric as the base material and epoxy resin as the binding phase, and has the advantages of high modulus, high strength, light weight, abrasion resistance, good toughness, self-lubricating properties and epoxy adhesiveness. It can effectively fit the liner material or anti-wear coating that is attached to the surface of the material to form a harsh friction environment, and has excellent processability and good development prospect [5–9]. Up to now, research reports on such composite materials have mostly focused on the preparation methods of materials, and there are fewer studies on the tribological modification of composite fillers. Therefore, this experiment selected nano-TiO<sub>2</sub> and multi-walled carbon nanotubes (MWNTs) as fillers, focused on the effect of filler content on the tribological performance of carbon fiber fabrics/epoxy substrates under

**Table 1:** The parameters of carbon fiber plane fabric

Type	Reinforcement Yarn		Weave	Fiber Count (10mm)		Weight (g/m <sup>2</sup> )	Width (mm)	Thickness (mm)
	Warp Yarn	Weft Yarn		Warp Ends	Weft Picks			
HY-1K-P	1K	1K	Plain	10.5	10.5	140	100	0.17

different friction conditions [10–15], analyzed the friction and wear mechanism, and discussed the synergistic relationship between nano-TiO<sub>2</sub> and multi-walled carbon nanotubes.

## 2 Experimental part

### 2.1 Experimental raw materials and main equipment

Epoxy resin (E-44, Zhenjiang Danbao Resin Co., Ltd.); Low molecular polyamide (650, Zhenjiang Danbao Resin Co., Ltd.); Butanone (AR, Xi'an Chemical Reagent Factory); Toluene (AR, Tianjin Damao Chemical Reagent Factory); Carbon fiber flat fabric (Parameters are shown in Table 1, Jiangsu Tianniao High-tech Incorporated Company); Nanometer TiO<sub>2</sub> (25nm, Shanghai Chaowei Nano Inc., Anatase); Multi-walled carbon nanotubes (purity >94.0%, Chengdu Institute of Organic Chemistry, Chinese Academy of Sciences); Silane coupling agent (KH550, Nanjing Dunning Coupling Agent Co., Ltd.); Ultrasonic cleaner (KQ3200E, Kunshan Ultrasonic Instrument Co., Ltd.); Magnetic stirrer (ZNCL-S, Zhengzhou Kaipeng Test Instrument Co., Ltd.); Friction and wear tester (MM-200, Xuanhua Tester Factory).

### 2.2 Sample preparation

#### 2.2.1 Formulation of epoxy resin components

The epoxy resin binder phase used in this test contains two components of A and B. In the A component, the base epoxy resin and diluent butanone were formulated according to the ratio of  $m_{\text{epoxy}}:v_{\text{butanone}} = 1:2.4$ ; in the B component, the curing agent polyamide and the diluent toluene were also formulated in the ratio of  $m_{\text{polyamide}}:v_{\text{toluene}} = 1:2.4$ .

#### 2.2.2 Surface treatment of carbon fiber fabrics and nanofillers

The appropriate size of carbon fiber fabrics was cut and soaked in acetone solution, ultrasonic cleaning at room temperature for 2h, and transferred to a constant temperature drying oven 80 °C drying 24h standby. According to the proportion of carbon fiber fabric/epoxy composite material of 2%, the appropriate mass of KH-550 silane coupling agent was weighed and formulated into a 90% ethanol solution. Nano TiO<sub>2</sub> and multi-wall carbon nanotubes were respectively added. And the mixture was magnetically stirred for 60 minutes at 120°C. The solution was evaporated to dryness and cooled to room temperature to prepare a modified nanofiller.

#### 2.2.3 Preparation of carbon fiber fabrics/epoxy composites

During adding component A, appropriate mass fraction of modified nanofiller was added. Then, the carbon fiber fabric was repeatedly impregnated and brushed in epoxy resin uniformly mixed with the B component in a mass ratio of 1:1 until the carbon fiber fabric accounted for 60% to 70% of the mass fraction of the composite material. Finally, the composite material was bonded to the surface of a 45<sup>#</sup> steel block [8] and solidified at 80° C for 2 hours under a vacuum condition of 0.1 MPa to prepare a test sample.

### 2.3 Experiment method

#### 2.3.1 Tribological performance test

The MM-200 ring-block friction and wear tester was used to evaluate the tribological properties of the material. The initial grind thickness of the carbon fiber fabric/epoxy resin composite is 1.5mm. The coated steel block size is 20 mm × 8 mm × 11 mm. The friction pair is a quenched 45<sup>#</sup> steel ring with a hardness which is from 40 to 50 HRC and a size of ø50 mm × 10 mm [16]. Before the friction and wear test, the surface of the dual steel ring was sanded with 800<sup>#</sup> and 1200<sup>#</sup> water-based sandpaper successively to

make surface roughness  $R_a$  reach 0.2–0.45  $\mu\text{m}$ , and cleaned with acetone. During the test, the sliding friction linear velocity was maintained at 0.54 m/s, the test time was fixed at 30 min for each group, the applied loads were 150 N and 200 N in sequence, and the ambient relative humidity was 50  $\pm$  5%. Dry friction test was conducted for all tests at room temperature.

The friction coefficient  $\mu$  of the material during the test can be calculated by reading the friction torque data on the tester and using the following formula:

$$\mu = M / (R \times P)$$

Where  $M$  – friction torque in the formula,  $N \cdot m$ ;  $R$  – pair steel ring radius, m;  $P$  – imposed load, N;

After the test was completed, the wear depth of the carbon fiber fabric/epoxy resin composite was measured by using a digital micrometer with an accuracy of 0.001 mm. And by using the sliding friction distance divided by the wear depth, the friction wear life of the composite was calculated [9]  $W$  to characterize the wear resistance of the material itself:

$$W = (V \times t) / H$$

Where  $V$  – friction line speed, m / s;  $t$  – friction test time, s;  $H$  – wear depth,  $\mu\text{m}$ .

### 2.3.2 Surface morphology and phase analysis of nanofillers

A small amount of nano-TiO<sub>2</sub> and multi-walled carbon nanotubes powders were added to anhydrous ethanol for 30 minutes to be fully dispersed. A few drops of the suspension were sucked with a dropper and carefully dropped onto the surface of a copper mesh covered with a support film. After the solvent was dried, the surface morphology was observed behind a high-resolution transmission electron microscope (HRTEM) of model JEOL-2010.

The D8 ADVANCE X-ray diffractometer (XRD) manufactured by Bruker Co., Germany was used to characterize the structure of nano-TiO<sub>2</sub> and multi-walled carbon nanotubes. Continuous spectroscopy was used, where the tube voltage was 50 kV, the tube current was 40 mA, the scanning angle was  $2\theta$ . 10–90°, and the scanning rate was 10°/min.

### 2.3.3 Wear and profile analysis of composite material

After the end of the test, the surface of the worn test specimen was sprayed with gold, and placed under a

JSM-5610LV scanning electron microscope for morphology analysis, where the acceleration voltage was 20 kV.

## 3 Results and discussion

### 3.1 Structural analysis of nanofillers

The transmission electron microscope images of nano-TiO<sub>2</sub> and multi-walled carbon nanotubes were respectively shown in Figure 1(a) and Figure 1(b).

From Figure 1(a), it can be seen that the nano-TiO<sub>2</sub> particles used in the experiment are all regular spherical shapes, most of which are between 20 nm and 30 nm in diameter, and the three-dimensional dimensions are within the nano-scale. As can be seen from Figure 1(b), the diameter of the wall of multi-walled carbon nanotubes is basically in the range of 10 nm to 20 nm. The walls of the multi-walled carbon nanotubes are intertwined with each other, and the aspect ratio is extremely large. The multi-walled carbon nanotubes still appear nearly transparent when they overlap. It can be inferred that its wall is very thin.

Figures 2(a) and 2(b) are the XRD patterns and electron diffraction (ED) images of nano-TiO<sub>2</sub>, respectively, and Figure 2(c) is corresponding to the XRD patterns of multi-walled carbon nanotubes.

As can be seen from Figure 2(a), there is a prominent main diffraction peak at  $2\theta = 25.5^\circ$  for nano-TiO<sub>2</sub>, and there are also relatively strong characteristic diffraction peaks at  $2\theta = 38.05^\circ$  and  $2\theta = 48.06^\circ$ , respectively. The characteristic peaks are generally more sharp, which proves that the nano-TiO<sub>2</sub> particles belong to the anatase TiO<sub>2</sub> with good crystallinity. At the same time, the characteristic bands of polycrystalline diffraction rings can also be seen in Figure 2(b), indicating that the selected nano-TiO<sub>2</sub> belongs to a crystal structure with good purity; from Figure 2(c), it can be seen that the material has sharp characteristic peaks at  $2\theta = 25.93^\circ$  and  $2\theta = 42.66^\circ$ , corresponding to the (002) plane and (100) plane, respectively. It shows that the multi-walled carbon nanotube also belongs to the crystal structure, and the main diffraction peak position is close to the (002) peak ( $2\theta = 26.3^\circ$ ) of the graphite material. It shows that the multi-walled carbon nanotubes may contain part of the amorphous carbon phase or graphite phase.

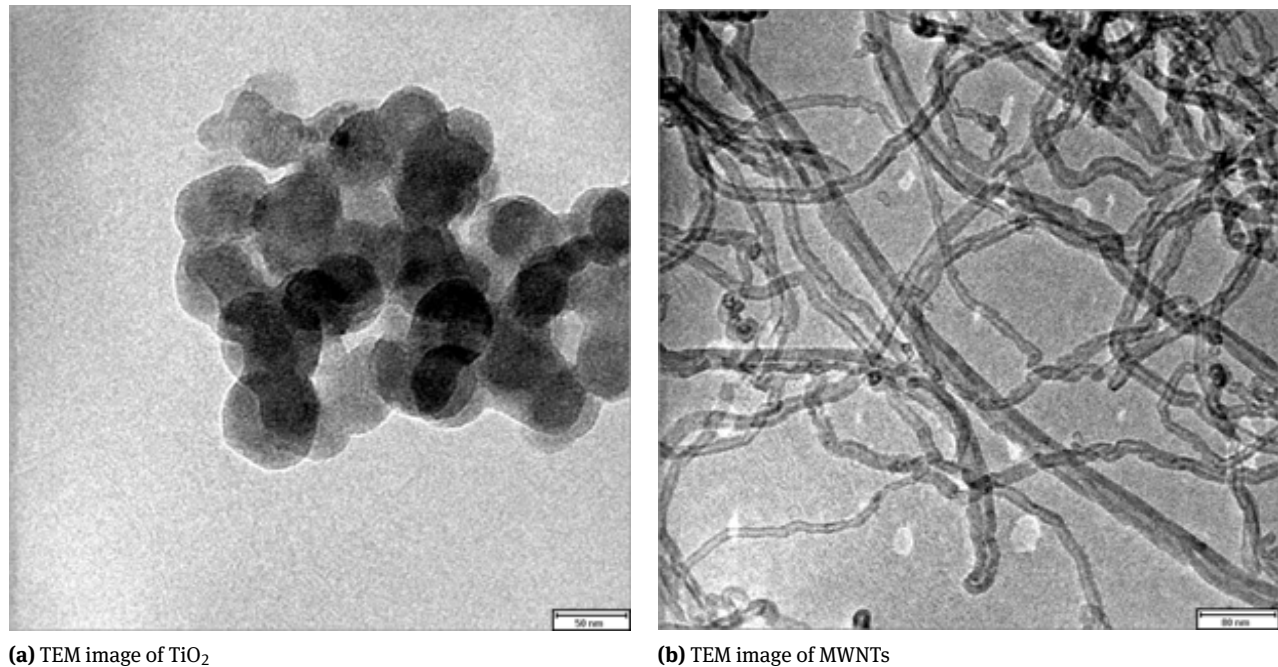


Figure 1: TEM images of the two kinds of nano filler particles

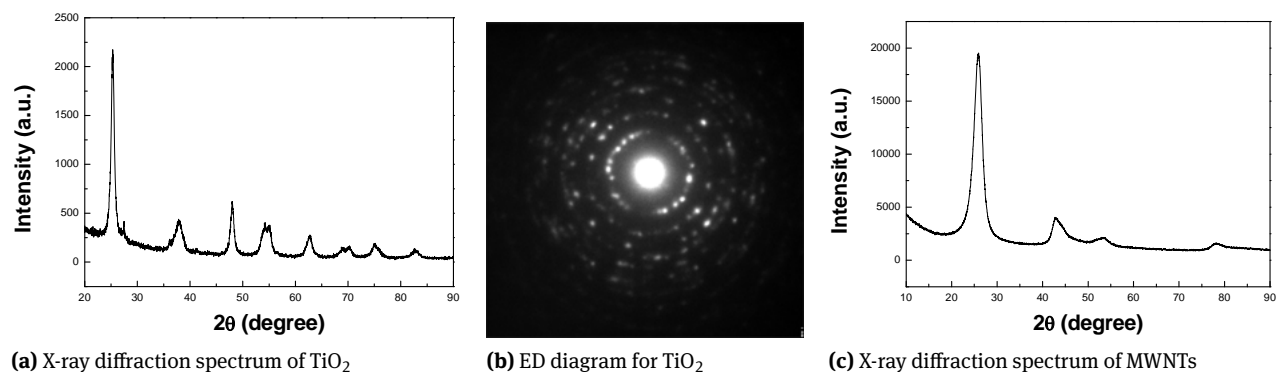


Figure 2: The crystal structure of the two kinds of nano filler particles

### 3.2 Friction and wear properties of carbon fiber fabric/epoxy resin composites

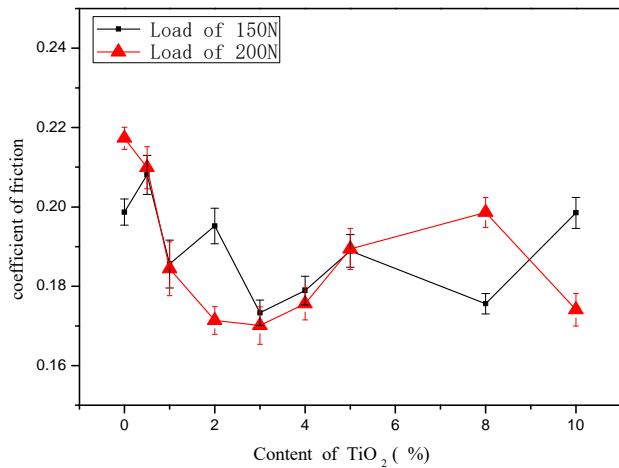
#### 3.2.1 Analysis of friction performance of CF/EP filled with nanometer $\text{TiO}_2$

Figure 3 shows the change of friction coefficient of carbon fiber fabric/epoxy resin composite material under 150N and 200N test conditions after nano- $\text{TiO}_2$  filling alone.

It can be seen from the figure that the friction coefficient of the pure carbon fiber fabric/epoxy resin composite is stable between 0.18 and 0.23, and the friction coefficient increases slightly with the increase of the load; under the condition of 150N load, the addition of different pro-

portions of nano- $\text{TiO}_2$  has little effect on the friction coefficient of the composites, and the friction coefficient shows fluctuation with the increase of filler addition. When the amount of filler added is 3%, the friction coefficient of the composite material is the lowest value of 0.1733. Compared with the pure carbon fiber fabric/epoxy resin composite, the friction coefficient is decreased by 12.78%. Under the 200N load condition, the friction coefficient of composites first decreases and then increases with the increase of the content of nano- $\text{TiO}_2$ . When the filler addition ratio is 3%, the friction coefficient of the composite material takes the lowest value of 0.1701. Compared with the pure material, the friction coefficient is reduced by 21.72%, and the improvement effect is significant [17–19].





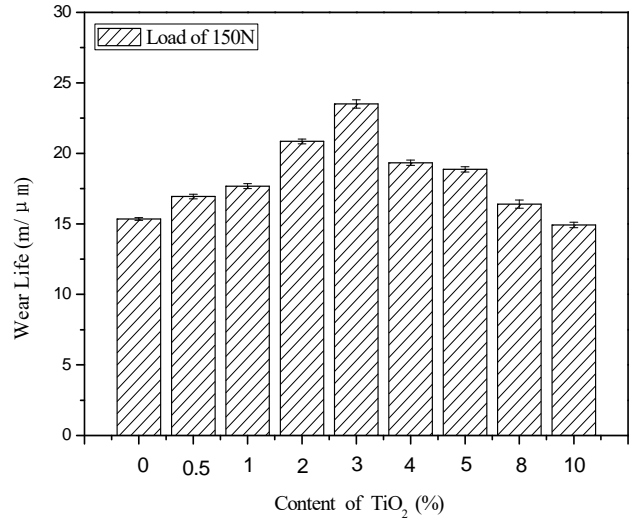
**Figure 3:** Effects of addition amount of nano-TiO<sub>2</sub> on the friction coefficient of CF/EP composites under different loads

Figure 4(a) and Figure 4(b) respectively show the friction and wear life relationships of carbon fiber/epoxy composites under 150 N and 200 N test conditions after sole nano-TiO<sub>2</sub> filling.

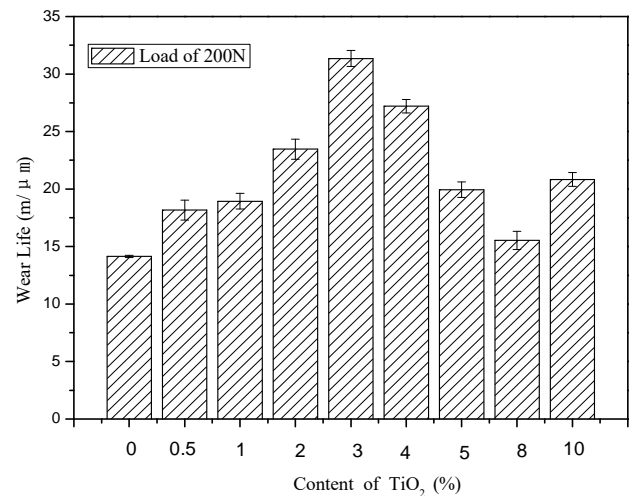
From Figure 4(a), it can be seen that under the load condition of 150N, with the increase of the content of nano-TiO<sub>2</sub> added, the friction/wear life of CF/EP composites first increases and then decreases; when the filler loading is 3%, the friction wear life of the modified composite is 23.51m/μm, which is 53.22% higher than that of the unmodified CF/EP material; when the content of nano-TiO<sub>2</sub> is more than 3%, the wear properties of the composites begin to deteriorate. When the load condition is increased to 200N, as shown in Figure 4(b), the change trend of the wear life of the composite material is larger than that under the 150N load condition, and the overall trend of the curve appears more "steep"; while the content of nano-TiO<sub>2</sub> increases from 0% to 3%, the tribological wear life of the composite changes from 14.15 m/μm to 31.35 m/μm, which is increased 121.55%; among them, when the load is increased from 150N to 200N, the enhanced wear life of the pure CF/EP material due to the external force shearing is reduced. After CF/EP composites is modified by the nano-TiO<sub>2</sub>, its friction and wear life is slightly increased[12]. It can be speculated that the anti-wear reinforcement effect of nano-TiO<sub>2</sub> on CF/EP substrates can be more fully used under higher loading conditions.

Scanning electron microscopy is used to further observe the wear morphology of unmodified CF/EP materials and CF/EP composites modified by 3% nano-TiO<sub>2</sub> respectively under 150N and 200N, as shown in Figure 5.

From Figure 5(a), it can be seen that after a certain period of friction and wear tests of the unmodified CF/EP



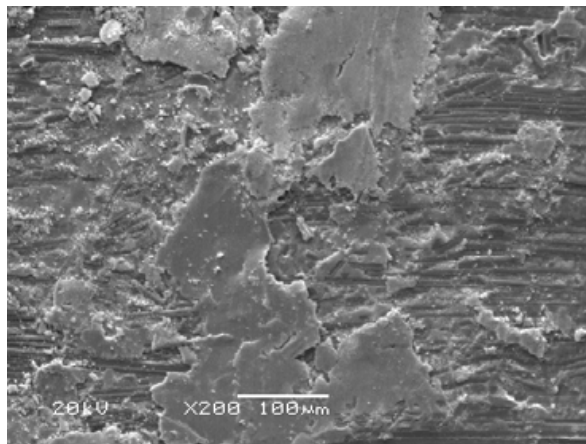
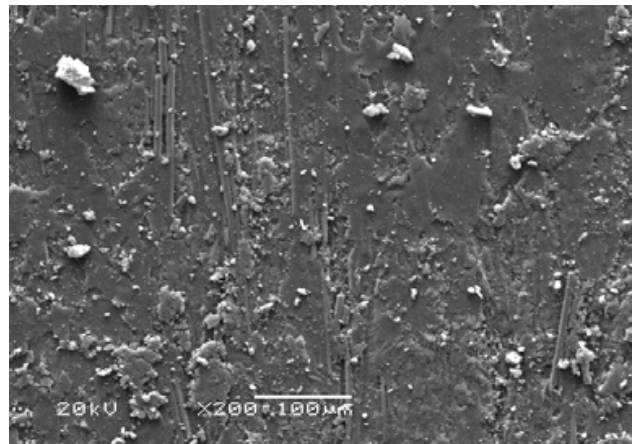
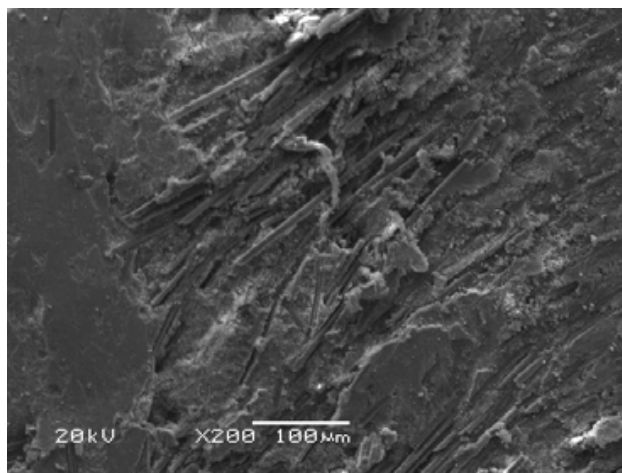
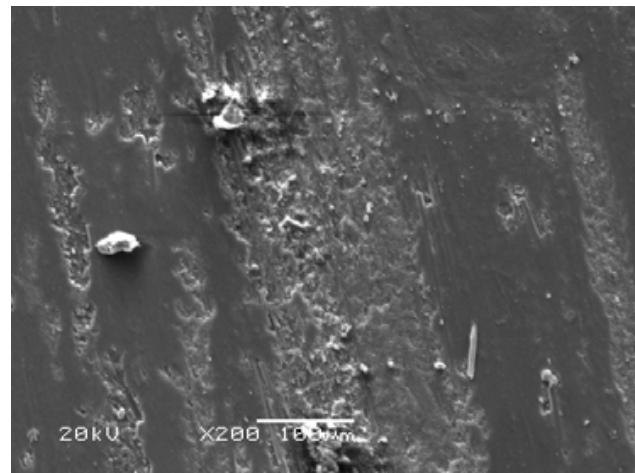
**(a)** Load of 150N



**(b)** Load of 200N

**Figure 4:** Variation of wear life of CF/EP composites with different nano-TiO<sub>2</sub> contents under different loads

matrix material under a load of 150 N, a deep groove-like scratch occurs at the interface of the wear surface. Large chunks of bonded resin phase of the block is destroyed and peeled off. The only part of the resin base material appears severe extrusion plastic deformation, and it is intermittently distributed on the surface of the material, exposed a lot of cut fibers, and shows the appearance of brittle peeling and fatigue wear as a whole; after being filled with 3% nano-TiO<sub>2</sub>, the peeling of the adhesive resin on the worn surface is effectively suppressed, the wear scar is relatively shallow, and a large amount of fiber is not exposed, as shown in Figure 5(b); when the load is increased to 200N, the unmodified CF/EP matrix material is subjected to a more severe shearing action. A large number

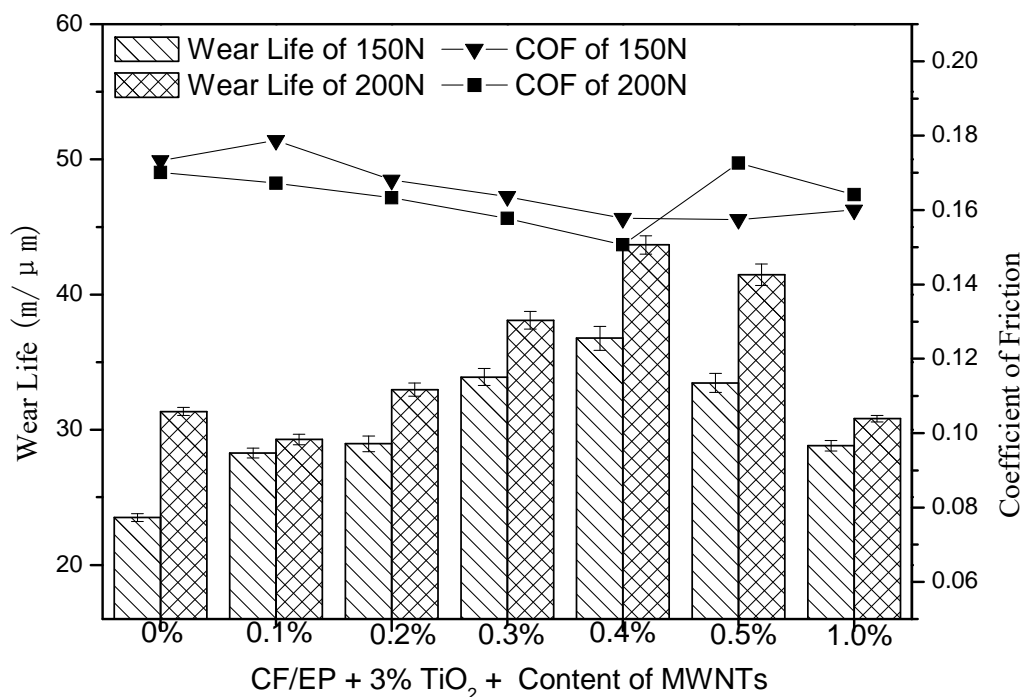
(a) 0% TiO<sub>2</sub> + CF/EP under load of 150N(b) 3.0% TiO<sub>2</sub> + CF/EP under load of 150N(c) 0% TiO<sub>2</sub> + CF/EP under load of 200N(d) 3.0% TiO<sub>2</sub> + CF/EP under load of 200N**Figure 5:** SEM micrographs of the worn surfaces of composites

of fibers in the surface layer are pulled out and cut off, and the interface is uneven. As shown in Figure 5(c), there is a more severe fatigue and wear pattern; Figure 5(d) shows the wear morphology of CF/EP composites modified by 3% nano-TiO<sub>2</sub> under 200N load. It can be seen that the structure of the material is maintained well, and some cluster-like abrasive particles are scattered in the surface layer. But it does not cause serious ploughing scratches, the overall surface is relatively flat, and the shape of the sheet is sticking and transferring along the sliding direction [20].

From the above characteristics, it can be seen that the adhesive phase of epoxy resin in the surface layer of the unmodified CF/EP material is brittle. Under the effect of the shearing force of the mating part, it is prone to cracking and spalling, and the fiber reinforced layer in the depth of the surface is also partially pulled out and cut off. Because the abrasion resistance of carbon fiber is much better than

that of epoxy resin, it can be inferred that the structural component that plays a major role in the friction process is still the carbon fiber fabric layer [21]. However, although carbon fiber can rely on high-strength, high-modulus anti-wear effects and self-lubrication, it is also a material with high brittleness. In the harsher friction environment, once the carbon fiber wears thin, it is easy to generate high-hardness debris residue, which in turn causes severe abrasive plunge cutting of the epoxy substrate. Until the carbon fiber begins to break, it will also mean that the material is resistant to wear.

After adding a certain amount of nano-TiO<sub>2</sub>, due to the small size effect and dispersion strengthening effect of nano-particles, the friction and wear properties of CF/EP materials have been correspondingly improved. Thereinto, the filling content of nano-TiO<sub>2</sub> is 3.0%, the CF/EP substrate has a better friction reduction effect. However, as a



**Figure 6:** Variation of wear life and friction coefficient of CF/EP composites modified by nano-TiO<sub>2</sub> with different MWNTs contents under different loads

whole, with the increase in the amount of filler added, the friction coefficient still shows a tendency to change, and there are still some brittle exfoliation pits on the worn surface. It is speculated that this may be related to the agglomeration and loss of nano-TiO<sub>2</sub> fillers in CF/EP substrates.

In order to further improve the tribological performance of CF/EP materials, the proportion of experimentally fixed nano-TiO<sub>2</sub> is 3.0%. Based on this, a multi-walled carbon nanotubes material is added to explore the effect of TiO<sub>2</sub>/MWNTs hybrid system on the friction and wear properties of CF/EP composite substrates.

### 3.2.2 Analysis of the frictional behavior of CF/EP composite filled with nanometer TiO<sub>2</sub> and MWNTs

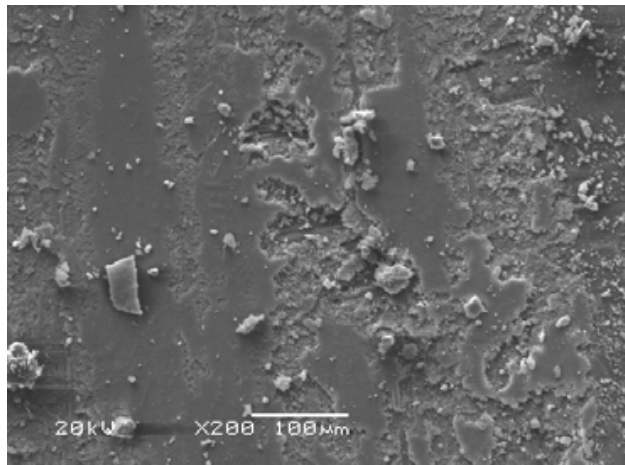
The nano-TiO<sub>2</sub>/MWNTs hybrid system (with a constant loading of 3.0% nano-TiO<sub>2</sub>) is shown in Figure 6. The friction coefficient and wear life of filled CF/EP composites under test conditions of 150N and 200N are plotted against the MWNTs content.

It can be seen from the figure that, under different load conditions, with the increase of the amount of MWNTs added, the friction wear life of the TiO<sub>2</sub>/MWNTs hybrid-filled CF/EP composites shows the law of first increase and then decrease, the friction coefficient phase shows

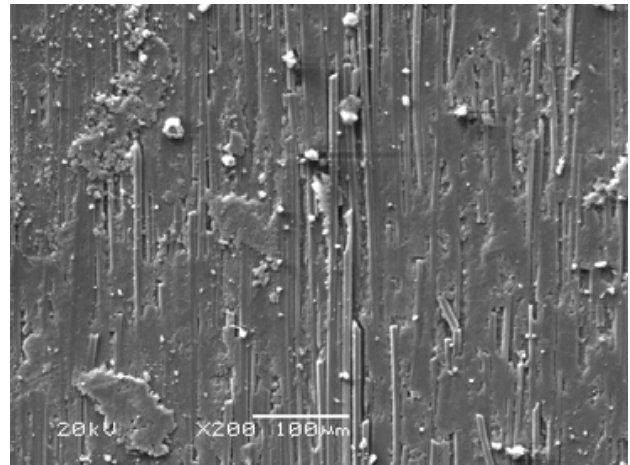
a gradual decline correspondingly; as a whole, the friction and wear properties of CF/EP composites modified by TiO<sub>2</sub>/MWNTs hybrid system are better than those of pure CF/EP, and the friction and wear properties of composites are more obvious under higher loading conditions; thereinto, the optimal addition of MWNTs is 0.4%. When the load is 150N, the added ratio of nano-TiO<sub>2</sub> is 3.0% and the added ratio of MWNTs is 0.4%, the friction wear life of the composite reaches 36.76 m/μm, which is increased by 1.40 times in comparison with the unmodified CF/EP material. While the friction coefficient is decreased by 20.58% compared with that before the modification; when the load is increased to 200N, the friction and wear life of the modified CF/EP composites is further increased to 43.66 m/μm, which is 2.08 times higher than before modification, and the improvement effect is very significant. The friction coefficient of the material is also reduced to the minimum value of 0.1506, and the relative pure CF/EP is reduced by 30.69%; therefore, in a comprehensive view, proper mixing of TiO<sub>2</sub>/MWNTs into the CF/EP matrix will greatly improve the antifriction and wear resistance of the material.

Figure 7 (a-f) is a scanning electron microscope photograph of the worn surface filled with CF/EP composites in the TiO<sub>2</sub>/MWNTs mixed system respectively under 150N and 200N load.

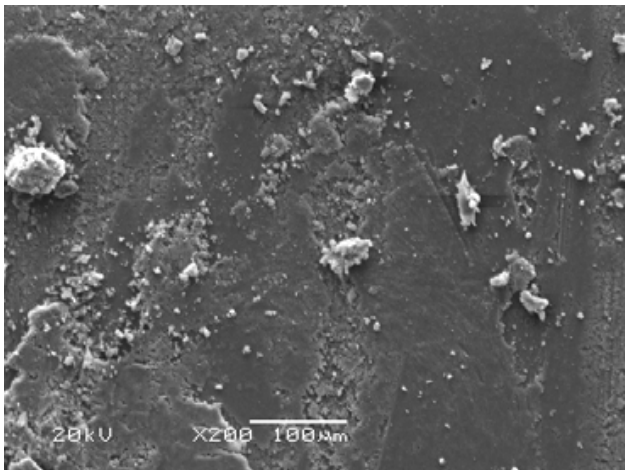




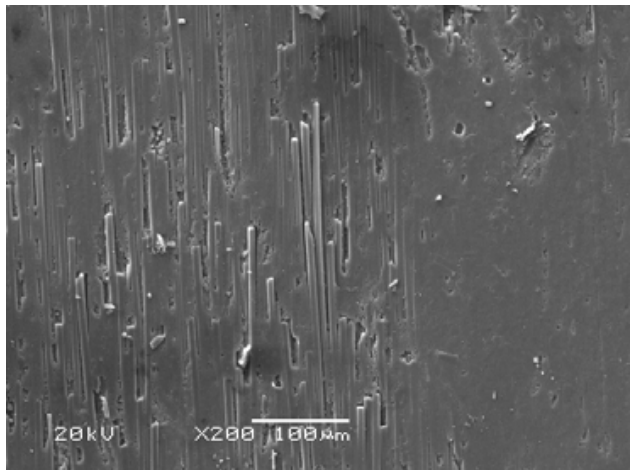
**(a)**  $\text{TiO}_2(3.0\%)/\text{MWNTs}(0.2\%) + \text{CF/EP}$  under load of 150N



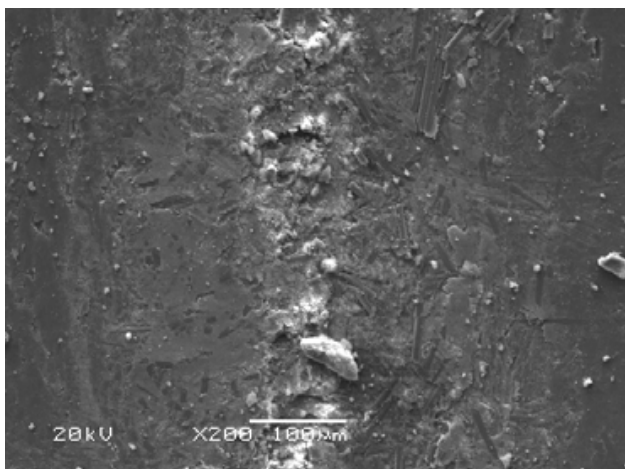
**(b)**  $\text{TiO}_2(3.0\%)/\text{MWNTs}(0.2\%) + \text{CF/EP}$  under load of 200N



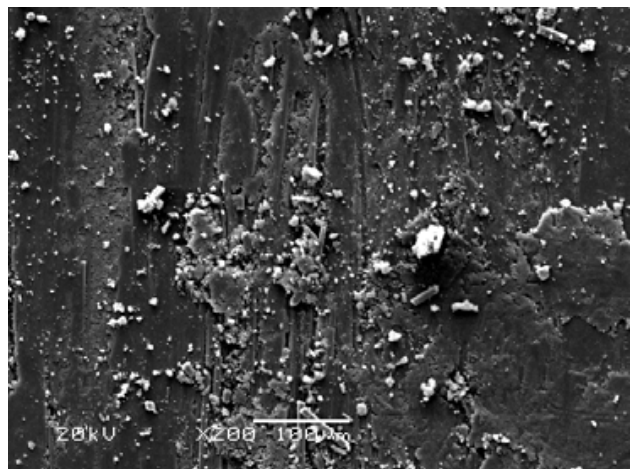
**(c)**  $\text{TiO}_2(3.0\%)/\text{MWNTs}(0.4\%) + \text{CF/EP}$  under load of 150N



**(d)**  $\text{TiO}_2(3.0\%)/\text{MWNTs}(0.4\%) + \text{CF/EP}$  under load of 200N



**(e)**  $\text{TiO}_2(3.0\%)/\text{MWNTs}(1.0\%) + \text{CF/EP}$  under load of 150N



**(f)**  $\text{TiO}_2(3.0\%)/\text{MWNTs}(1.0\%) + \text{CF/EP}$  under load of 200N

**Figure 7:** (a-f) SEM micrographs of the worn surfaces of composites



From Figure 7(a), 7(c) and 7(e), it can be seen that the wear surface of the modified CF/EP composite is dotted with some of the resin-phase flaking pits and the rim of the flaking pit is sharp and neat, which is in the brittle exfoliated form, when the system is filled with TiO<sub>2</sub>(3.0%)/MWNTs (0.2%) under the condition of 150N load. A small amount of fiber debris is found inside the pit, but no deep scratches is found on the outer surface of the pit. The overall wear of the material is still dominated by fatigue wear, as shown in Figure 7(a); when the content of MWNTs is increased to 0.4%, the pit structure on the wear surface of the material is significantly reduced, the scratch surface is flat and continuous, but the layered topography is exhibited along the sliding direction, exhibiting the wear characteristics of adhesion transfer, see Figure 7(c); it is speculated that the addition of MWNTs improves the brittleness of the CF/EP matrix material, which makes it easier for the composite to form a transfer film during friction with the metal friction pair, thereby playing a role in isolation, lubrication, friction reduction and wear resistance [22, 23]. When the added content of MWNTs is further increased to 1.0%, as shown in Figure 7(e), it can be seen that scattered fiber heads are distributed on the friction interface. The surface of the wear surface appears a rough and deep scratch in the direction of the sliding friction. The scratches are surrounded by pits left by the abrasive grain cutting, showing a characteristic appearance of abrasive wear. It is speculated that the wear debris particles constitute a micron abrasive particle, which increases the wear of the material surface and the mating surface.

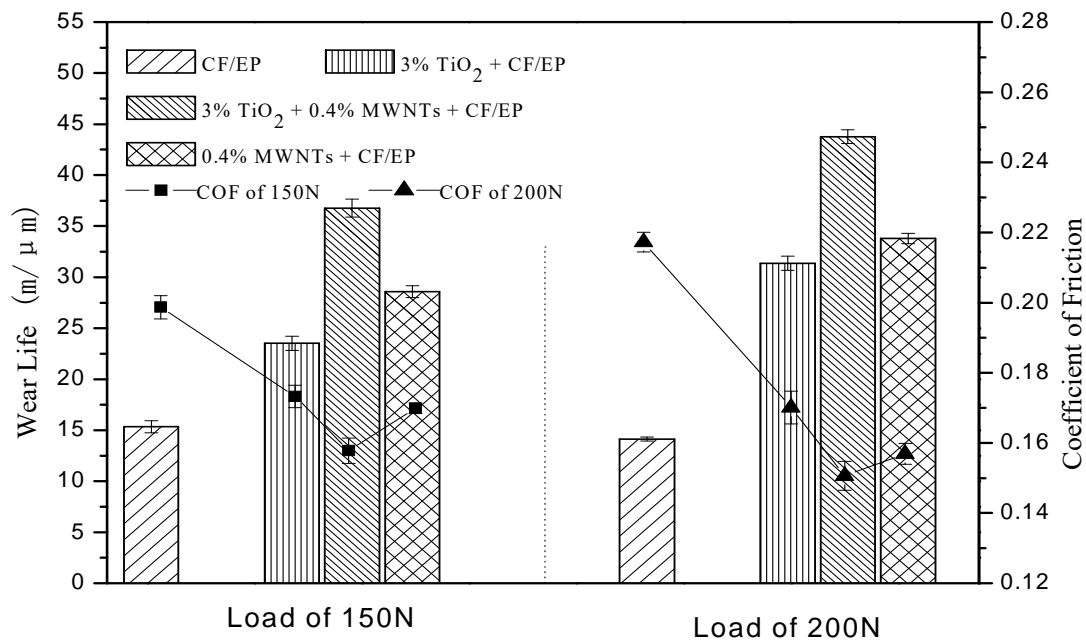
When the load condition is increased to 200N, as shown in Figure 7(b), 7(d) and 7(f), the wear surface of the modified CF/EP composite material has obvious changes with the change of the addition of MWNTs from 0.2% to 1.0%. When the content of MWNTs is low, microscopic avulsion on the surface layer occurs under the action of periodic shearing force, which exposes the bonding interface between the resin phase and the fiber. There is a wide gap between the two phases, and the surrounding is attached by flaky resin-bonded block. However, no brittle exfoliation pit appears under low-load conditions, and the overall appearance is adhesive wear. This is presumably because the added MWNTs are distributed in the state of interpenetrating network and the coiled state in the CF/EP substrate, and form a chemical bond with the CF/EP substrate through the “bridge function” of the coupling agent. As a result, the interfacial area and interfacial bonding strength of the internal structure of the composite material are increased, thereby improving the shear resistance of the composite material. When the composite material begins to bear a large load, MWNTs particles can

induce the yield strain of the resin around the filler to absorb a large amount of impact energy through the “cavitation and silver streaking effect”, thereby achieving the toughening effect of the material and avoiding the material Brittle fracture. When the filling content of MWNTs is 0.4%, see Figure 7(d), it can be seen that the smoothness of the wear surface of the material is improved, the gap between the fiber bundles is repaired, and no “scar block” of melt-deformed resin is found. This may be attributed to the excellent thermal conductivity and self-lubrication of MWNTs. It accelerates the dissipation of frictional heat of the composite during the friction process, inhibits the excessive temperature rise of the material, and prevents the adhesion phenomenon of the resin phase from undergoing welding due to high temperature melting and the metal dual friction pair. At the same time, the MWNTs in the surface layer of the material can also be enriched in the friction interface and the resin phase to form a lubrication transfer film of wear resistance and friction reduction, thereby significantly improving the wear resistance of the material. When the added content of MWNTs is further increased to 1.0%, the interfacial cracks on the wear surface of the composite are basically repaired, but a new abrasive plow-groove appears, and the number of surface wear debris increases significantly, as shown in Figure 7(f). The reason for this phenomenon may be that, when the content of the nano-filler particles is high, the dispersibility of the nano-filler particles will decrease, and the weak interface between the particles will easily form. Due to the high hardness of the nano-particles themselves, the material will form stress concentration centers around the hard nano-filler particles. When the composite material is subject to periodic shearing and fatigue occurs, the molecular chain can easily break off at this place, thus enabling the nanoparticles to separate from the matrix surface and form abrasive particles. After the nano-filler runs off, the stress-bearing effect of the material is weakened, resulting in a decline in its wear resistance.

### 3.3 Study on the synergistic effect of composite of nano-TiO<sub>2</sub> and MWNTs filled with CF/EP

#### 3.3.1 Synergistic effect of TiO<sub>2</sub>/MWNTs hybrid filling system

Figure 8 shows the relationship between friction coefficient and wear life of pure CF/EP and nano-composite fillers under different loads.



**Figure 8:** The comparison of wear life and friction coefficient of CF/EP composites modified by different nano filler particles under different loads

It can be seen from the figure that, compared to unmodified CF/EP substrates, for both the TiO<sub>2</sub>/CF/EP composite prepared by separately filling 3.0% of nano-TiO<sub>2</sub> and MWNTs/CF/EP composite materials prepared by separately filling 0.4% of multi-walled carbon nanotube, their friction and wear properties are greatly improved. When the TiO<sub>2</sub>-MWNTs/CF/EP composites are prepared by adding 3.0% TiO<sub>2</sub> and 0.4% MWNTs to the matrix, the friction coefficient is lower than that of the single filler system, and the wear life is higher than that of the single particle-filled system. This shows that compared to the individual particle filling system, TiO<sub>2</sub>/MWNTs hybrid system has a good synergistic effect on tribological filling and modification of CF/EP substrates.

### 3.3.2 Synergistic mechanism of TiO<sub>2</sub>/MWNTs hybrid filling system

The friction and wear properties of polymer composites usually depend on several factors: first, the structure of the polymer. Second, the frictional interface between material and duality. Third, the friction and wear environment. In addition, we need to see whether chemical changes and chemical reactions occur in the friction process. CF/EP coating materials use carbon fiber as the reinforcing base and epoxy resin as the bonding phase. Despite the large mechanical strength, the flaw that brittleness is relatively

large still exists, which leads to a layered structure of the worn surface layer of the material during frictional dynamics process: due to the breakage of the epoxy-based side chains, the epoxy resin wears faster in the three-dimensional network structure, and the thickness of the coating at the place is also decreased quickly. The wear rate of carbon fiber is slower, and the thickness of the coating layer is also reduced accordingly. The resin and fiber form a concave-convex structure of high and low layers.

The rough and uneven surface structure not only reduces the real contact area between the material and the pair, but also increases the unit friction force the surface bears. And it is very easy to cause the instantaneous high temperature at the contact surface of the material, which promotes further crosslinking and brittleness. On the one hand, the addition of nano-TiO<sub>2</sub> and MWNTs can effectively use the dispersion strengthening effect to increase the stress carrying capacity of epoxy matrix. Both of them can absorb a large amount of impact energy and delay the brittle fracture of materials by using the silver grains and hollowing out effect in the process that the material undergoes the repeated shearing action of the steel ring; on the other hand, small-sized filler particles can be filled into the defects of the substrate and the metal dual surface, and repair the material and metal duality [14]. In addition, the nano-TiO<sub>2</sub> particles can also be dispersed in the friction interface to form a rolling lubrication similar to the bearing micro-beads. MWNTs with a very large aspect ra-

tio use their excellent thermal conductivity to form a heat-conducting network in the substrate, thereby accelerating the disperse of the frictional heat and inhibits the melting of the resin. At the same time, because of the small size, large specific surface area, and free radicals of active groups, the two filler particles have free points of active group. Therefore, the binding force between the metal pairs is strong, which can effectively enhance the adhesion strength of the friction transfer film on the metal surface, and exert a pinning effect to improve the wear resistance of the material.

However, when nano-TiO<sub>2</sub> is filled separately, the non-uniform dispersion of particles may increase the stress concentration of the material and make the wear larger. After adding MWNTs on this basis, it can utilize its larger ratio of length to diameter to form a network-like contact phase interface inside the substrate, thereby playing the role of dispersing stress. At the same time, the addition of MWNTs can also suppress and block the microscopic crack propagation of the surface layer caused by stress concentration, and prevent brittle peeling of the material [23]. Correspondingly, if only MWNTs are filled individually, they do not reach the nanometer level in the length dimension, and therefore some microscopic defects will be left when they are filled. Nano-TiO<sub>2</sub> can be added to these defect spaces better, making the material more compact. Therefore, the comprehensive utilization of the synergistic relationship between nano-TiO<sub>2</sub> and MWNTs can better improve the tribological properties of CF/EP [24].

## 4 Conclusions

- a) An appropriate content of nano-TiO<sub>2</sub> can be filled in the carbon fiber fabric/epoxy composite and play a good role in friction reduction and wear resistance. The optimal addition amount of nano-TiO<sub>2</sub> is 3.0%. And under the condition that load is higher, the composite material has lower friction coefficient and higher wear life.
- b) The TiO<sub>2</sub>/MWNTs hybrid system filled with CF/EP can exert a synergistic effect, significantly reduce the friction coefficient of the matrix material and increase the wear life. When the addition amount of nano-TiO<sub>2</sub> is 3.0% and the addition amount of MWNTs is 0.4%, the composite material achieves the best antifriction and wear reduction effect.
- c) Unmodified carbon fiber fabrics/epoxy composites exhibit mainly fatigue wear and wear patterns of brittle exfoliation. With the increase of the filling

amount of two kinds of nano-fillers, the wear patterns of the materials gradually change to the adhesive wear and abrasive wear.

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