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The friction and wear properties of carbon nanotubes/graphite/carbon fabric reinforced phenolic polymer composites

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In this paper, either graphite (Gr) or carbon nanotubes (CNTs), or both of them were incorporated into carbon fabric reinforced phenolic (CFRP) composites, preparing by a dip-coating and heat molding process, the tribological properties of the resulting composites were investigated using a block-on-ring arrangement. The worn surfaces were observed by scanning electron microscope to understand the mechanism. Experimental results showed that the optimal Gr was more beneficial than CNTs in improving the tribological properties of the CFRP composites when they were singly incorporated. It is well worth noting that the friction and wear behavior of the CNTs-filled CFRP composites were improved further when Gr was added, indicating that there is a synergistic effect between them. Tribological tests under different sliding conditions revealed that the Gr and CNTs-filled CFRP composites seemed to be the most suitable for tribological applications under higher sliding speed and load, and oil lubrication.

Keywords: fabric composites; tribological properties; nanocomposites; synergistic effect

1. Introduction

Nowadays, polymer composites have found great potentials in tribological applications in various fields of engineering to replace metallic materials owing to their easy manufacturability and excellent wear resistance.[1–5] When the polymer matrix must withstand high mechanical and tribological load, it is usually reinforced with various fillers, such as clay,[6] carbon nanotubes (CNTs),[7] mesoporous silica,[8] graphene,[9] fibers,[10] or inorganic nanoparticles.[11,12] Among these reinforcing elements, fiber-based fabrics are very unique and outstanding because of their high structure ordering and tightness. Reinforcement with carbon fabric is the most preferred fabric for composites due to its interesting properties such as high specific strength, thermal conductivity, thermal and thermo-oxidative resistance, low expansion coefficient, and self-lubricity.[13,14] Moreover, by introducing small amounts of CNTs or graphene oxide, the mechanical and the tribological properties of non-fabric reinforced polymer composite materials can be improved tremendously.[15,16] Chang et al. [17] studied the friction and wear properties of short carbon fiber/CNT/PA6 hybrid composites under dry sliding conditions. It was found that CNTs significantly decreased the friction

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coefficient and increased the wear resistance of CF/PA6 composites. Diez-Pascual et al. [18] investigated the tribological properties of CNTs/thermoplastic nanocomposites incorporating inorganic fullerene-like WS$_2$ nanoparticles, and the results showed that CNTs and fullerene-like WS$_2$ nanoparticles had a synergistic reinforcement effect in improving the tribological behavior of polymer composites. However, we know of only a relatively few studies on the friction and wear behavior of CNTs-filled fabric composites to date.[19,20] Moreover, the synergistic effects of CNTs and solid lubricant on the tribological behavior of fabric composites have not been reported to our knowledge. Apart from the fabric composites composition, sliding conditions can also exert much influence on the tribological behavior.[17,21]

In our work, graphite (Gr) powder and CNTs were incorporated into carbon fabric reinforced phenolic (CFRP) composites in the presence of phenolic adhesive resin. The purpose of this study was to investigate the synergistic effect of the two fillers on the tribological behavior of CFRP composites. The wear mechanisms are comparatively discussed, based on scanning electron microscopy examination. It is believed that this work will contribute to the understanding of the effect of conventional filler and CNTs on the tribological properties of fabric composites.

2. Experimental

2.1. Materials and specimen preparation

In the present study, the adhesive resin (204 phenolic resin adhesive) was provided by Shanghai Xing-guang Chemical Plant of China. The carbon fabric used was supplied by Shanghai Sxcarbon Technology Co., Ltd, China. The properties of the carbon fabric are shown in Table 1. Gr powder ($<$1.5 $\mu$m) was provided by Shanghai Colloid Chemical Plant, China. The multi-walled CNTs (purity:$>$95%, diameter: $<$ 8 nm, length: 10–30 $\mu$m) were provided by Chengdu Organic Chemistry Co. Ltd., Chinese Academy of Sciences.

The commercial carbon fabrics were dipped in acetone for 24 h, then cleaned ultrasonically with acetone for 0.5 h; finally, they were dried before use. The untreated Gr powder or/and CNTs were uniformly mixed with a phenolic resin at chosen mass fractions with the assistance of magnetic stirring and ultrasonic stirring. The composites were prepared by a dip-coating and heat molding process. To get the prepregs, the cleaned carbon fabric was first immersed into the phenolic resin solution containing the Gr and/or CNTs and then dipped into an ultrasonic bath for 10 min; the fabric was then placed into an oven (40 °C) to evaporate the solvent. The above process was repeated several times until the mass fraction of the carbon fabric was about 60%. The resulting prepregs were cut into long pieces of 50 mm × 30 mm and placed into a mold with plies orientations of [0°/0°], after which the prepregs were compressed and heated to

| Table 1. Properties of plain weave carbon fabric. |
|------------------|--------|
| Carbon fabric    | Plain  |
| Type             | PAN    |
| Tow              | 1K     |
| Density (g/cm$^3$)| 1.76   |
| Thickness (mm)   | 0.18   |
| End per inch (filament/mm) | 10 |
| Pick per inch (filament/mm)  | 10 |
180 °C in the mold. The pressure was held at 15 MPa for 240 min to allow full compression sintering with intermittent deflation. At the end of each run of compression sintering, the resulting specimens were cooled in the press in air, and then cut into pre-set sizes for friction and wear tests.

2.2. Characterization

The friction and wear tests were conducted on an M-2000 model friction and wear tester (Jinan Test Factory, China). A schematic diagram of the block-on-ring-type friction and wear tester used in this study is shown in Figure 1. The specimens for the wear tests were machined with a geometry of 30 mm × 2 mm × 7 mm. The stainless GCr15 steel rings (G means bearing steel) with a roughness (Ra) of 0.30 μm served as counterparts. The chemical composition of the GCr15 steel is given in Table 2. In this study, sliding was performed under ambient conditions over a period of 120 min at a sliding velocity of 0.431 m/s or 0.862 m/s and load range from 200 N to 500 N. The water lubrication between the sliding surfaces was realized by continuous dropping of distilled water onto the sliding surface at a rate of 80–90 drops per minute. Liquid paraffin was also used as a lubricating oil in one set of experiments, and it was added to the sliding surfaces at a rate of 60 drops per minute during the tests. Before each test, the surfaces of the block specimens and counterpart rings were polished to a Ra of about 0.3 μm and cleaned with acetone-dipped cotton. During the friction process, the block specimen was static and the steel ring slid against the block unidirectionally. The friction force was measured using a torque shaft equipped with strain gauges mounted on a vertical arm that carried the block, which was used to calculate the friction coefficient (μ) by taking into account the normal load applied. The specimens were removed and cleaned after predetermined sliding durations to measure the length of the wear scratches with a three-dimensional profilometer. Then the specific wear rate (ω) of the specimen was calculated from Equation (1) as follows:

![Figure 1. The contact schematic for the friction couple.](image-url)
where $B$ is the width of the specimen (mm), $r$ is the semi-diameter of the stainless steel ring (mm), $b$ is the length of the wear trace (mm), $L$ is the sliding distance in m, and $P$ is the load in N. In this study, three replicated wear results were averaged and taken as the wear results. The morphologies of the worn surfaces of the CFRP composites and the transfer films formed on the counterpart steel rings were analyzed on a JSM-5600LV scanning electron microscope (SEM, JEOL Co., Japan). In order to increase the resolution for the SEM observation, the tested composite specimens were gold coated to render them electrically conductive.

### 3 Results and discussion

#### 3.1. Friction and wear behavior of CFRP composites

The effect of the content of Gr on the friction coefficient and wear rate of the CFRP composites sliding against the GCr15 steel ring is shown in Figure 2. It can be seen that the friction coefficient and wear rate of the unfilled carbon fabric was high. The friction and wear behavior of the CFRP composites were improved remarkably when Gr was incorporated. The Gr debris forms a thin, lubricating film on the counterface, thereby reducing the abrasion process drastically. This results in low friction coefficient and low wear of the composite. In the tested system regarding the friction coefficient

![Figure 2. Friction coefficient and wear rate of Gr-filled CFRP composites (200 N, 0.431 m/s).](image-url)
and wear rate, the optimum content of Gr was about 15 wt.%. With a further increase in the concentration of Gr, the tribological properties deteriorated. Excessive Gr tended to aggregate and led to less uniformity of the system, a serious abrasive wear took a dominant place, and thus, impaired the friction-reduction and anti-wear abilities of the composites.

The effect of the content of CNTs on the friction and wear of the filled CFRP composites is shown in Figure 3. As shown in Figure 3, the addition of a small amount of CNTs (≤4 wt.%) can decrease the friction coefficient and wear rate slightly. A significant reduction of friction coefficient and wear rate was observed when the proportion was increased to 6 wt.%. Then further addition of CNTs led to an increase in the friction coefficient and wear rate. In all samples, the surface was smooth before the wear test, and the external resin was worn down when the abrasive wear took the dominant place, then the carbon fabric emerged and the surface became rougher. CNTs and carbon fabric were then exposed to the sliding interface during the friction process. Then the exposed CNTs and carbon fabric bore most of the load and transferred the heat and stress effectively, protecting the polymer matrix from being further destroyed. The favorable effect of CNTs on the tribological properties is attributed to the high strength of the CNT that restrain the scuffing and adhesion of the matrix during the sliding process, combined with the increase in thermal conductivity that lowers the temperature in the sliding contact. Since the optimal tribological properties were obtained when the Gr and CNTs proportions were 15 and 6 wt.% separately, these contents were chosen to investigate the synergistic effect of the Gr and CNTs, and different sliding conditions on the friction and wear behavior of carbon fabric composites. The combined effect of Gr and CNTs on the friction coefficient and wear rate of CFRP composites is shown in Figure 4. It can be seen that the addition of 15 wt.% Gr can enhance the anti-wear properties of the 6 wt.% CNTs-filled CFRP composites to a significant extent. A combination of Gr and CNTs was the most effective way to improve the friction and wear behavior of the CFRP composites, which is related to their synergistic effects. The wear rate of Gr/CFRP, CNTs/CFRP, and Gr/CNTs/CFRP decreased by 61.4, 42.2, and 66.5%, respectively. It is well worth noting that the simultaneous addition of Gr and CNTs can effectively improve the anti-wear ability owing to the synergistic effects between them. The lubricating nature of the Gr filler played an important role in

![Figure 3. Friction coefficient and wear rate of CNTs-filled CFRP composites (200 N, 0.431 m/s).](image-url)
reducing the friction coefficient and wear rate, and the reinforcing CNTs can effectively reduce the adhesion force and the plow. Addition of the CNTs strengthened the interfacial adhesion between the transfer film and the counterpart steel ring. As is well known, the tribological behavior of polymer composites largely depends on the formation of a transfer film on the sliding counterface.[22,23] The transfer film can easily form owing to the increase in adhesive force between the film and counterpart. With the formation of a relatively uniform and coherent transfer film, subsequent sliding occurs between the surface of the CFRP composites and the transfer film; then the friction process can be quickly transferred from severe friction to steady friction quickly. Consequently, a better tribological behavior is obtained.

Variations of the friction and wear behavior of the CFRP composites with load are shown in Figure 5. The friction coefficient and wear rate decreased steadily with an increase in contact pressure. With the increase of applied load, the adhesive wear became dominant. This mechanism is generally less damaging for polymer composite

Figure 4. The combined effect of Gr and CNTs on the friction coefficient and wear rate of CFRP composites (200 N, 0.431 m/s).

Figure 5. Effect of load on the friction coefficient and wear rate of CFRP composites (0.431 m/s).
sliding surfaces. The rate of transfer film formation may be enhanced at higher load, which can shorten the running-in period and lessen the plowing and scuffing and is favorable for improving the tribological properties of the polymer composites. Moreover, with further increase in applied load, the newly formed wear debris form a more integrated but thinner layer on the worn surface, which plays an important role in improving the tribological properties.[24] Figure 6 shows the friction and wear behavior of the Gr/CNTs/CFRP composites under low speed (0.431 m/s, 200 N) and high speed (0.862 m/s, 200 N). The friction coefficient and wear rate decreased under high sliding speed compared with that under low sliding speed. It is assumed that, under a small load, the interfacial temperature is a crucial factor determining the tribological characteristics.[25] Friction-induced heat is expected to have caused an increase in the contact temperature owing to the low thermal conductivity of the phenolic matrix, and an increase in the sliding speed will cause a higher contact temperature. The adhesion between the carbon fabric, Gr, CNTs, and phenolic matrix decreased under high temperature owing to the softening phenomenon of the polymer resin, Gr has a layer structure, the shear force between layers is small. Moreover, the particle size of CNTs is far less than Gr, the adhesion between CNTs, fabric and polymer resin was higher than the adhesion between Gr, fabric and polymer resin. So, Gr can transfer to the counterpart more easily. The Gr debris can be more easily transferred to the counterpart and form a more uniform film, which plays an important role in reducing the friction coefficient. The CNTs debris can enhance the adhesion between the transfer film and counterpart. The exposed carbon fibers and CNTs largely bore the applied load between the contact surface and protected the polymer matrix from further cutting action of the counterpart, thus, decreasing the wear rate. As a result, adhesive wear was the dominant effect, and the friction force component from adhesion can be greatly reduced.[26] Table 3 presents the friction and wear properties of the Gr and CNTs-filled phenolic composites under dry, water and oil (liquid paraffin) lubricated sliding conditions. The CFRP composites exhibited the best wear behavior under oil lubrication. This is attributed to the cooling and boundary lubricating ability of the liquid paraffin, which
considerably decreased the friction-induced heat and hence, reduced the plastic deformation and breakage of the matrix by the thermal effect.[25] An excellent lubricative oil film can be formed, and thus, reduce the direct contact between the filled CFRP composites and the counterpart steel ring. Under water lubrication, the water might first be absorbed into the voids associated with the interface between the carbon fiber and phenolic matrix, which diffused slowly into the voids between carbon fabric, Gr, CNT, and phenolic matrix and lead to a decrease of the shear strength of the composites. In addition, carbon fibers broke out from the phenolic matrix easily and were pulverized and cut; thus, severe abrasion occurred and weakened the effect of water lubrication. Therefore, the Gr and CNTs-filled phenolic composites exhibited the best friction and wear properties under liquid paraffin lubrication, as compared with that under dry sliding and under water lubrication.

3.2. **SEM analysis of the worn surface and transfer film**

Figure 7 shows the SEM images of the worn surfaces of the CFRP composites under 200 N and 0.431 m/s. Numerous carbon fibers were pulled out and cut from the pure CFRP composites, which resulted in high abrasive wear (Figure 7(a)). Contrary to the unfilled one, the worn surface of 15% Gr-filled CFRP composites (Figure 7(b)) was

<table>
<thead>
<tr>
<th>Sliding conditions</th>
<th>Friction coefficient</th>
<th>Wear rate/10^{-6}mm^3(N m)^{-1}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry sliding</td>
<td>0.22</td>
<td>1.8</td>
</tr>
<tr>
<td>Water lubrication</td>
<td>0.13</td>
<td>0.39</td>
</tr>
<tr>
<td>Oil lubrication</td>
<td>0.16</td>
<td>0.05</td>
</tr>
</tbody>
</table>

Table 3. Friction and wear properties of Gr and CNTs-filled CFRP composites under dry and water and oil (liquid paraffin) lubrication.

![Figure 7. SEM images of the worn surface of the CFRP composites (200 N, 0.431 m/s)](image-url) (a) Unfilled CFRP composites; (b) Gr/CFRP composites; (c) CNTs/CFRP composites; (d) Gr/CNTs/CFRP composites.
very smooth and the pulling-out and exposure of fiber was not seen, which corresponded to its better tribological properties. The worn surface of 6% CNTs-filled CFRP composites (Figure 7(c)) was rough and showed signs of carbon fiber pulling-out, which corresponds to the unsatisfied tribological properties as compared with the 15% Gr-filled CFRP composites. The worn surface of the Gr and CNTs-filled fabric composites (Figure 7(d)) was the smoothest, the carbon fibers were not pulled out from the phenolic matrix, and only a few wear debris appeared on the worn surface, which indicated that slight abrasive wear was the dominant mechanism.

The SEM morphologies of the transfer film of the CFRP composites are shown in Figure 8. The transfer film of the unfilled CFRP composite (Figure 8(a)) was rough, non-uniform, and lots of wear debris appeared on the counterpart, which correspond to the poor tribological properties. However, the transfer film of the 15% Gr-filled CFRP composites (Figure 8(b)) was smooth, uniform and continuous, which conformed to the significantly improved tribological behavior. The transfer film of the 6% CNTs-filled CFRP composites (Figure 8(c)) was relatively smooth and continuous but showed signs of scuffing. This indicated that 6% CNTs-filled CFRP composites experienced abrasive wear and it was not possible to obtain a satisfactory tribological behavior. The transfer

Figure 8. SEM images of the transfer film of the CFRP composites (200 N, 0.431 m/s). (a) Unfilled CFRP composites; (b) Gr/CFRP composites; (c) CNTs/CFRP composites; (d) Gr/CNTs/CFRP composites.
film of the Gr and CNTs-filled fabric composites (Figure 8(d)) was somewhat smooth, the scuffing phenomena abated, and few wear debris appeared, which corresponded to the improved tribological properties as compared with single CNTs-filled CFRP composite.

The worn surface and transfer film of the Gr and CNTs-filled CFRP composite sliding at 500 N and 0.431 m/s are shown in Figure 9. The worn surface (Figure 9(a)) was smooth and fiber pulling-out phenomena were not seen. Moreover, there existed a more integrated layer on the worn surface. With an increase in load, any large particle shaped or flaky debris on the wear surface would be crushed or sheared into smaller particles or thinner flakes, which generally resulted in the formation of compacted wear debris layer which acted as a lubricant. The transfer film (Figure 9(b)) became thinner, more coherent and uniform. With the formation of a more uniform and coherent transfer film; subsequent sliding occurred between the surface of the CFRP composites and the transfer film. As a result, the reduced ‘direct contact’ between the filled carbon fabric composite and the counterpart would bring about a small friction coefficient and wear rate.

The worn surface and transfer film of the Gr/CNTs filled CFRP composites sliding at 200 N and 0.862 m/s are shown in Figure 10. The worn surface of the Gr/CNTs-filled fabric composite was relatively smooth, a few fine wear debris appeared on the worn surface (Figure 10(a)). Moreover, lots of wear debris layer oriented in rows along the sliding direction can be formed when sliding at high sliding speed, the transfer film became thinner and more uniform (Figure 10(b)), which conform to its better tribological properties compared with that under low sliding speed.
Figure 11 shows the SEM morphologies of the worn surface and transfer film of the CFRP composites under water and oil lubricated conditions. As for water lubricated samples, severe plough and scuffing phenomena, and lots of carbon fibers broken out from the phenolic matrix (Figure 11(a)), while the transfer film was thin and discontinuous and lots of wear debris appeared on the counterpart (Figure 11(c)). On one hand, the cooling and boundary lubricating abilities of water would reduce the friction coefficient and wear rate. On the other hand, the absorbed water would penetrate and corrode the filler–matrix interface, and hinder the formation of a transfer film, which led to the abrasive wear. This mechanism is generally more damaging for polymer composites than an adhesive one. Thus, the final tribological behavior under water lubrication was determined by the two main competitive effects. For this experiment, the cooling and boundary lubricating abilities of water took the dominant place and the erosive effect of water reduced the improvement. Furthermore, we found that the worn surfaces under liquid paraffin lubrication were smooth, and exhibited little scuff (Figure 11(b)). Accordingly, there appears an excellent lubricative oil film on the counterpart (Figure 11(d)), which agrees well with it having the best tribological properties as compared with those under other lubrication conditions.

4. Conclusions
A systematic investigation of the tribological properties of Gr and CNT-filled CFRP composites was carried out. The friction and wear properties of the Gr/CNTs-filled carbon fabric composite materials depended on the synergetic effects of the ingredients.
The combined addition of Gr and CNTs were the most effective in improving the tribological properties of the CFRP composites. The Gr/CNTs-filled CFRP composites showed the best friction and wear behavior under oil lubrication compared with that under dry and water-lubricated sliding conditions.

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