

Investigations of the Tribological Properties of Carbon Fabric Reinforced Phenolic Polymer Composites Filled with Several Nanoparticles

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ABSTRACT: The carbon fabric composites filled with several nanoparticles were prepared by dip-coating and hot press molding technique. The friction and wear behavior of the resulting composites were studied systematically using a block-on-ring arrangement. Experimental results showed that the optimal content of nanoparticles as fillers contributed to improve the tribological properties of the carbon fabric composites. Moreover, the friction and wear properties of the fabric

composites were closely dependent with the sliding conditions. The differences in the transfer film formed on the counterpart surface during the friction process also accounted for the friction and wear behavior of carbon fabric composites. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 123: 3081–3089, 2012

Key words: fabric composites; tribological properties; nanoparticles

INTRODUCTION

Polymer and polymer–matrix composites have been extensively studied because of the increasing industrial and martial applications.^{1–6} Especially, polymer matrix composites reinforced with fibers have been widely accepted as tribo-materials and used on the components supposed to run without any external lubricants.^{7,8} Carbon fibers combine exceptional mechanical properties and low weight, making them ideal reinforcements for polymer composites.^{9,10} The structure ordering and tightness of fabrics are much higher than those of fibers. Thus, fabric reinforced polymer composites have higher mechanical strength, which has been considered as advanced materials for tribological applications in many high-tech industries, such as aerospace, aviation, automobile.^{11,12} The tribological performance of fabric reinforced composites is a complex phenomena, which depends on the type of fabric and matrix, fabric composites composition, sliding conditions

and so on.^{13,14} Typical wear mechanisms of fabric reinforced polymer matrix composites are: fiber breaking, fiber–matrix debonding and matrix fracture.^{15–18} Many studies have shown that the fiber surface treatment, solid lubricants and nanoparticles have great effect on the friction and wear behavior of fabric composites.^{19–24} Nanoparticles most often used in plastics are carbon nanomaterials,²⁵ layered clayey minerals²⁶ and nanoparticles of metals or their organic and inorganic compounds.²⁷ These nanoparticles can enhance the friction and wear behavior of the polymer composites owing to the interfacial reinforcing action of the nanoparticles and/or the self-lubricating effects of nanoparticles.

This article deals with the preparation, friction, and wear properties of carbon fabric composites (CFC) filled with nano-Si₃N₄, nano-CaCO₃, nano-TiO₂, nano-CuO, nano-SiO₂, and multiwalled carbon nanotubes (MWNT), respectively. The object was to investigate and compare the effect of different nanoparticles on the tribological behavior of the carbon fabric composites. It is expected that this work will bring a new tribological application of carbon fabric reinforced polymer composites.

EXPERIMENTAL

Materials and specimen preparation

In this study, the adhesive resin (204 phenolic resin) was provided by Shanghai Xing-guang Chemical Plant of China. Carbon fabric (CF) used was

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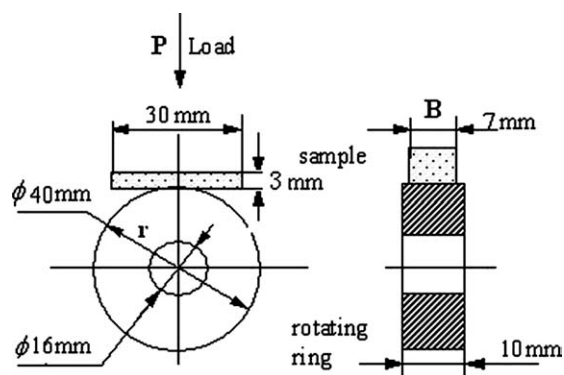


Figure 1 The contact schematic for the friction couple.

supplied from Shanghai Sxcarbon Technology (Shanghai, China). Nano-Si₃N₄ (<20 nm), nano-CaCO₃ (<50 nm), nano-TiO₂ (<10 nm), nano-CuO (<60 nm), and nano-SiO₂ (<50 nm) were supplied by Zhoushan Nanomaterials, China. The multi-walled carbon nanotubes (MWNT) (purity: >95%, diameter: <8 nm, length: 10–30 μm) were provided by Chengdu Organic Chemistry, Chinese Academy of Sciences. The mixed acetone/absolute ethyl alcohol/ethyl acetate in a volume fraction of 1 : 1 : 1 was employed as the mixed solvent.

The concentration of nanofiller in this work was the ratio of the weight of nanofiller and the phenolic resin. The phenolic resin was weight and added to the mixed solvent [the ratios of phenolic resin (g) and the mixed solvent (mL) is 1 : 3]. The nanoparticles were uniformly mixed with the phenolic resin with the assistance of mechanical and ultrasonic stirring. A dip-coating process was used to prepare the prepreps of the composites. First, the cleaned carbon fabric was dipped into phenolic resin solution containing different nanoparticles. Then the fabric was put into an oven at 40°C to evaporate the solvent. A series of repeated dipping and coating of the carbon fabric were performed until the fraction of carbon fabric was about 60 wt %. The final carbon fabric composites were fabricated by means of hot press molding technique. The prepreps were compressed and heated to 180°C in the mould with intermittent deflation. The pressure was held at 15 MPa for 240 min to allow full compression sintering. At the end of each run of compression sintering, the resulting specimens were cooled with the mold in air, and then cut into preset sizes for friction and wear tests.

Characterization

The friction and wear tests were conducted on an M-2000 model friction and wear tester. 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 wear tests were machined with geom-

etry of 30 mm × 3 mm × 7 mm. The stainless GCr15 steel rings with a hardened and smoothly polished surface served as counterparts. The chemical composition of the GCr15 steel was given in Table I. Sliding was performed under ambient conditions over a period of 120 min at sliding velocities of 0.431 and 0.862 m/s, normal load ranging from 200 to 500 N. Before each test, the surfaces of the block specimens and counterpart rings were polished to a roughness (Ra) of about 0.3 μm and cleaned with acetone-dipped cotton. In this study, three replicated wear results were averaged and taken as the wear results. 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 width of the wear tracks was measured with a reading microscope to an accuracy of 0.01 mm. Then the specific wear rate (ω) of the specimen was calculated from eq. (1) as follows.

$$\omega = \frac{B}{L * P} \left[\frac{\pi r^2}{180} \left(\arcsin \frac{b}{2r} \right) - \frac{b}{2} \sqrt{r^2 - \frac{b^2}{4}} \right] (\text{mm}^3/\text{N m}) \quad (1)$$

where B is the width of the specimen (mm), r is the semidiameter of the stainless steel ring (mm), and b is the width of the wear trace (mm), L is the sliding distance in meter, P is the load in Newton.

RESULTS AND DISCUSSION

Figure 2(a,b) shows the variation and wear rate of the nanoparticles-filled carbon fabric composites with the content of nanoparticles at 200N and 0.431 m/s. It is seen that 2% nano-Si₃N₄ or nano-CuO decreases the friction coefficient and wear rate, while further addition harms the friction and wear properties. It also can be seen that the friction coefficient and wear rate of nano-SiO₂, nano-CaCO₃, and MWNT-filled carbon fabric composites assumes an obvious decrease with increasing content up to 6%, and then increases with the further increase of content. As for nano-TiO₂-filled carbon fabric composites, the friction coefficient and wear rate shows a decrease with increasing content up to 10%, and then increases with increasing content. For the combination of friction coefficient and wear rate, the optimal content of nano-Si₃N₄, nano-CuO, nano-

TABLE I
Chemical Composition of the GCr15 Steel Ring

Chemical composition (mass fraction, %)					
C	Mn	Si	P	S	Cr
0.95–1.05	0.25–0.45	0.15–0.35	≤ 0.025	≤ 0.025	1.40–1.65

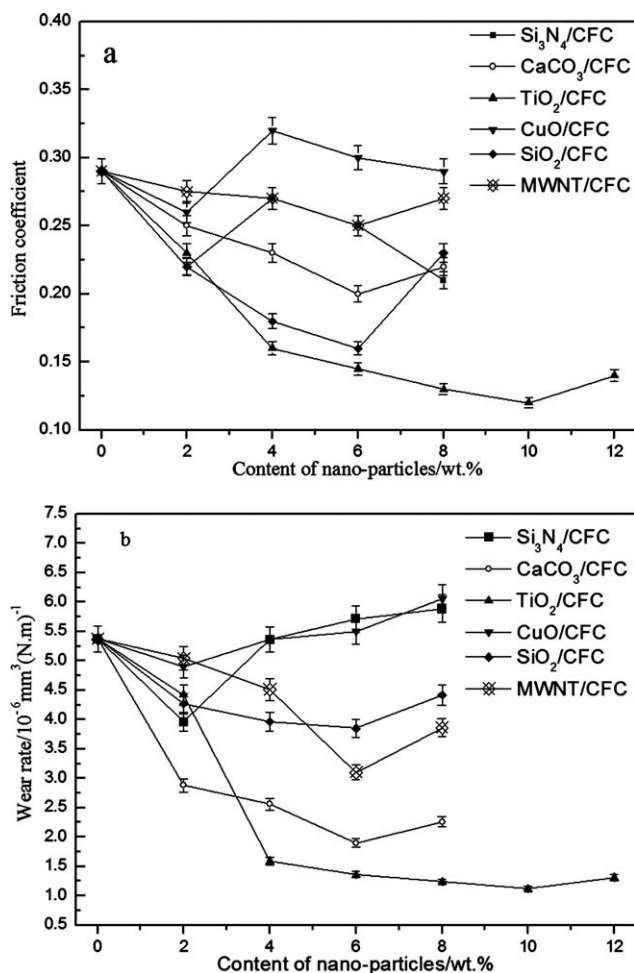


Figure 2 Friction coefficient and wear rate of nanoparticles-filled CF composites.

SiO₂, nano-CaCO₃, MWNT, and nano-TiO₂ in the carbon fabric composites appears to be 2, 2, 6, 6, 10%, respectively.

The friction and wear behavior of carbon fabric composites filled with different optimal nanoparticles are comparatively shown in Figure 3(a,b). It is seen that all the filled carbon fabric composites show better friction-reducing and antiwear abilities than the unfilled one. It also can be seen that nano-TiO₂ as filler is the most effective in improving the tribological properties of carbon fabric composites. The friction coefficient of carbon fabric composites is reduced by 24.1, 10.3, 44.8, 31, 13.8, and 58.6%, respectively, by the optimal addition of nano-Si₃N₄, nano-CuO, nano-SiO₂, nano-CaCO₃, MWNT, and nano-TiO₂.

The variation of the friction coefficient and wear rate of the filled and unfilled carbon fabric composites with load under dry sliding against the stainless steel counterface is shown in Figure 4(a,b). Compared with the unfilled one, all the nanoparticles-filled carbon fabric composites exhibited a lower value of friction coefficient under all condi-

tions in this work. It also can be found that the friction coefficient of all carbon fabric composites exhibited a similar decreasing trend with an increase in load. Moreover, it is seen that the carbon fabric composite filled with nano-TiO₂ shows the best friction-reducing ability, and the carbon fabric composite filled with nano-SiO₂ is next to the best. It can be found that the wear rate of all carbon fabric composite also exhibited a similar decreasing trend with an increase in load. The antiwear abilities of the carbon fabric composites filled with nano-Si₃N₄, nano-CaCO₃, MWNT, and nano-TiO₂ were obviously better than the unfilled one under all conditions. With an increase in load, the carbon fabric composite filled with nano-CuO shows a higher wear rate than the unfilled one. Nano-SiO₂ as filler shows slight effect on the improvement of the wear resistance of the carbon fabric composites with the increase in load. Moreover, it can be found nano-TiO₂ as filler has greatest effect on the improvement of the wear resistance of the carbon fabric composites under all conditions and nano-CaCO₃ ranks second.

Figure 5 shows the friction and wear behavior of the CF composites under low speed (0.431 m/s) and high speed (0.862 m/s). It is clearly seen that the

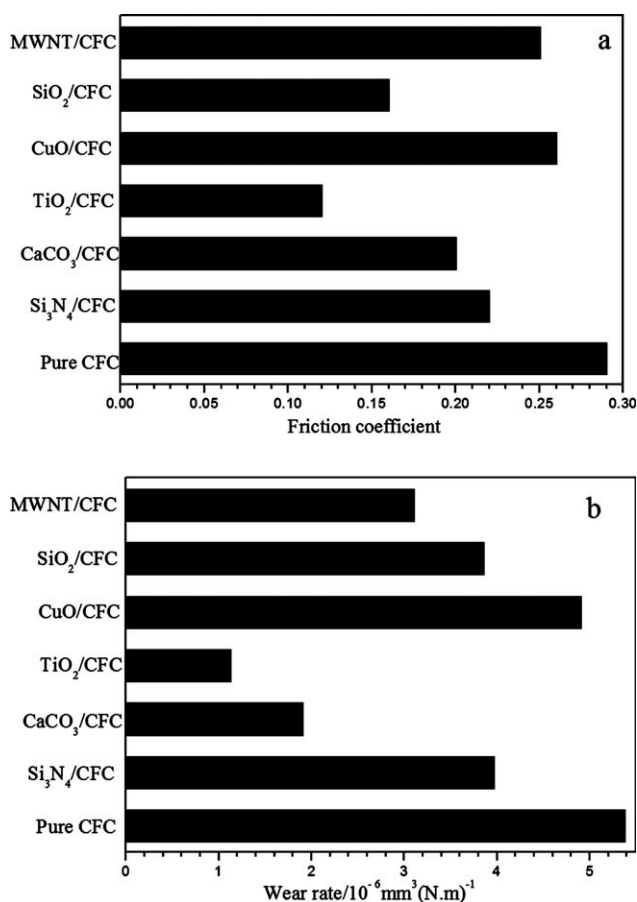


Figure 3 Comparison of friction coefficient and wear rate of nanoparticles-filled CF composites.

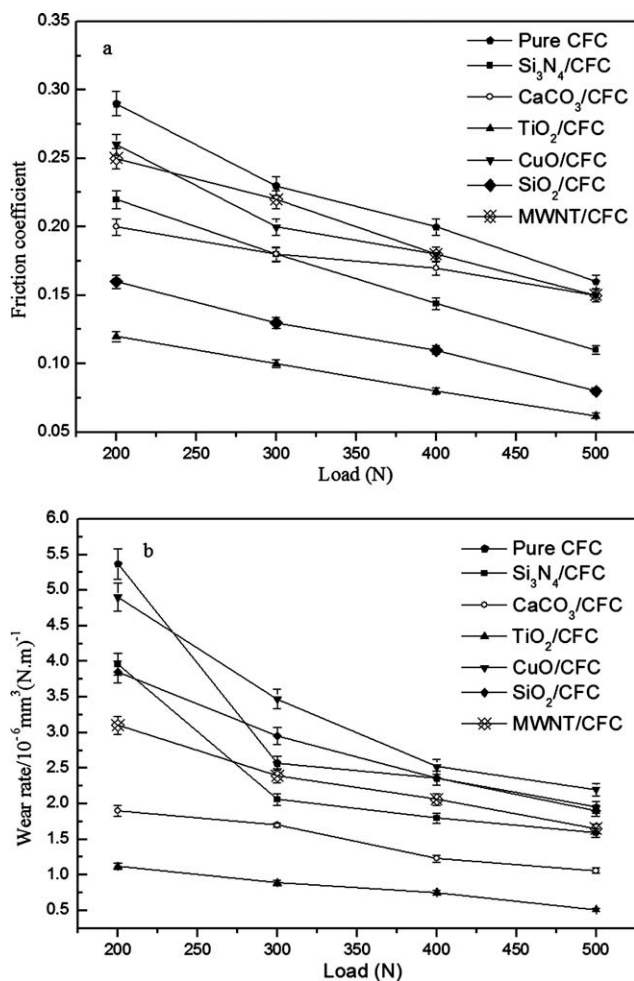


Figure 4 Effect of load on the friction coefficient of CF composites.

unfilled and nano-CuO, nano-CaCO₃, and MWNT-filled CF composites assumed a higher friction coefficient under high sliding speed compared with that under low sliding speed. With an increase in sliding speed, the temperature between the contact surface increased drastically, which would result in two competitive effects. First, the adhesion between the filler, fabric and polymer matrix decreased, filler and fiber can easily fell out from the matrix and ruptured without the support and protection of the phenolic matrix, and the worn surface enter the transfer period from viscoelastic state to viscous state. Then the serious abrasive wear took the dominant place, which resulted in a drastic increase in the friction coefficient. Second, the exposed carbon fibers on the worn surface can inhibit the cutting action of micro-convexity to the matrix of the CF composites. The exposed carbon fibers bore most of the load between the contact surface and reduced the real contact area. So, the final friction coefficient and wear rate is determined by their competitive effect. Nano-Si₃N₄, nano-SiO₂, and nano-TiO₂-filled CF composites exhibited a lower friction coefficient

under high sliding speed. The polymer matrix was softened but not molten, and the filler and fabric were still strong bonded with the polymer matrix. The adhesive wear took the dominant place, which is less dangerous than severe wear.

As shown in Figure 6(a), the pulling-out and cutting phenomena of carbon fibers are obviously observed on the worn surface, which is indicative of abrasive wear. Thus, the friction coefficient and wear rate is high. Contrary to the unfilled one, the worn surfaces of nano-Si₃N₄ [Fig. 6(b)], nano-CaCO₃ [Fig. 6(c)], nano-TiO₂ [Fig. 6(d)], and nano-SiO₂ [Fig. 6(e)] filled CF composites are smooth and the pulling-out and exposure of fiber are invisible. The friction heat for these nanoparticles-filled carbon fabric composites is less than the unfilled one. These nano particles can increase the interfacial bonding between carbon fiber and phenolic matrix, and hence to improve the tribological properties of the composites. However, some large patches of resin are broken, and lots of wear debris are observed on the worn surface of nano-CuO-filled CF composites [Fig. 6(f)], which conforms to its slight effect in

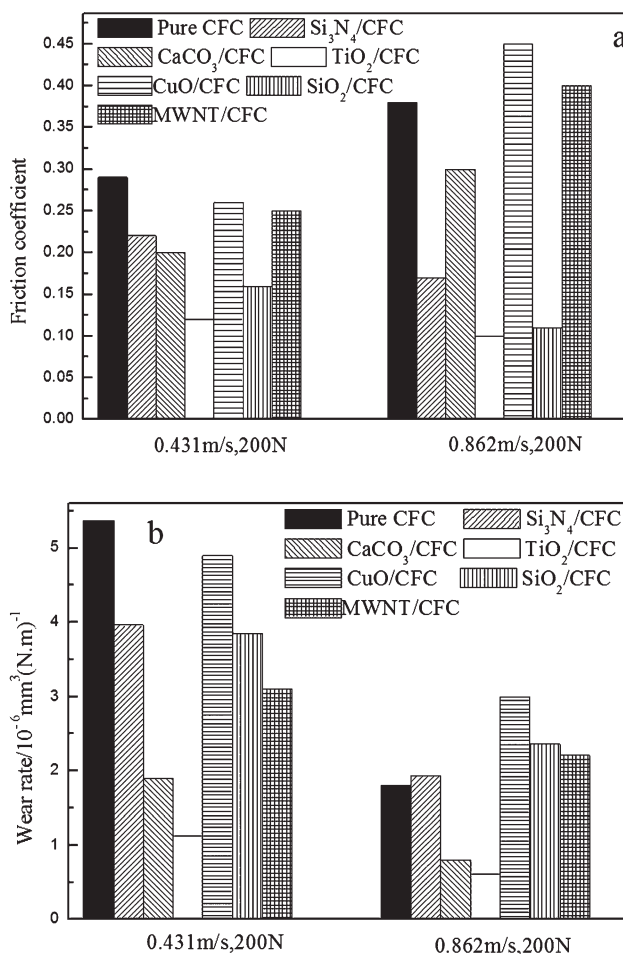


Figure 5 Effects of sliding speed on the friction coefficient and wear rate of CF composites.

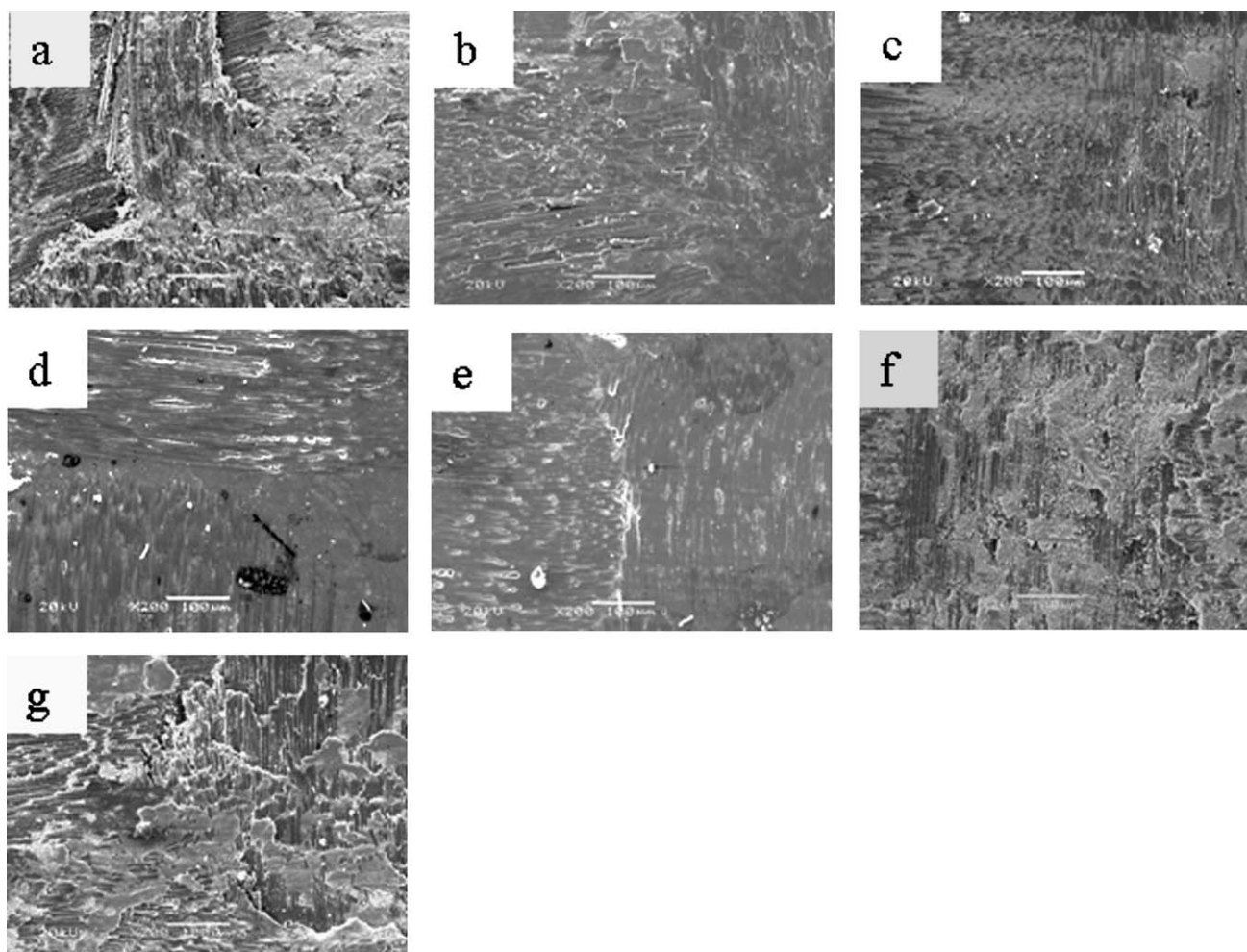


Figure 6 SEM morphologies of the worn surface of nanoparticles-filled CF composites (200N, 0.431 m/s). (a) Pure CFC; (b) nano-Si₃N₄/CFC; (c) nano-CaCO₃/CFC; (d) nano-TiO₂/CFC; (e) nano-SiO₂/CFC; (f) nano-CuO/CFC; (g) MWNT/CFC.

decreasing the friction coefficient and wear rate of the CF composites. As for MWNT-filled CF composite [Fig. 6(f)], some patched of resin were broken, some cracks and pulling-out and cutting phenomena of carbon fibers are also observed, which corresponds to its poorer friction-reducing abilities. SEM micrographs of the transfer film of the unfilled and nanoparticles-filled CF composites formed on the counterpart steel ring at 200 N and 0.431 m/s are shown in Figure 7. It can be seen from Figure 7(a) that transfer film of the unfilled one appears rough, ununiform, lots of wear debris and obvious signs of scuffing also can be observed, which corresponds to the poor tribological properties. As for nano-Si₃N₄ [Fig. 7(b)], nano-SiO₂ [Fig. 7(e)], nano-CaCO₃ [Fig. 7(c)] and nano-TiO₂ [Fig. 7(d)] filled CF composites, the transfer films become relatively smooth, scuffing phenomena abate, and few wear debris are seen. Moreover, the transfer film of nano-TiO₂ [Fig. 7(d)] filled CF composite appears thinnest, most coherent, and uniform. With the formation of a most uniform and coherent transfer film, subsequent

sliding occurred between the surface of the CF composites and the transfer film, a decrease in the friction coefficient and wear rate is inevitable. The transfer film of nano-CuO-filled CF composite [Fig. 7(f)] is relatively thin but lots of wear debris appear on the counterpart, and scuffing phenomena also can be seen clearly, which correspond to its poor wear-resistance. As for MWNT-filled CF composites, the transfer film [Fig. 7(g)] is thick and ununiform, scuffing phenomena is obviously observed. So, it can be concluded that the formation of a transfer film on the sliding counterpart largely respond for the tribological properties of polymer composites, which is in accordance with Su.²² It can be concluded that the influences of nanofiller particulates on the tribo-performance of some fabric composites were dependent with the intrinsic properties of the filler particulates themselves, the influence of the filler particulates on the structure of the filled fabric composites, and the properties of the transfer films formed on the counterface.

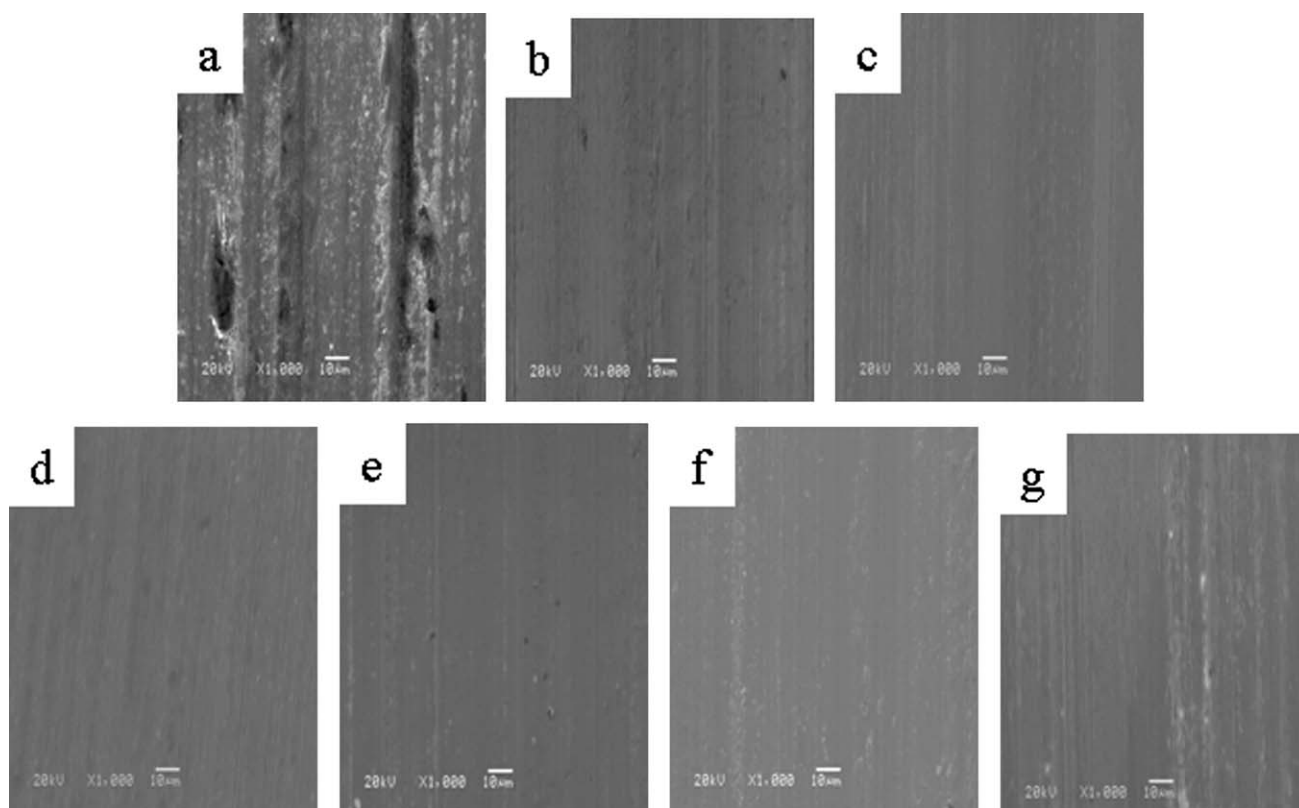


Figure 7 SEM morphologies of the transfer film of nanoparticles-filled CF composites (200N, 0.431m/s). (a) Pure CFC; (b) nano-Si₃N₄/CFC; (c) nano-CaCO₃/CFC; (d) nano-TiO₂/CFC; (e) nano-SiO₂/CFC; (f) nano-CuO/CFC; (g) MWNT/CFC.

The worn surfaces of the unfilled and nanoparticles-filled CF composites sliding at 500 N and 0.431 m/s are shown in Figure 8. It can be seen that the worn surface becomes smoother under 500N compared with those under 200 N. As for the unfilled one, the worn surface is relatively smooth [Fig. 8(a)], and fiber pulling-out and of cutting phenomena abate. Moreover, a few wear debris are crushed into the worn surface [Fig. 8(a)]. In agreement with their excellent wear resistance of nano-Si₃N₄ [Fig. 8(b)], nano-CaCO₃ [Fig. 8(c)], nano-TiO₂ [Fig. 8(d)], and MWNT [Fig. 8(g)] filled CF composites, fiber pulling-out and of cutting phenomena on the worn surface is invisible, and the fillers are strongly bonded with polymer matrix. Moreover, there exists a more compacted wear debris layer on the worn surface, thus prevent the polymer composites from the cutting of the counterpart. As for nano-CuO-filled CF composite [Fig. 8(f)], slight scuffing and ploughing signs are shown on the worn surface, and some wear debris are also crushed into the worn surface, which confirms its higher wear rate than the unfilled one under 500 N. A few wear debris are observed on the worn surface of nano-SiO₂-filled CF composites [Fig. 8(e)], some patches of polymer matrix are broken and crushed together. It can be concluded that

some big particle-shaped or flaky debris in the wear surface would be crushed or sheared into smaller particles or thinner flakes and acted as lubricants under higher load, and reduced the cutting action of counterpart to the worn surface. Thus, a decrease in the friction coefficient and wear rate is inevitable.

Figure 9 shows the SEM images of the worn surface of the unfilled and nanoparticles-filled CF composites sliding at 200 N and 0.862 m/s. It can be seen the phenolic matrix of the unfilled [Fig. 9(a)] and nano-CuO [Fig. 9(f)] and MWNT [Fig. 9(g)] filled fabric composites experienced molten phenomena resulted from the lots of friction heat and entered the transfer period from viscoelastic state to viscous state. Carbon fibers can easily fell out from the matrix and ruptured without the support and protection of the phenolic matrix, which correspond to their worse tribological behavior compared with that sliding under low sliding speed. As for nano-Si₃N₄-filled CF composite [Fig. 9(b)], the worn surface appears smooth, and the wear debris were sheared into a compacted layer oriented along the sliding direction. The pulling-out and cutting phenomena of carbon fibers are obviously observed on the worn surface of nano-CaCO₃-filled CF composite [Fig. 9(c)], thus, results in an increase in the friction

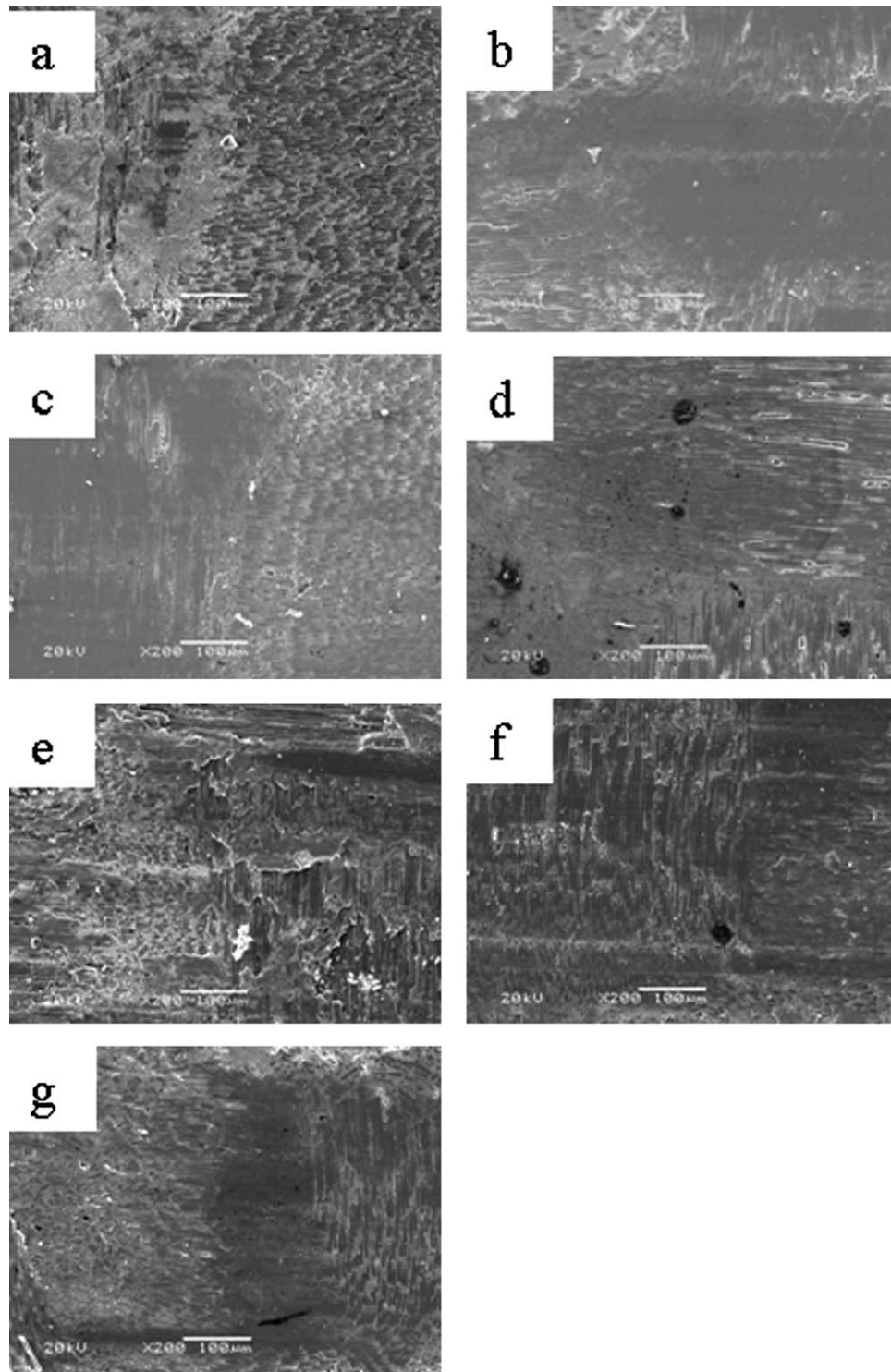


Figure 8 SEM morphologies of the worn surface of nanoparticles-filled CF composites (500N, 0.431 m/s. (a) Pure CFC; (b) nano-Si₃N₄/CFC; (c) nano-CaCO₃/CFC; (d) nano-TiO₂/CFC; (e) nano-SiO₂/CFC; (f) nano-CuO/CFC; (g) MWNT/CFC.

coefficient. The worn surface of nano-TiO₂-filled CF composite [Fig. 9(d)] is smoothest. The phenolic matrix was sheared into a most integrated layer on the worn surface and strongly bonded with carbon fibers. The pulling-out and cutting phenomena of carbon fibers are also obviously observed on the worn surface of nano-SiO₂-filled CF composite

[Fig. 9(e)]. Moreover, lots of flaky debris appear on the worn surface.

CONCLUSIONS

A systematic investigation on the tribological properties of several nanoparticles-filled carbon fabric

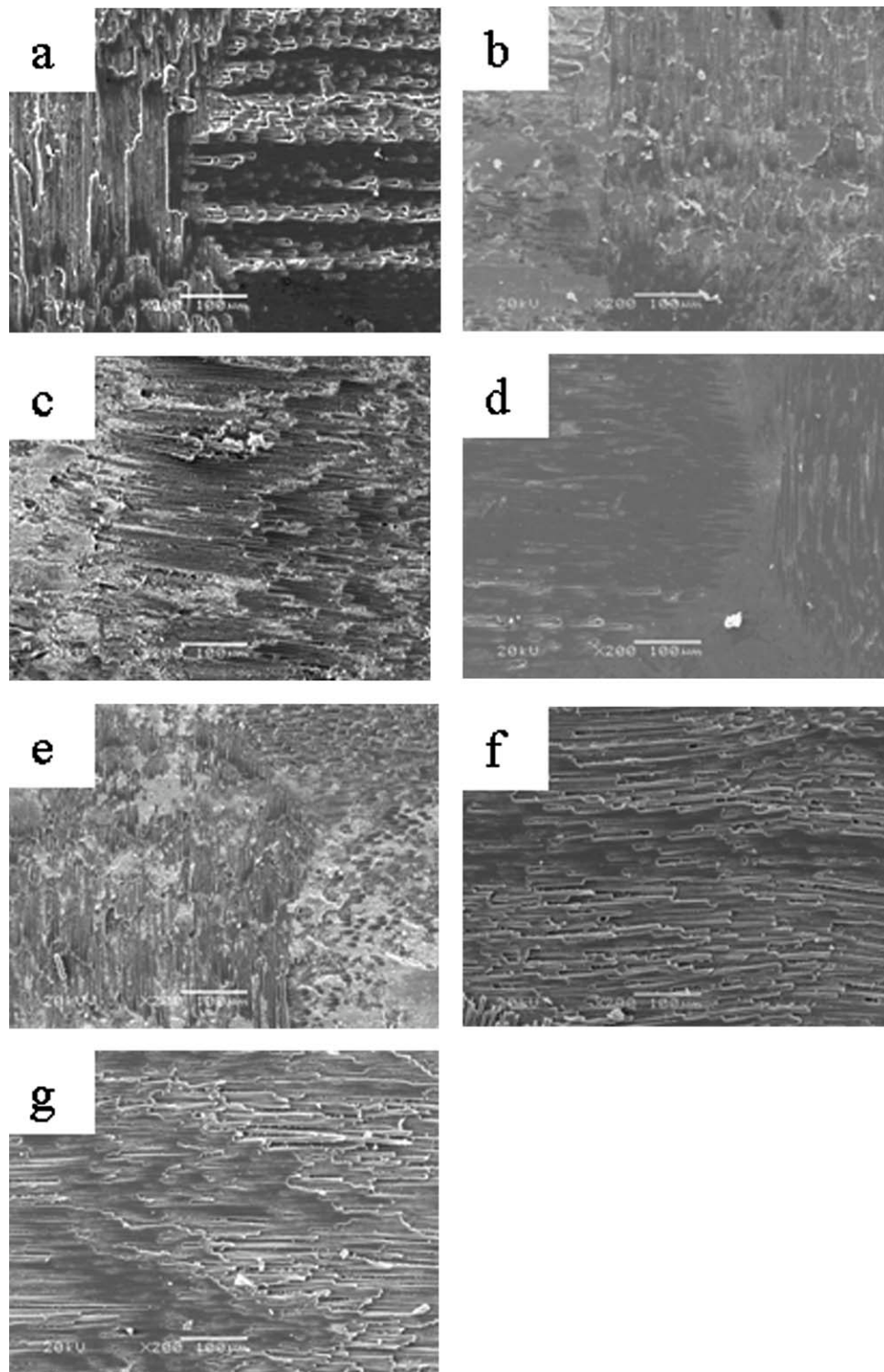


Figure 9 SEM morphologies of worn surface of nanoparticles-filled CF composites (200N, 0.862 m/s) (a) Pure CFC; (b) nano-Si₃N₄/CFC; (c) nano-CaCO₃/CFC; (d) nano-TiO₂/CFC; (e) nano-SiO₂/CFC; (f) nano-CuO/CFC; (g) MWNT/CFC.

reinforced phenolic composites was carried out in this work. The results are as follows:

1. An appropriate content of nanoparticles can improve the tribological properties of CF composites. The differences of nanofiller particulates on

the tribo-performance of carbon fabric composites were dependent with the intrinsic properties of the filler particulates themselves, the influence of the filler particulates on the structure of the filled carbon fabric composites, and the properties of the transfer films formed on the counterface.

2. The differences in the friction and wear properties of CF composites are closely related with the sliding conditions such as load and sliding speed.

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