Tribological behavior of hybrid PTFE/Kevlar fabric composites with nano-Si$_3$N$_4$ and submicron size WS$_2$ fillers

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A B S T R A C T
Hybrid PTFE/Kevlar fabric composite specimens were prepared with nano-Si$_3$N$_4$ and/or submicron size WS$_2$ as fillers. The tribological behaviors of these composites were studied. The morphologies of the worn surface, transfer film and debris were analyzed by means of scanning electron microscopy. In addition, an energy-dispersive X-ray spectrometer was used for analysis of the elemental distribution and content in the transfer film. The results indicate that single nano-Si$_3$N$_4$ fillers can effectively reduce the wear rate of composites, but they do not reduce the friction coefficient. Hybrid Si$_3$N$_4$ and WS$_2$ fillers can significantly reduce the wear rate and friction coefficient of composites.

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1. Introduction

Fabric composites play an important role in materials and mechanical engineering, not only for their ease in manufacturing and low unit cost but also for their potentially excellent tribological performance in engineered forms; therefore, they are very attractive materials for use as advanced bearing liner materials. Hybrid PTFE/Kevlar fabric composites, which are woven out of PTFE and Kevlar fibers, are one of the most popularly used bearing liner materials. The good lubrication of the PTFE fiber side was used as the friction surface, and the Kevlar fiber side, with its good mechanical properties, was used as the binding surface [1–3]. However, it is well known that PTFE fibers exhibit a high wear rate in the pristine form; as a result, hybrid PTFE/Kevlar fabric composites would also not satisfy most of the tribological requirements. Therefore, a modification is necessary to improve the tribological properties of hybrid PTFE/Kevlar fabric composites.

Many researchers have developed polymer-based nanocomposites for tribological applications [4–8]. Li et al. filled PTFE with nanoparticles of ZnO and found that using nanometer ZnO powders as a filler in PTFE changed the microstructure of PTFE and prevented the destruction of PTFE banded structures during the friction process [9]. Sawyer et al. studied the wear and friction properties of nanofiller-containing PTFE composites and found that at filler concentrations of 20 wt%, the wear resistance improved by 600 × [10]. Sebastian et al. studied the tribological behavior of polyphenylensulfide composites filled with short carbon fibers and/or carbon nanotubes. They found that due to the fast formation of a groove-filling transfer film on the counterpart, these composites exhibited an excellent tribological property [8]. Wang et al. filled polyetheretherketone (PEEK) with various weight fractions of nano-Si$_3$N$_4$ and found that nano-Si$_3$N$_4$ particles could significantly improve the wear resistance and reduce the friction coefficient. This improvement was closely related to the improved characteristics of the transfer film [11]. Chang et al. observed the tribological properties of polyamide composites filled with TiO$_2$ nanoparticles, short carbon fibers, and graphite flakes. It was found that nano-TiO$_2$ could effectively reduce the frictional coefficient and wear rate. One mechanism of the remarkable improvement of the tribological properties of the composites was the positive rolling effect of nanoparticles between the material pairs [12,13].

Recently, some research on nanoparticle-filled fabric composites revealed their significant potential in producing materials with good comprehensive friction properties [14–19]. Professor Zhang and his coworkers at the Lanzhou Institute of Chemical Physics have performed a significant amount of work in the area of fabric composites filled with nanoparticles. Su et al. investigated the tribological properties of nano-TiO$_2$ and nano-ZnO-filled hybrid glass/PTFE fabric composites, and the results indicated that the incorporation of TiO$_2$ and ZnO nanoparticles could significantly improve the wear resistance of the composites [14–17]. Zhang et al. studied the influence of nano-TiO$_2$ and nano-SiO$_2$ on the tribological behavior of hybrid PTFE/Kevlar fabric/phenolic composites. The incorporation of TiO$_2$ or SiO$_2$ nanoparticles was found to reduce the wear rate of the fabric composite at elevated temperatures, but it did not have an important influence on the wear resistance of the composites at room temperature.

Nanoparticles can be effective in reducing the wear rate of fabric composites, and in some cases, the coefficient of friction can also be reduced. However, in practice, fabric composites filled with
ultrasonic vibration was used to disperse the nano-Si$_3$N$_4$ and agglomerated [14]. To prevent agglomeration of the particles, between the nanoparticles is strong, and the particles are easily particles, and their surface energy is high. Thus, the adhesive force much higher surface area-to-volume ratio than do larger-sized submicron size WS$_2$ particles in a modiﬁcation. Thus, a combination of nano-Si$_3$N$_4$ and submicron size WS$_2$ fillers.

properties of nano-Si$_3$N$_4$ and submicron size WS$_2$. Table 1.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Si$_3$N$_4$</th>
<th>WS$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grain size (nm)</td>
<td>80–100</td>
<td>600</td>
</tr>
<tr>
<td>Purity (%)</td>
<td>99.9</td>
<td>99.9</td>
</tr>
<tr>
<td>Specific surface area (m$^2$/g)</td>
<td>71.0</td>
<td>3.2</td>
</tr>
<tr>
<td>Tap density (g/cm$^3$)</td>
<td>1.14</td>
<td>2.04</td>
</tr>
<tr>
<td>Bulk density (g/cm$^3$)</td>
<td>0.49</td>
<td>0.44</td>
</tr>
</tbody>
</table>

2. Experimental section

2.1. Materials and specimen preparation

The PTFE/Kevlar fabric used in this study was woven from PTFE fibers and Kevlar fibers, and a picture of the fabric is shown in Fig. 1. As shown in Fig. 1, the two sides of the fabric have different proportions of PTFE and Kevlar. The front face was rich in PTFE fiber and was always used as a friction surface. The back face was rich in Kevlar fiber and was used as a binding surface. In this way, the low friction of PTFE and high strength of Kevlar were combined to a great extent [1]. The fillers used in this study are commercially available, and the material properties are listed in Table 1.

Due to the very small diameter of nano-Si$_3$N$_4$, nano-Si$_3$N$_4$ has a much higher surface area-to-volume ratio than do larger-sized particles, and their surface energy is high. Thus, the adhesive force between the nanoparticles is strong, and the particles are easily agglomerated [14]. To prevent agglomeration of the particles, ultrasonic vibration was used to disperse the nano-Si$_3$N$_4$ and submicron size WS$_2$ particles in a modiﬁed polyimide resin. The hybrid PTFE/Kevlar fabrics were ultrasonically cleaned in an acetone bath for 1 h, boiled 30 min in distilled water, dried in an oven at 80 °C for 1 h, and then the dried hybrid PTFE/Kevlar fabrics were weighed by a precision balance (accuracy: 0.1 mg). The fillers were mixed uniformly with modiﬁed polyimide adhesive resin at the proper mass fractions with the assistance of ultrasonic stirring. Afterwards, the hybrid PTFE/Kevlar fabrics were immersed in the mixed adhesive containing the fillers. Subsequently, the immersed PTFE/Kevlar fabrics were dried in a nitrogen-purged environment at a rate of 50 °C/h to 130 °C, where they were held for 1 h.

The specimens were then cooled at a rate of 50 °C/h back to room temperature. After this, the specimens were weighed and the relative mass fraction of fabrics was calculated. The immersion was repeated several times until the relative mass fraction of fabrics was 70 ± 5%. And then, a laboratory press was used to consolidate the fabrics under pressure of 5 MPa at 210 °C for 30 min. Finally, the ﬁlled PTFE/Kevlar fabric composites (which were composed of the PTFE/Kevlar fabric, the adhesive resin, and the ﬁllers) and unfilled PTFE/Kevlar fabric composites were affixed onto the 440c stainless steel using the modiﬁed polyimide adhesive resin and then cured at 210 °C for 15 min under pressure of 0.2–0.3 MPa.

2.2. Tribological test

Tribological tests were performed using a pin-on-disc tribometer (RTEC MFT-5000, made in the USA) under dry friction conditions. All of the experiments were performed under laboratory conditions (temperature, $T=25$ °C, relative humidity ~50%). Fig. 2 shows the schematics of the test assembly. In the pin-on-disc tester, a stationary steel pin slid against a rotating steel disc that was afﬁxed with the PTFE/Kevlar fabric composite specimens. The ﬂat-ended bearing steel pin (diameter of 3.3 mm) was secured to the load arm with a chuck. The distance between the center of the pin and the center of the disc was 16 mm. The pin remained over the disc with two degrees of freedom: the vertical one for normal load application by direct contact with the disc and the horizontal one for friction measurement.

The sliding was performed under dry friction conditions at a sliding speed of 1 m/s and at a normal load of 513 N (60 MPa), and the sliding distance used was 1.8 km. For self-lubricating fabric composites these contact pressures are typical for industrial applications. The normal load and friction force were measured by normal force sensor (range: 50–5000 N, resolution: 0.25 N) and friction force sensor (range: 1–100 N, resolution: 0.005 N), and the frequency of sampling is 1000 Hz. The friction coefficient $\mu$ of the
Energy dispersive x-ray spectroscopy (EDS) was used for the elemental analysis of the samples. In addition, each sample was examined by Scanning electron microscopy (SEM), and the ones which results in the strengthening of the mechanical properties of the fabric composite. Therefore, the wear resistance is significantly improved.

3. Results and discussion

3.1. Friction and wear properties

Fig. 4a shows the variation of the friction coefficient and the wear rate of hybrid PTFE/Kevlar fabric composites containing different contents of Si$_3$N$_4$ nanoparticles under the load of 513 N (60 MPa) at the speed of 1 m/s. The use of the fillers remarkably reduced the wear rate of the composites. Compared to unfilled PTFE/Kevlar fabric composites, the composites with 12.5 wt% nano-Si$_3$N$_4$ exhibit the best wear resistance. In contrast, with the increase in the content of filler, the friction coefficient increased. Contrary to the above case, submicron size WS$_2$ filler was favorable for the reduction of the friction coefficient and the wear rate of composites, as shown in Fig. 4b. When the content of filler increased to 7.5 wt%, the composites exhibited lower wear rate, and the minimum friction coefficient. Therefore, this content was selected to investigate the combined effects of two types of fillers on the tribological properties of hybrid PTFE/Kevlar fabric composites. Fig. 4c shows the variation of the friction coefficient and the wear rate of the PTFE/Kevlar fabric composite filled with hybrid nano-Si$_3$N$_4$ and submicron size WS$_2$ fillers (the content of WS$_2$ is a constant value of 7.5 wt%, and the content of Si$_3$N$_4$ is varied from 2.5 wt% to 12.5 wt%). The friction condition was the same as that mentioned above. The wear rate was found to sharply decrease with the increase in the content of Si$_3$N$_4$ nanoparticles, and the composites with 7.5 wt% WS$_2$ + 12.5 wt% nano-Si$_3$N$_4$ exhibits the lowest wear rate. Fig. 4d and e shows the variations of the friction coefficient and the wear rate of all types of composites. It can be observed from the figures that hybrid fillers exhibit the best wear resistance and friction properties.

3.2. SEM observations of the worn surfaces

Fig. 5a–d shows the SEM images of the worn surface of unfilled and WS$_2$ + Si$_3$N$_4$-filled PTFE/Kevlar fabric composites. Fig. 5a and b shows the SEM image of the worn surface of unfilled PTFE/Kevlar fabric composites. A large number of PTFE and Kevlar fibers significantly peel, and there are many long and deep cracks on the worn surface, which is indicative of severe wear. Fig. 5c and d shows the SEM images of the worn surfaces of 7.5 wt% WS$_2$ + 12.5 wt% Si$_3$N$_4$-filled composites. The worn surface of the WS$_2$ + Si$_3$N$_4$-filled composites is quite smooth, and the fibers are strongly combined with the matrix. This observation indicates that the addition of WS$_2$ and Si$_3$N$_4$ filler in the hybrid PTFE/Kevlar fabric composite results in strong adhesion of fibers to the matrix, which results in the strengthening of the mechanical properties of the fabric composite. Therefore, the wear resistance is significantly improved.

3.3. SEM and EDS analysis of the transfer films

It is well known that achieving the appropriate characteristics of the transfer film is a very important factor affecting the tribological properties of polymer composites. To better understand the role of fillers in tribological processes, SEM was used to explore the morphologies of the transfer films formed on the steel pin surface for unfilled and filled hybrid PTFE/Kevlar fabric composites. In addition, an energy-dispersive X-ray spectrometer (EDS) was used for analysis of the elemental distribution and content in the transfer films.

The results of the EDS elemental analysis are shown in Fig. 6. The F element and O element were found in the transfer films for unfilled fabric composites. The F element, O element, N element and Si element were found in transfer films for 7.5 wt% WS$_2$ + 12.5 wt% Si$_3$N$_4$-filled PTFE/Kevlar fabric composites. These findings indicate that the transfer of PTFE, resin and filler occurred during sliding [21,22]. It is also observed from Fig. 6 that the F element and O element content in the transfer film for unfilled composites are higher and that the Fe element content is lower than that of the filled composites. This observation might suggest that the transfer film for unfilled composites formed on the steel pin is thicker than that of the 7.5 wt% WS$_2$ + 12.5 wt% Si$_3$N$_4$-filled hybrid PTFE/Kevlar fabric composites. It can be seen from Fig. 6a that the transfer film formed on the unfilled composites is characterized as thick and lumpy. This type of transfer film has poor adhesive properties with the substrate and was easily peeled off from the counterface. Therefore, it can be inferred that adding nanoparticles to composites can significantly improve the performance of the transfer film formed on the
counterface, which results in a much lower wear rate for the filled composite in comparison with the unfilled one.

The SEM image of the transfer film formed on the pin’s surface is shown in Fig. 7. For unfilled composites, the transfer film formed on the pin’s surface is thick and lumpy. According to former research, this type of transfer film was easily scaled off of the counterface and formed debris during wear process, which resulted in the high wear rate of unfilled hybrid PTFE/Kevlar fabric composites. Whereas a uniform and thin transfer film is formed on the pin sliding against the 7.5 wt% WS$_2$ + 12.5 Si$_3$N$_4$-filled hybrid PTFE/Kevlar fabric composites. The thin and uniform transfer film will firmly adhere onto the counterface and is not easily scaled off during sliding. The tenacious transfer film can prevent the direct contact between the steel pin and fabric composites, thereby significantly reducing the wear rate. Moreover, by careful observation of Fig. 7d, we find that there are many nanoparticles on the transfer film surface; those nanoparticles between the material pairs may have acted as roller bearings and further reduced the wear rate [12,14,23].

3.4. SEM examination of the wear debris

Debris is a product of the frictional experiment, and analyzing debris is helpful to understand the tribological mechanisms. Fig. 8 shows the SEM images of the wear debris of unfilled hybrid
PTFE/Kevlar fabric composites and 7.5 wt% WS$_2$ + 12.5 wt% Si$_3$N$_4$-filled composites. It can be observed from Fig. 8a and b that unfilled composites generate debris that mainly consists of wide ribbon debris and lumpy slabs, which is indicative of delamination. Contrary to the unfilled composites, the wear debris of 7.5 wt% WS$_2$ + 12.5 wt% Si$_3$N$_4$-filled hybrid PTFE/Kevlar fabric composites is much smaller and mainly consists of tiny flakes and filamentous wear debris. This observation indicates that adding nanoparticles to PTFE/Kevlar fabric composites can restrain the formation of larger debris. Moreover, wide ribbon and lumpy slab debris cannot easily fill in the grooves on the fabric surface, and hence, they pile up during repeated sliding and subsequently are discarded as debris. Wear debris composed of tiny flakes is easily trapped in the gap of a worn surface and can repair the damaged surface, and this trapped debris can be considered as a secondary source of lubricant that permeates to the surface to reduce the friction and retard the galling during sliding. Therefore, adding hybrid fillers to PTFE/Kevlar fabric composites can sharply improve the friction and wear properties of the composites.

4. Conclusion

This work presents investigations on the tribological behavior of hybrid PTFE/Kevlar fabric composites with nano-Si$_3$N$_4$ and/or submicron size WS$_2$ filler samples against bearing steel at dry friction conditions. The following conclusions can be drawn from the present study:

(a) It was found that under the experimental conditions, Si$_3$N$_4$ nanoparticles could effectively reduce the wear rate of hybrid PTFE/Kevlar fabric composites.
(b) Submicron size WS$_2$ filler was favorable for the reduction of the friction coefficient and the wear rate of composites compared to the unfilled samples; the 7.5 wt% WS$_2$ filled composites exhibited lowest friction coefficient, and the value is 0.045.
(c) The wear rate and friction coefficient of 7.5 wt% WS$_2$ + 12.5 wt% Si$_3$N$_4$-filled hybrid PTFE/Kevlar fabric composites were much less than those of the unfilled composites. The wear rate was reduced greatly, from $8.75 \times 10^{-14}$ m$^3$/Nm to...
0.41 × 10^{-14} \text{m}^3/(\text{Nm})$, and the uncertainty of wear rate of unfilled composites and the 7.5 wt% WS$_2$ + 12.5 wt% Si$_3$N$_4$-filled composites are 0.069 × 10^{-14} \text{m}^3/(\text{Nm}) and 0.073 × 10^{-14} \text{m}^3/(\text{Nm})$, respectively. The friction coefficient also decreased from unfilled (0.059) to filled with hybrid fillers (0.040). Thus, hybrid fillers could achieve the desired comprehensive tribological properties in dry sliding.

(d) The transfer films of 7.5 wt% WS$_2$ + 12.5 wt% Si$_3$N$_4$-filled hybrid PTFE/Kevlar fabric composites were thin, uniform and full of nanoparticles. The tenacious transfer film can prevent the direct contact between the steel pin and the fabric composites, and those nanoparticles between the material pairs are thought to have acted as roller bearings, thereby further reducing the wear rate.

Fig. 7. The scanning electron micrographs of the transfer film formed on the counterpart pin: (a) unfilled, (b) magnification of (a), (c) filled with 7.5 wt% WS$_2$ and 12.5 wt% Si$_3$N$_4$, and (d) magnification of (c).

Fig. 8. SEM images of the wear debris of hybrid PTFE/Kevlar fabric composites: (a) lumpy slabs debris (unfilled), (b) wide ribbon debris (unfilled), (c) tiny flake debris (filled) and (d) filamentous debris (filled).
Acknowledgments

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