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Enhancement effect of nanoparticles on the sliding wear of short fiber-reinforced polymer composites: A critical discussion of wear mechanisms

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ABSTRACT

Short fiber-reinforced polymers (SFRPs) form an important class of tribo-materials owing to their high specific strength, good load-carrying capacity and rapid, low-cost processibility. Nevertheless, further developments are still under way to tailor their properties for more extreme loading conditions and to explore new fields of application for these materials. Recently, nano-sized inorganic particles have come under consideration. It was found that the addition of a small percentage of rigid nanoparticles to SFRPs may significantly improve their wear resistance, especially under high pv (the product of p (pressure) and ν (velocity)) conditions. However, the detailed mechanisms of such improvement have not been fully understood yet.

The objective of this study is to achieve an in-depth understanding of the role of the nanoparticles in modifying the sliding wear behavior of SFRPs. In particular, the effects of nanoparticles on contact mechanics and wear behavior of the transfer film were investigated. It was found that the additional nanoparticles do not directly contribute to the formation of a high performance transfer film. However, the presence of nanoparticles in the contact region can effectively reduce the adhesion between the transfer film and the polymeric specimen, resulting in a lower coefficient of friction. In particular, the rolling behavior of nanoparticles can significantly enhance the tribological performance of SFRPs especially under extreme sliding conditions.

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1. State of the art

Tailored polymeric composites, such as short fiber-reinforced engineering polymers (SFRPs), have been widely used as dry sliding materials, in particular as lower weight alternatives to metal materials, with the attractive advantages of self-lubrication and superior cleanliness [\[1–3\]](#page-9-0). The beneficial effect on the tribological behavior of polymer composites by short fibers has been attributed to a reduced ability of plowing, tearing and other non-adhesive components of wear [\[4,5\].](#page-9-0) Moreover, in comparison with continuous fiber-reinforced polymers, SFRPs have the advantage of rapid, lower-cost processibility by injection/compression molding or by extrusion [\[6\]](#page-9-0). However, due to the fiber breakage and the thermal failure of the polymeric matrix, SFRPs may suffer the risk of severe wear or sometimes sudden seizure especially under high loading conditions, which is normally related to the increase in friction as well as contact temperature [\[7,8\]](#page-9-0). The current trends in

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development of SFRPs are to tailor their properties for more extreme loading and environmental conditions and to explore new fields of application for these materials.

Integrating various functional fillers is a principal route to develop high performance composite materials which cannot be achieved by using the single filler alone [\[9\]](#page-9-0). Considerable attempts have been made to incorporate different additional fillers into SFRPs in order to further improve their tribological performance. In particular, lubricating particulates such as polytetrafluoroethylene (PTFE), graphite and molybdenum disulfide $(MoS₂)$ have been successfully used to reduce the friction coefficient and the wear rate of SFRPs [\[3,9–12\].](#page-9-0) These solid lubricants are generally helpful in developing a uniform transfer layer on the surface of metallic counterparts, which protects fibers from severe abrasive wear. More recently, with the booming of nanophased materials, nano-sized inorganic particles have also come under consideration. For instance, Cho and Bahadur [\[13\]](#page-9-0) reported that the addition of 2 vol% nano-CuO could generally enhance the wear resistance of short fiber-reinforced polyphenylene sulfide. The beneficial effect of nanoparticles was attributed to the development of a thin and uniform transfer film. Chang and Zhang [\[7\]](#page-9-0) and Chang et al. [\[14\]](#page-9-0) systematically studied the effect of nano-TiO₂ on short fiber-reinforced epoxy under different

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loading conditions. It was found that the addition of 5 vol% nano-TiO2 could significantly reduce the friction coefficient and the wear rate of epoxy composites filled only with traditional fillers. The reduction was more pronounced at high pv (the product of p (pressure) and v (velocity)) conditions. The rolling effect of nanoparticles was proposed to explain the low friction and wear loss of the nanocomposites. Guo et al. [\[15\]](#page-9-0) used surface modified nano- $SiO₂$ filler to enhance the tribo-properties of epoxy composites filled with short carbon fibers. In order to improve the interface bonding between nanoparticles and the polymeric matrix, the nanoparticles were pretreated by graft polymerization. Again, the additional nanoparticles (4 wt%) proved to be useful in enhancing the wear resistance and reducing the friction of the SFRPs. The authors indicated that the improvement mechanisms of nanoparticles could be caused by the increased strength of the matrix and better properties of the transfer film. These results have clearly shown that the addition of nanoparticles is potentially useful to improve the tribological performance of SFRPs, even at a relatively low content. Nevertheless, the improvement mechanisms using nanoparticles have not been deeply understood, although the pioneer researchers have addressed a number of significant factors affecting the wear behavior of these materials.

It was, therefore, the objective of the present work to bring further light into the open questions mentioned above.

2. Experimental details

2.1. Materials

Two kinds of polymers, i.e. epoxy (EP) and polyamide 66 (PA 66), were used as matrices, and the short carbon fiber (SCF) and two solid lubricants, i.e. graphite and PTFE, acted as conventional tribo-fillers.

Fig. 1. SEM picture of the fracture surface of an epoxy matrix composite containing short (smaller diameter, PAN based) carbon fibers, graphite flakes and 300 nm sized $TiO₂$ nanoparticles.

The average diameter of the pitch based SCF was \sim 14.5 μ m, with an average fiber length of \sim 90 µm. The size of the graphite flakes and the PTFE powder particles amounted to \sim 20 and \sim 4 µm, respectively. Nano-sized TiO₂ particles were used as the additional filler, at a volume content of 5%. The average diameter of the particles was 300 nm (Fig. 1). Technical details of the fillers and matrix, as well as the compositions and the compounding procedures have been reported previously [\[8,14\]](#page-9-0) (cf. Table 1). In terms of the epoxy composites, a composition of 15 vol% SCF+5 vol% graphite+5 vol% PTFE was used as a benchmark for the conventional SFRP composites, which was formulated as the optimum content according to the results from a series of SCF/graphite/PTFE/epoxy-based composites [\[14,16\]](#page-9-0). For the PA 66 composites, a composition of 15 vol% SCF+5 vol% graphite was used as the conventional SFRP composite.

2.2. Wear test procedure

Fig. 2 shows a schematic diagram of the pin-on-disk apparatus, with which the wear tests were conducted. The specimen pin $(4 \times 4 \times 12 \text{ mm}^3)$ was rotated against a hardened and polished carbon steel disk (German Standard 100Cr6), with an initial surface roughness R_a of \sim 220 nm. All tests in this study were conducted for 20 h under dry condition at room temperature. During the test, the friction coefficient was recorded and calculated by the ratio of tangential force to normal load. The reduction in specimen's height was measured by a displacement transducer, which could be used to characterize the development of the wear process. An additional monitoring of the temperature rise during testing was carried out by an iron–constantan thermocouple positioned on the edge of the steel disk.

[Fig. 3](#page-2-0) shows the typical sliding process of a polymeric sample sliding against the steel disk. The sliding process can be generally divided into two stages, a running-in stage and a steady wear stage, which are further discussed in Section 5.3. In most cases the sliding behavior in the steady stage is of primary concern, since it determines the wear life and thus the applicability of a component. Therefore, in this paper, the values of the friction coefficient and temperature of the steel disk refer to the mean values in the steady stage, and each result is an average value from at least three repeated tests. The specific wear rate is determined by the mass loss

Fig. 2. Pin-on-disk configuration under which the wear tests were performed.

Table 1

Compositions of the tested materials and their compounding methods [\[8,14\].](#page-9-0)

Fig. 3. Typical sliding performance of polymeric composite against metallic disk. Polymeric pin: 5 vol% TiO₂+5 vol% graphite+15 vol% SCF/PA 66. Loading conditions: normal pressure = $2MPa$ and sliding velocity = 1 m/s.

of the specimen after the test, according to the following equation:

$$
w_s = \frac{\Delta m}{\rho F_N L} \left[\text{mm}^3 / \text{Nm} \right] \tag{1}
$$

where Δm is the specimen's mass loss, ρ the density of the specimen, F_N the normal load applied on the specimen during sliding and L the total sliding distance.

2.3. Microscopic characterization of the worn surfaces

After the wear testing, the worn surfaces and the wear tracks on the steel disk were observed by scanning electron microscopy (SEM, JEOL-5400). In addition, an SEM (JSM-T330A), equipped with a wavelength dispersive X-ray (WDX) spectrometry, was used to characterize the titanium elements (nano-TiO₂) in wear region on the steel disk. For more exact and detailed information, an atomic force microscope (AFM; Digital Instruments) was employed to study highly localized damage and/or topographical changes. The surface morphology of steel disks covered with a polymer transfer film was investigated with a laser profilometer (UBM Messtechnik).

3. Wear test results

Fig. 4a summarizes the wear test results of the polymeric composites in comparison with that of the pure polymers. The applied tribo-fillers enhanced the wear resistance of the polymers by about one order of magnitude at 1 MPa m/s. In this case, it is also noticed that the wear rates of the SFRP composites are in the range of 10^{-6} mm³/Nm, which is in agreement with results typically found for carbon fiber-reinforced polymers sliding against various steel counterfaces [\[6,17\].](#page-9-0) With an increase in pv , the wear rate of the composites filled with traditional fillers progressively increased, suggesting changes in the dominant wear mechanisms. For the composite with additional nanoparticles, however, the wear rate of the nanocomposite was relatively stable (within a range between 1 and 3×10^{-6} mm³/Nm), even under high pv conditions. This means that the limiting pv of the nanocomposite was clearly improved, which would promote the use of these materials for triboapplications in which more severe wear conditions are dominant.

Fig. 4b compares the friction coefficient of the specimens tested under different sliding conditions. It was found that the addition of nanoparticles could effectively reduce the friction coefficient of SFRPs under all the testing conditions applied here. There is, however, no general relationship between the trends in friction coefficient and specific wear rate as a function of pv

Fig. 4. Wear test results of various polymer composites subjected to different sliding conditions: (a) specific wear rate and (b) friction coefficient. Dashed lines: wear results of the composite with nanoparticles; full lines: wear results of the composite without nanoparticles.

product. Nevertheless, a high friction force/coefficient is normally undesirable for polymeric materials, not only because it may accelerate the wear loss of the materials, but also it will lead to a high contact temperature due to the frictional heating, and thus a thermal–mechanical failure of the material. In the following sections, the wear mechanisms of SFRP composites are further discussed based on microscopic observations. In particular, the mechanisms for the favorable effects of nanoparticles on the wear behavior of SFRPs are discussed in more detail.

4. Analysis of wear mechanisms

It is known that the wear performance of SFRP composites is determined to a great extent by the properties of the fibers [\[6,17\].](#page-9-0) This is also true for hybrid SFRP composites filled with additional particulate fillers, such as the materials considered in this study. [Fig. 5](#page-3-0) shows the microscopic view of fibers exposed on the worn surfaces of epoxy-based SFRP composites filled without and with nanoparticles. It can be observed that the fibers clearly stand out from the polymeric matrix and are fully exposed to the counterparts. By using atomic force microscopy (AFM), the height from the matrix surface to the exposed fiber can be accurately

Fig. 5. Tilted SEM image with an angle of 45° for the short fibers in the worn surfaces of (a) graphite+SCF+PTFE/epoxy and (b) nano-TiO₂+graphite+SCF+PTFE/epoxy. Loading conditions: normal pressure = 1 MPa and sliding velocity = 1 m/s.

Fig. 6. (a) AFM picture of the exposed fiber in the worn surface of nano-TiO₂+graphite+SCF+PTFE/epoxy and (b) a cross-sectional measurement. Loading conditions: normal pressure = 1 MPa and sliding velocity = 1 m/s.

measured (Fig. 6). After examination of more samples, it was found that the height of the exposed fiber always agreed with the original surface roughness of the steel counterpart (which is \sim 220 nm), regardless of the type of the matrix [\[7,8\]](#page-9-0). Hence, during the wear process, the short fibers had to carry most of the load. To fully explore the strengthening effect of short fibers, it is critical to ensure that the fibers are only gradually removed from the polymer matrix, i.e. without serious breakage.

[Fig. 7](#page-4-0) compares the worn surfaces of the two epoxy-based composites without and with nanoparticles subjected to different loading conditions at a sliding speed of 1 m/s. For the composite without nanoparticles, the worn surface is relatively smooth under the low loading condition (Fig. [7a](#page-4-0)), which indicates a gradual removal process of the fibers, normally occurring in the sequence of fiber thinning, fiber fracture and final removal of broken fiber pieces [\[1\].](#page-9-0) However, with an increase in the applied contact pressure, breakage of the epoxy matrix occurs, especially at the interfacial region around the fibers [\(Fig. 7b](#page-4-0)). As a result, the fibers are removed more easily, because the local support of the matrix is missing. The large fiber debris can further reduce the wear resistance of the composite because of a third body abrasive wear effect. Consequently, the wear rate of the material progressively increases (cf. [Fig. 4a](#page-2-0)). When the pressure increases to 4 MPa, the specimen failed by the formation of macro-cracks ([Fig. 7](#page-4-0)c), which contributed to a further increase in the specific wear rate. With the addition of nanoparticles, however, the situation was much different. As shown in [Fig. 7](#page-4-0)d–f, the worn surfaces appear much smoother, even at a severe wear condition of 12 MPa and 1 m/s. The fibers were always removed gradually and fully contributed to the wear resistance of the composites. As a result, the specific wear rate of the material was much more stable (cf. [Fig. 4a](#page-2-0)), and the load-carrying capacity of the material was significantly improved.

[Fig. 8](#page-4-0) compares the worn surfaces of the PA 66 based composites, without and with nanoparticles, tested under different loading conditions. The fiber removal in the composite without nanoparticles was also very much aggravated with an increase in applied pressure. However, in comparison with the brittle epoxy system, the breakage of the matrix at the interfacial regions was much more limited because of the higher ductility of the polyamide matrix, which deformed through elongation rather than breakage [\[7\]](#page-9-0). However, due to the thermal softening of the polymer matrix caused by frictional heating, serious fiber removal also happened at higher loading conditions, leaving large grooves on the worn surfaces ([Fig. 8b](#page-4-0)). At 8 MPa, even some melting features (double arrow) of the PA 66 matrix could be observed on the worn surface ([Fig. 8c](#page-4-0)). As a result, the wear rate was greatly increased because the reinforced fibers could not contribute to wear resistance any more. Again, the addition of nanoparticles resulted in smoother worn surfaces under all test conditions (cf. [Fig. 8d](#page-4-0)–f). Accordingly, the specific wear rates of the nanocomposites were much lower than those of the composites without nanoparticles, especially under extreme loading conditions (cf. [Fig. 2](#page-1-0)).

On the basis of the microscopic observations shown above, [Fig. 9](#page-5-0) gives a schematic illustration of the failure mechanisms during sliding wear of SFRP composites without nanoparticles.

Fig. 7. Comparisons of the damage characteristics of the fibers in the worn surfaces of epoxy-based composites without and with additional nanoparticles: (a), (b) and (c) are the representative SEM images for graphite+SCF+PTFE/epoxy tested under 1, 2 and 4 MPa, respectively; (e), (d) and (f) are the representative SEM images for nano- $TiO₂ + graphite + SCF + PTFE/epoxy tested under 1, 4 and 12 MPa, respectively. The sliding velocity remained constant at 1 m/s. The white arrow indicates the sliding$ direction of the counterpart.

Fig. 8. Comparisons of the damage characteristics of the fibers in the worn surfaces of PA 66-based composites without and with the additional nanoparticles: (a), (b) and (c) are the representative SEM images for graphite+SCF/PA 66 tested under 1, 4 and 8 MPa, respectively and (e), (d) and (f) are the representative SEM images for nano-TiO₂+graphite+SCF/PA 66 tested under 1, 4 and 8 MPa, respectively. The sliding velocity is constant at 1 m/s. The letters in (f) have the following meaning: F=fibers and CWD=compacted wear debris, piled up in front of up-standing fiber edges.

The continuous transfer film formed during the running-in stage is mainly composed of worn matrix material and can effectively reduce the 'direct contact' of the composite with asperities of the hard metallic counterface [\[18–20\].](#page-9-0) Nevertheless, the worn fibers are exposed to most of the normal load and the resulting shear forces during the wear process. They often slide directly against the counterpart, which results in special stress concentrations at the interfacial regions between fibers and matrix. Moreover, due to the frictional heating induced by the fibers, the temperature of the matrix around the fibers is relatively high. As a result, with an increase in the pv factor, failure of the material occurs first in the interfacial region. The specific failure mechanism is dependent on the thermal–mechanical properties of the polymeric matrix, e.g. brittle fractures occurred in case of the epoxy-based composites (cf. Fig. 7c), whereas thermal softening/melting was evident for the PA 66 based composites (cf. Fig. 8c). When the matrix failed to support the short fibers, serious fiber removal could occur and thus a rapid increase in the composite's wear rate. Finally, the material can no longer be employed.

For the nanocomposites, a three-body contact condition was induced by the additional nanoparticles between the contact surfaces, which is evidenced by the nano-grooves/indents on the fiber surfaces (cf. Figs. 6–8). To further confirm the presence of nanoparticles in the contact region, the transfer film developed by the epoxy nanocomposite was analyzed with WDX spectrometry. As shown in [Fig. 10,](#page-5-0) the peaks of titanium elements (representing nano-TiO₂) can be clearly observed in the wear region. Hence, as illustrated in [Fig. 11](#page-5-0), it was proposed that during the sliding process many of the hard particles were embedded in the soft polymeric transfer film on the counterface and grooved the exposed fibers. In this way, the distance between the steel and the composite material was also enhanced, i.e. the particle acted as 'spacers'. This, in turn, can cause a reduction in the adhesion between the contacting surfaces. Therefore, the friction coefficient of the nanocomposites

Fig. 9. Schematic illustration of the failure mechanism for the sliding wear of SFRP composites without nanoparticles (for better illustration purposes: fiber diameter too small relative to roughness of steel counterpart). During the wear process, the short fibers undergo the most of load and wear against the counterpart. In this case, the polymeric matrix in the interfacial region around fibers suffers higher stress and temperature. With the increase in pv, thermal–mechanical failure of the material in this region may occur, due to the high friction and heating. As a result, the fibers will be removed more easily, associated with a progressive increase in the wear rate of the composites (cf. [Figs. 4c](#page-2-0) and [5c](#page-3-0)).

Fig. 10. WDX analysis of Ti-K_{α} and Ti-K_B on the steel counterpart covered with the transfer film. Scanning area: $100 \times 100~\mu$ m². Polymeric pin: nano-TiO₂+graphite+SCF+PTFE/epoxy. Loading conditions: normal pressure=1 MPa and sliding velocity = 1 m/s.

was always lower than that of the composites without nanoparticles (cf. Fig. [4](#page-2-0)b). Moreover, as the nanoparticles were free to move, they tend to be dispersed uniformly over the transfer film during the wear process, which would result in a more uniform contact stress between the contacting surfaces, and thus minimize the stress concentration on the individual fibers. As a result, the thermal failure of polymer matrix in the interfacial region between SCF/ matrix was avoided, and a more gradual removal process of short fibers occurred. This ensured that the wear rate of the nanocomposites was lower, even under extreme loading conditions. In the following section, the role of nanoparticles in modifying the wear behavior of SFRPs is further discussed according to the contact mode illustrated in Fig. 9.

5. Role of nanoparticles in the wear behavior of SFRPs

5.1. Nanopolishing effect

As mentioned above, the additional nanoparticles changed the contact conditions for SFRP vs. steel and effectively reduced the friction force. Due to the abrasiveness of the hard nanoparticles, also a polishing effect on the worn surfaces could be expected (and seen on Figs. 7 and 8). [Fig. 12](#page-6-0) compares the surface roughness of the worn surfaces of four SFRP composites tested under different sliding conditions. The worn surfaces of the composites without nanoparticles are normally rougher under higher pv conditions because of more serious surface damage (cf. Figs. [7\(](#page-4-0)b) and [8](#page-4-0)(b)). However, it is interesting to note that the roughness of the worn surfaces of the composites filled with nanoparticles remained stable at \sim 300 nm, which is in agreement with the size of nanoparticles used in this study.

Therefore, there are two competitive effects of nanoparticles on the wear resistance of SFRP composites. On one hand, nanoparticles tend to reduce the wear rate of composite by a reduction in the friction. On the other hand, abrasive nanopolishing is simultaneously induced by hard nanoparticles acting as third bodies, and this would counteract the former effect to a certain extent. This can explain that the wear rate of SFRP composites could sometime slightly increase with the addition of nanoparticles, especially

Fig. 11. (a) Contact mode for the SFRP composites reinforced with additional nanoparticles (for better illustration purposes: fiber diameter too small relative to roughness of steel counterpart and size of nanoparticles) and (b) force analysis for a single nanoparticle with the radius of R. F_{SCF} : shear force added on the particle by SCF, which also constitutes the friction for the sample; F_{tf} : sum of the force contributed by the counterface covered with the transferred material, which embeds the particle against the fibers and f_{TF} : the resulted internal friction due to the rotation moment, $M_{SCF} = F_{SCF}\delta$.

Fig. 12. Surface roughness R_a of the worn SFRP composites without and with nanoparticles. Due to the polishing effect of nanoparticles, the surface roughness of the composites with nano-TiO₂ is stable at \sim 300 nm and independent of the p v conditions.

under relatively lower pv conditions when the abrasive effect of nanoparticle is dominant [\[8,21\]](#page-9-0).

5.2. Rolling effect under extreme sliding conditions

Experiments have shown that the movement pattern of the particles, e.g. sliding or rolling, plays an important role in the wear performance of the system [\[22–24\].](#page-9-0) It was found that the particles could be embedded in the softer surface, thus scratching the harder one [\[22\].](#page-9-0) The scratching depth is dependent on the hardness and size of the particles [\[22,23\]](#page-9-0). However, depending on the sliding conditions and the properties of the particles, the particle may also roll within the contact interface, resulting in low friction and wear [\[24\].](#page-9-0) Based on such understanding, [Fig. 11b](#page-5-0) shows the force analysis for a spherical nanoparticle during the sliding process. The particle was trapped in the softer polymeric transfer film and scratched the exposed fiber. In this case, the friction force F_{SCF} must be balanced by the supporting force F_{TF} from the transfer film. Accordingly, a rotation moment, $M_{SCF} = F_{SCF}\delta$ is applied on the particle, causing internal friction f_{TF} between the particle and the surrounding polymeric material. When the transfer film is strong enough to resist the moment, the particle can be firmly held and slides against the fiber. As a result, the sliding nanoparticle induces nano-cutting or nano-plowing wear on the surface of the fiber, resulting in continuous nano-grooves (cf. [Figs. 7e](#page-4-0) and [8d](#page-4-0)). However, when the applied friction rotation moment M_{SCF} is higher than the maximum internal holding moment provided by the transfer film, $M_{TF} = f_{TF}R$, the nanoparticle tends to rotate or tumble. As a result, the surface of the fiber (SCF) would be relatively smooth, sometime with discontinuous indents due to the tumbling effect of particle (cf. [Figs. 7](#page-4-0)f and [8](#page-4-0)e).

The rolling/tumbling effect of particles, in turn, also restricts the further increase in the friction force of the system, especially under extreme loading conditions. For example, Fig. 13a compares the friction forces of the hybrid composites filled without and with nanoparticles under different loading conditions. For the polymer composites without nanoparticles, the friction force proportionally increased with an increase in the load (e.g. from 1 to 4 MPa), until yielding of the polymeric material occurred in the contact region. Then the friction force of the SCF+graphite/PA 66 composite increased only slightly (in the pressure range 4–8 MPa) due to melting effects of the PA 66 matrix. However, with the addition of nanoparticles, the

Fig. 13. Effects of the additional nanoparticles on (a) the friction force of SFRP composites and (b) the corresponding temperature rise of the steel disk due to the frictional heating. The sliding velocity is 1 m/s.

maximum friction force was concentrated on a much lower level due to the rolling effect of particles. As shown in the figure, the friction force of the nanocomposites slightly increased when the pressure increased from 1 to 4 MPa; then it remained stable despite a further increase in the load. Accordingly, there were less continuous nanogrooves on the worn SCF under higher loading conditions (cf Figs. 7 and 8). As a result, the temperature rise for the nanocomposites was much less than that for the composites without nanoparticles, especially under higher pv conditions (cf. Fig. 13b).

5.3. On the transfer film

With the use of solid lubricants, i.e. graphite and PTFE, continuous transfer films are usually formed during the sliding of all the composites, i.e. with and without nanoparticles, against steel counterparts [\[8,19\].](#page-9-0) It was reported that the properties of the transfer films might also be influenced by the additional nanoparticles, which finally have an effect on the wear performance of polymeric composites [\[13,15\]](#page-9-0). However, it is difficult to quantitatively study the wear reducing properties of the transfer films after the wear tests, because their wear behavior is determined by the real contact conditions, especially the temperature rise at the interface. Therefore, in the present work, a special comparative

study was carried out in order to investigate the effect of the additional nanoparticles on the wear performance of a transfer film.

Fig. 14 compares the friction and wear processes of composites without and with nanoparticles, using three different contact conditions. During the first 10 h (Test 1), the sliding tests were conducted against clean disks. As shown in Fig. 14a, for the composite without nanoparticles, the friction coefficient initially increases and then becomes stable after the formation of the continuous transfer film. With the addition of nanoparticles (cf. Fig. 14b), the friction coefficient shows a similar increasing tendency at the beginning but then decreases remarkably. The results are in agreement with our earlier observations reported in Ref. [\[8\]](#page-9-0). It was proposed that during the running-in stage the transfer film is gradually formed out of the wear debris under a certain compaction pressure. This was associated with an increase in the coefficient of friction because of the increased real contact area and thus a higher adhesive force. However, for the nanocomposite, the nanoparticles in the wear debris were also gathered and distributed on the counterpart surface in the running-in

Fig. 14. Comparative study on the tribological performances of the transfer films developed without and with nanoparticles: (a) the sliding processes for graphite+SCF/PA 66 against the disk with the transfer film developed without (the first 20 h) and with nanoparticles (the last 10 h) and (b) the sliding processes for nano- $TiO₂ + graphite + SCF/PA$ 66 against the disk with the transfer film developed with (the first 20 h) and without nanoparticles (the last 10 h). Loading conditions: normal pressure = 2 MPa and sliding velocity = 1 m/s.

stage. Therefore, the friction was reduced after a while (still within the running-in period), once a certain amount of nanoparticles was present in the contact region, due to the three-body contact effect. For comparison, the wear processes of the materials were given in the figures as the variation in wear depth. Due to the effect of thermal expansion, the initial changes in depth should normally not be used for the accurate calculation of the wear rate. However, it is useful to on-line monitor the wear process in this way. In particular, the linear behavior of the change in wear depth generally indicates a steady wear process with a constant wear rate. As shown in [Fig. 14,](#page-7-0) according to the variations in friction coefficient, the wear processes can also be divided into two stages, i.e. the initially unstable 'runningin' behavior and then the steady wear stage.

After 10 h, the sliding wear tests were paused for 2 h in order to cool the tribo-system down to room temperature. Then, the sliding tests were continued for another 10 h (Test 2). In this case, the wear track on the steel disk was already fully covered with a continuous transfer film (cf. Fig. 15). As a result, the friction and wear behavior was quickly stabilized without an observed "running-in" process. Instead, the value of the steady friction coefficient remained almost unchanged, compared with the one observed during the first 10 h. The result confirms quite well that the variations in the friction and wear in the running-in stage are mainly caused by the evolution process of the transfer film.

During the last period of testing, i.e. between 20 and 30 h (Test 3), the effect of nanoparticles on the wear behavior of the transfer film was compared. Before the sliding tests, the steel disks covered with various transfer films were exchanged, i.e. pin-I was running against disk-II, whereas pin-II was sliding against disk-I. Here, disk-I and disk-II refer to the steel disks used as the counterparts for pin-I and pin-II, respectively, in the first 20 h (cf. [Fig. 14](#page-7-0)). As shown in Fig. 15, the width of the wear track covered with the transfer film agrees quite well with the size of the pin (which is 4 mm). Since the size of all the pins is the same, this allows us to carry out the wear tests on the same wear track even after changing the disks. [Fig. 14b](#page-7-0) gives the sliding behavior of the nanocomposite, i.e. pin-II against the disk-I covered with the transfer film, which was formed by the composite without nanoparticles. The friction coefficient sharply decreased and then reached a stable value, which agreed well with the friction coefficient during the steady states of Tests 1 and 2. Such friction reduction can also be explained by the process of collection and distribution of nanoparticles on the counterpart surface, which has been noticed in the running-in stage during the first 10 h. For the composite without nanoparticles, i.e. pin-I, the friction coefficient gradually increased when the test started with disk-II. This is apparently similar to the running-in process observed in Tests 1 and 2 (cf. [Fig. 14a](#page-7-0)). However, it can be noticed that the wear processes of the materials were actually quickly stabilized, which is significantly different from the normal running-in behavior. Therefore, the increase in friction coefficient in case of [Fig. 14a](#page-7-0) was not caused by the development of the transfer film, but could be reasonably explained by the gradual removal process of the trapped nanoparticles in the transfer film (which was originally formed with the nanocomposite). Again, it is noted that the friction coefficient in steady stage remained almost unchanged regardless of the swap of disks. Hence, in our case, the additional nanoparticles did not directly contribute to the formation of a high performance transfer film. The friction reduction for nanocomposites is mainly caused by a change in the contact mechanisms due to the presence of nanoparticles, such as the rolling effect.

Fig. 15. Surface profile of the worn region on the steel disk tested against the pin of nano-TiO₂+graphite+SCF/PA 66 under a contact pressure of 2 MPa and the sliding velocity of 1 m/s. The inset SEM picture shows a magnified view of the boundary region on the steel disk.

5.4. Additional remarks

The tribological performance of SFRPs could be remarkably improved by using nanoparticles as additional fillers. Meanwhile, a three-body mild abrasive wear was suggested due to the presence of hard nanoparticles in the contact region. However, the three-body contact problem is very complex and depends on many variables, including particle characteristics such as size, hardness and shape and properties of the counterparts such as surface topography and lubricating and loading conditions. The presence of so many factors, and the interactions among them, makes a full characterization of the roles of these factors in friction and wear very difficult. Up to now, there is still a lack of fundamental understanding of the wear mechanisms when using nanoparticles in such wear conditions. This means that systematic investigation of all the relevant characteristics and properties of nanoparticles is still a matter of further research. In particular, the following two questions should be addressed first:

- 1. What is the size effect of nanoparticles in their interaction with the surface profile (or roughness) of the counterparts?
- 2. What is the influence of the mechanical characteristics (e.g. hardness) of particles on rolling mechanisms in relation to the properties of the counterparts?

The knowledge obtained will advance the current wear principles in tribology of SFRPs and may offer a promising novel route to the design of high performance tribo-materials.

6. Conclusions

In this work, the wear mechanisms of the hybrid SFRPs filled with nanoparticles were investigated. It was found that the load-carrying capacity of the SFRPs is mainly determined by the properties of the fibers. However, the tribological performance of SFRPs can be significantly improved by using nanoparticles due to their friction reducing abilities, especially under extreme loading conditions. In particular, the advantages produced by additional nanoparticles can be attributed to the following effects:

- 1. Adhesion between the contact surfaces was reduced with the presence of nanoparticles, due to the increased distance between the steel and the composite material, i.e. the particles acted as 'spacers'.
- 2. Stress concentration on the individual fibers was minimized with the dispersed nanoparticles in the contact region, which consequently protected the polymer matrix in the interfacial regions from the thermal–mechanical failure. This finally led to the gradual removal process of short fibers and the high wear resistance of the composites.
- 3. Rolling ability of nanoparticles could significantly restrict the increase in the friction force, especially under extreme loading conditions. As a result, the specific wear of the nanocomposites remained stable even under relatively high pv conditions, i.e. the limiting pv of the nanocomposite was clearly improved.

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References

- [1] Friedrich K. Wear of reinforced polymers by different abrasive counterparts. In: Friedrich K, editor. Friction and wear of polymer composites. Elsevier Science Publishers, BV; 1986. p. 233–87.
- [2] Kukureka SN, Hooke CJ, Rao M, Liao P, Chen YK. The effect of fiber reinforcement on the friction and wear of polyamide 6,6 under dry rollingsliding contact. Tribology International 1999;32:107–16.
- [3] Bijwe J, Rajesh JJ, Jeyakumar A, Ghosh A, Tewari US. Influence of solid lubricants and fiber reinforcement on wear behavior of polyethersulphone. Tribology International 2000;33:697–706.
- [4] Häger AM, Davies M. Short-fiber reinforced, high-temperature resistant polymers for a wide field of tribological applicants. In: Friedrich K, editor. Advances in composites tribology. Elsevier Science Publishers, BV; 1993. p. 104–57.
- [5] Voss H, Friedrich K. On the wear behavior of short-fiber-reinforced PEEK composites. Wear 1987;116:1–18.
- [6] Tewari US, Bijwe J. Recent development in tribology of fiber reinforced composites with thermoplastic and thermosetting matrices. In: Friedrich K, editor. Advances in composites tribology. Elsevier Science Publishers, B.V; 1993. p. 159–207.
- [7] Chang L, Zhang Z. Tribological properties of epoxy nanocomposites: II. A combinative effect of short carbon fiber and nano-TiO2. Wear 2006;206:869–78.
- [8] Chang L, Zhang Z, Zhang H, Schlarb AK. On the sliding wear of nanoparticles filled polyamide 6,6. Composites Science and Technology 2006;66:3188–98.
- [9] Friedrich K, Zhang Z, Klein P. Wear of polymer composites. In: Stachowiak GW, editor. Wear—materials, mechanisms and practice, as part of ''Handbook of measuring system design'' edited by Sydenham P. and Thorn R. John Wiley & Sons; 2005. p. 269–90.
- [10] Wang J, Gua M, Bai S, Ge S. Investigation of the influence of $MoS₂$ filler on the tribological properties of carbon fiber reinforced nylon 1010 composites. Wear 2003;255:774–9.
- [11] Bijwe J, Naidu V, Bhatnagar N, Fahim M. Optimum concentration of reinforcement and solid lubricant in polyamide 12 composites for best tribo-performance in two wear modes. Tribology Letters 2006;21:59–66.
- [12] Zhang XR, Pei XQ, Wang QH. Effect of solid lubricant on the tribological properties of polyimide composites reinforced with carbon fibers. Journal of Reinforced Plastics and Composites 2009;27:2005–12.
- [13] Cho MH, Bahadur S. Study of the tribological synergistic effects in CuO-filled and fiber-reinforced polyphenylene sulfide composites. Wear 2005;258:835–45.
- [14] Chang L, Zhang Z, Breidt C, Friedrich K. Tribological properties of epoxy nanocomposites: I. Enhancement of the wear resistance by nano-TiO₂ particles. Wear 2005;258:141–8.
- [15] Guo Q, Rong MZ, Jia GL, Lau KT, Zhang MQ. Sliding wear performance of nano-SiO2/short carbon fiber/epoxy hybrid composites. Wear 2009;266:658–65.
- [16] Zhang Z, Breidt C, Chang L, Haupert F, Friedrich K. Enhancement of the wear resistance of epoxy: short carbon fiber, graphite, PTFE and nano-TiO2. Composites Part A 2004;35:1385–92.
- [17] Friedrich K. Wear models for multiphase materials and synergistic effects in polymeric hybrid composites. In: Friedrich K, editor. Advances in composite tribology. Elsevier Science Publishers, B.V; 1993. p. 209–73.
- [18] Bahadur S. The development of transfer layers and their role in polymer tribology. Wear 2000;245:92–9.
- [19] Myshkin NK, Petrokovets MI, Kovalev AV. Tribology of polymers: Adhesion, friction, wear, and mass-transfer. Tribology International 2005;38:910–21.
- [20] Chang L, Zhang Z, Ye L, Friedrich K. Tribological properties of epoxy nanocomposites III. Characteristics of transfer films. Wear 2007;262:699–706.
- [21] Chang L, Zhang Z, Ye L, Friedrich K. Tribological properties of high temperature resistant polymer composites with fine particles. Tribology International 2007;40:1170–8.
- [22] Dwyer-Joyce RS, Sayles RS, Ioannides E. An investigation into the mechanisms of closed three-body abrasive wear. Wear 1994;175:133–42.
- [23] Stachowiak GB, Stachowiak GW. The effects of particle characteristics on three-body abrasive wear. Wear 2001;249:201–7.
- [24] Fang L, Kong XL, Su JY, Zhou QD. Movement patterns of abrasive particles in three-body abrasion. Wear 1993;162–164:782–9.