

# NEW INSIGHTS INTO THE TRIBOLOGICAL EFFECTS OF NANOPARTICLES ON THE SLIDING WEAR PERFORMANCE OF POLYMER NANOCOMPOSITES

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## Abstract

*In the present work, the role of the nanoparticles in modifying the sliding wear behavior of hybrid polymer composites was studied. It was found the presence of nanoparticles in the contact region can effectively reduce the friction between the worn surface of polymeric specimen and the metallic counterface covered with transferred films, owing to their “spacer” effect and the rolling ability. Meanwhile, such low-friction conditions for nanocomposites are also helpful for the formation of TFLs on the steel counterparts, particularly under extreme sliding conditions. As a result, a high load-carry capacity of hybrid nanocomposites can be finally achieved by integrating inorganic nanoparticles with traditional micro-sized tribo-fillers.*

## 1 Introduction

Advanced polymeric composites, such as short fibre-reinforced polymers (SFRPs) have been widely used as dry sliding materials as lower weight alternatives to metal materials, with the attractive advantage of self-lubrication and superior cleanliness. 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. To achieve high wear resistant polymer composites, it is a traditional route to integrate various functional fillers [1]. Now, more and more evidences have shown that the hybrid composites by integrating inorganic nanoparticles with traditional micro-sized fillers could be a new promising way to develop high performance wear resistant polymeric materials. In particular, the synergistic effect between nanoparticles and fibrous reinforcements on the sliding wear behavior of polymer composites was observed by Bahadur et al [2] and Lin et al [3], respectively. It was proposed that nanoparticles could effectively inhibited the fibre failures through reducing the stress concentration on the carbon fibers interface and the shear stress between two sliding surfaces [3]. Whilst, Zhang et al [4] indicated that the incorporation of nanoparticles with optimised contents could further increase the wear-resistance of carbon fabric composites. The beneficial effect of additional nanoparticles on wear performance of the composites could be caused by an increased mechanical strength of the fabric composites and a better bonding strength of the transfer film developed on the metallic counterfaces. However, the

improvement mechanisms by 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 is therefore, the objective of the present work to bring further light into the open questions mentioned above.

## 2 Materials and testing methods

Two different polymers i.e. epoxy and polyamide 66 (PA 66) were chosen as matrices. The short carbon fiber (SCF) and two solid lubricants, graphite and PTFE were used as traditional tribo-fillers. The average diameter of the SCF was  $\sim 14.5 \mu\text{m}$ , with an average fiber length of  $\sim 90 \mu\text{m}$ . The sizes of the graphite flakes and the PTFE powders amounted to  $\sim 20 \mu\text{m}$  and  $\sim 4 \mu\text{m}$  respectively. Nano-sized  $\text{TiO}_2$ -inorganic particles were applied as additional fillers. The average diameter of the particles was 300 nm.

Wear tests were performed on a Wazau pin-on-disc (P-o-D) apparatus according to ASTM D3702. To evaluate the load-carrying capacity of these materials, selected compositions were tested in a wide range of  $pv$  factors, e.g. the nominal pressure in a range from 0.5 to 12 MPa, and the sliding velocity from 0.5 to 3 m/s. During the tests, the frictional coefficient was recorded and calculated by the ratio between the tangential and the normal force. The test temperature was monitored by an iron-constantan thermocouple positioned at the edge of the disc. After the tests, measurements of the mass loss of the specimens took place in order to calculate the specific wear rate, using the following equation,

$$w_s = \frac{\Delta m}{\rho F_N L} \quad [\text{mm}^3/\text{Nm}] \quad (1)$$

where  $\Delta m$  is the specimen's mass loss,  $\rho$  is the density of the specimen,  $F_N$  is the normal load applied on the specimen during sliding, and  $L$  is the total sliding distance. To understand the wear mechanisms of the composite samples, worn surfaces were examined by a JEOL-5400 scanning electron microscopy (SEM). To measure the thickness of transfer films, nanoindentation experiments were conducted on a nano-Triboindentation Device (Hysitron Inc., USA) using a Berkovich nano-indenter. All the indentation tests were carried out at a peak load of 3 mN, with a holding time of 5 s at the maximum load to minimize time-dependent creep effects. The loading and unloading rates were 0.3 mN/s.

## 3 Wear results

Figure 1 summarizes the wear test results of the polymeric composites in comparison with that of the pure polymers. As shown in the figure, the applied tribo-fillers enhanced the wear resistance of the polymers about one order of magnitude at 1 MPa·m/s. In this case, it is also noticed that the wear rates of all the composites are narrowly ranged between  $10^{-7}$  and  $10^{-6} \text{mm}^3/\text{Nm}$ , which agree well with results for carbon fibre-reinforced-polymers sliding against various steel counterfaces [5]. With an increase of  $pv$ , the wear factor of the composite filled with traditional fillers only was progressively increased, suggesting changes in the dominant wear mechanisms. For the composite with additional nano-particles, however, the wear factor of the nano-composite was relatively stable at  $\sim 1 \times 10^{-6} \text{mm}^3/(\text{Nm})$  even under high  $pv$  conditions. This means that the limiting  $pv$  of the composite was clearly improved, which would promote the use of this material for tribo-applications with more severe wear conditions. It was also noticed that the addition nanoparticles could effectively reduce the friction coefficient of composite materials under all the testing conditions. There is no general relationship between friction and wear. However, a high friction force/coefficient is normally

undesirable for polymeric materials not only because it may accelerate the wear loss of the materials, but it also will lead to a high contact temperature due to the frictional heating and thus the thermal-mechanical failure of the material. In the following sections, the wear mechanisms of SFRP composites will be further discussed based on microscopic observations. In particular, the mechanism for the favorable effects of nanoparticles on the wear behavior of SFRPs will be investigated in details.

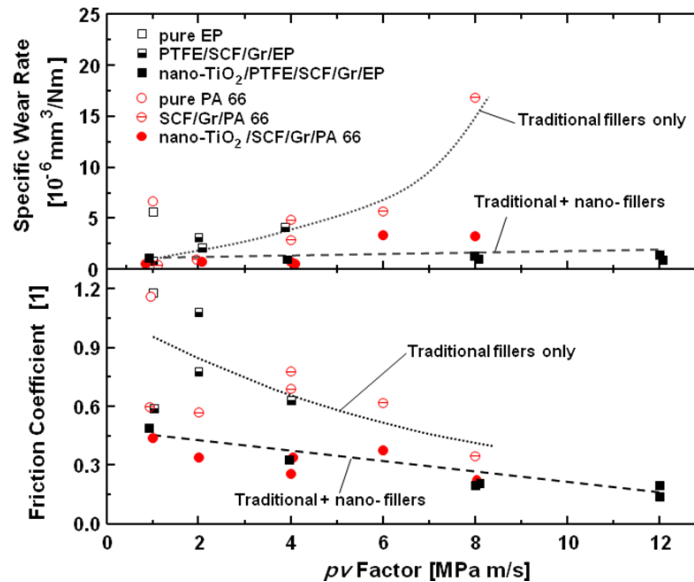
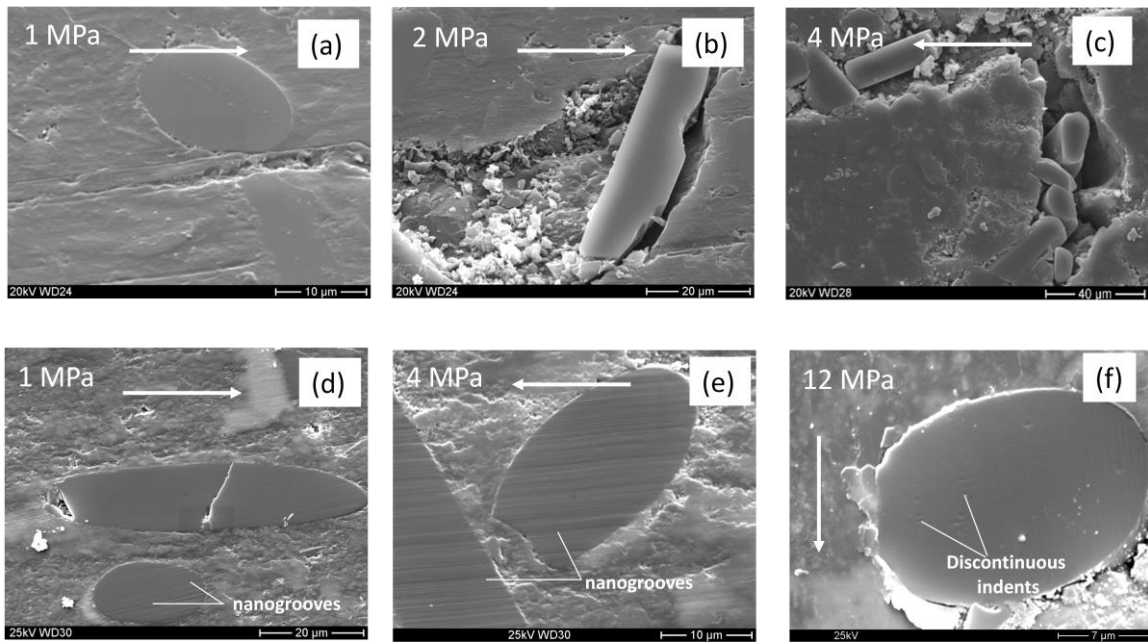


Figure 1. Wear results for the polymer composites tested under different sliding conditions.

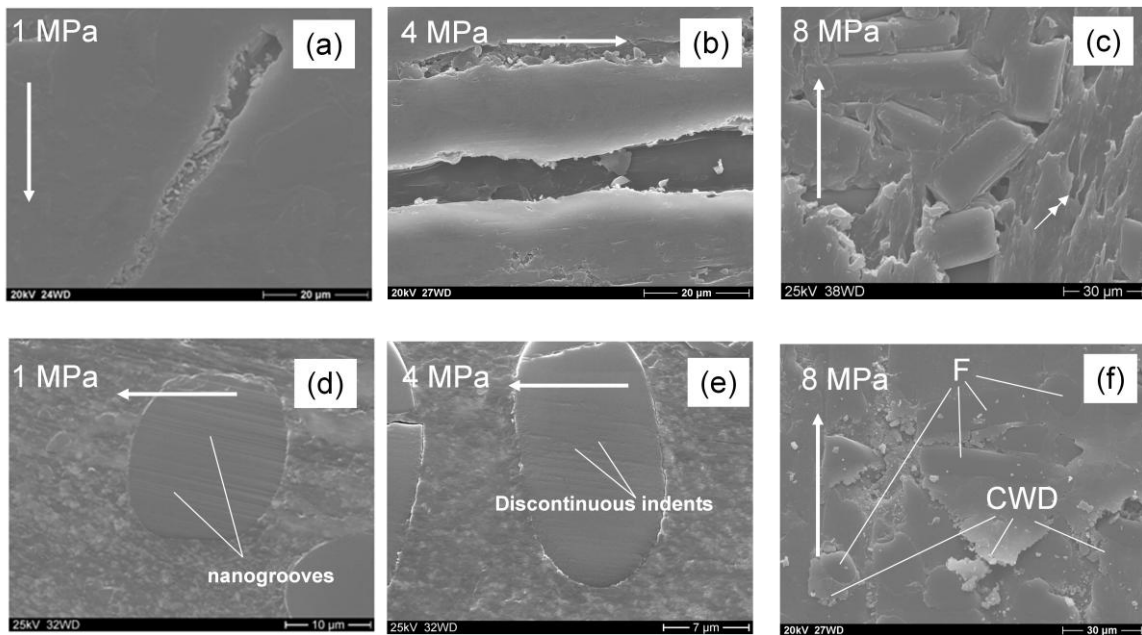
## 4 The tribological role of the nanoparticles in wear performance of polymeric hybrid composites

### 4.1 On the removal process of short fibre

It is known that the wear performance of SFRPs is to a great extent determined by the properties of the fibers [5]. 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. Figure 2 compares the patterns of fiber removal for the epoxy composite filled without and with additional nanoparticles tested under 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 (Figure 2a), which indicates a gradual removal process of the fibers. However, with an increase in the applied contact pressure, breakage of the epoxy matrix occurs, especially at the interfacial region around the fibers (Figure 2b). 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. Figure 1). When the pressure increases to 4 MPa, the specimen failed by the formation of macro-cracks (Figure 2c), which contributed to a further increase in the specific wear rate. With the addition of nanoparticles, the situation was much different. As shown in Figures 2 (d) (e) and (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. Figure 1), and the load carrying capacity of the material was significantly improved.



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



**Figure 3.** 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), (c) are the representative SEM images for graphite + SCF/PA 66 tested under 1MPa, 4MPa and 8MPa respectively; (e), (d), (f) are the representative SEM images for nano-TiO<sub>2</sub> + graphite + SCF/PA 66 tested under 1MPa, 4MPa and 8MPa respectively. The sliding velocity is constant with 1m/s. The letters on (f) have the following meaning: F = fibers; CWD = compacted wear debris, piled up in front of up-standing fiber edges.

The similar behavior was observed for the thermoplastic composites. As shown in Figure 3, the fiber removal in the PA 66 based composite filled only traditional fillers was also very much aggravated with an increase of applied pressure. Nevertheless, 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. But, 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 (Figure 3b). At 8 MPa, even some melting features (double arrow) of the PA 66 matrix could be observed on the worn surface (Figure 3c). 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. Figure 3 (d) (e) (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. Figure 1).

Thus, with the addition of nanoparticles, the fibers could be maintained in the polymeric matrix (with a gradual wear process even at high  $p\nu$  conditions), which finally led to an enhanced load-carrying capacity of the material (Figure 1).

#### 4.2 On the formation of transfer films

It is known that the sliding wear of polymeric specimens is greatly affected by the transfer films developed on the steel counterparts [6]. Therefore, to fully understand the tribological role of nanoparticles, it is crucial to examine their effect on the formation of transfer films.

The beneficial effect of the TFL on the wear performance of a polymer-on-steel tribo-system is normally attributed to its protection of the polymeric partner from severe abrasive wear caused by the hard roughness tips of the metallic counterface [6]. In order to describe the effectiveness of such protection, a new term, namely the “transfer film efficiency factor”,  $\lambda$ , was introduced [7],

$$\lambda = h_f / R_a \quad (2)$$

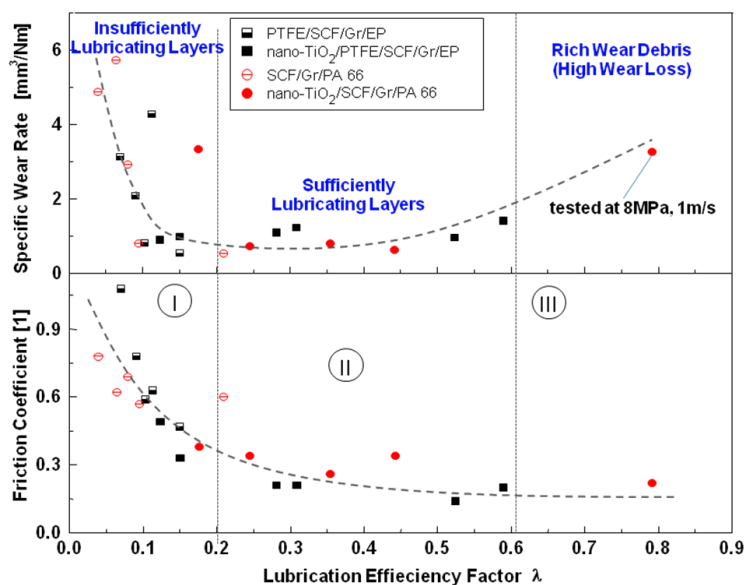
where  $h_f$  is thickness of the TFL, and  $R_a$  is the surface roughness of the steel counterface. The factor considers mainly the relative contributions of the TFL and the metallic counterpart to the wear process of the sliding system. At a given value of  $R_a$ , a larger value of  $\lambda$  suggests a thicker TFL, so that the surface properties are more governed by the TFL. The thickness of the localized TFL can be further determined by using nanoindentations, according to the following equation [7, 8],

$$h_f = h_t - h_s = h_t - h_t \times \sqrt{\frac{(H_c - H_f)}{(H_s - H_f)}} = h_t \left[ 1 - \sqrt{\frac{(H_c - H_f)}{(H_s - H_f)}} \right] \quad (3)$$

where  $h_t$  is the total indent depth and  $h_s$  indent depth in the substrate.  $H_f$  and  $H_s$  are intrinsic hardness of the film and substrate respectively.

Figure 4 shows the friction coefficient and the wear rate of polymer composites as functions of  $\lambda$ . It is interesting to note that the  $w_s$  - and  $\mu$  -  $\lambda$  curves showed apparent resemblance to the well-known Stribeck curves, which describe the effect of a liquid film on the friction and wear of a lubricated sliding system (in terms of the lubricant thickness related to the average roughness between the contacting partners). It is clearly shown in Figure 4 that effective TFLs were more likely formed with the addition of nanoparticles under all the tested conditions. Accordingly, polymer nanocomposites showed improved tribo-performance, especially under extreme sliding conditions (Figure 1). In general, the higher values of  $\lambda$ , were associated with a desirable tribological performance of the polymer composites i.e., a low friction coefficient and a low wear rate. However, if the amount of TFL becomes too large, this may again result in a relatively high wear rate, e.g. for the PA 66-based nanocomposites tested at 8 MPa, 1m/s (which belongs to the category of “rich wear debris” shown in Figure 4). In this case, the thick

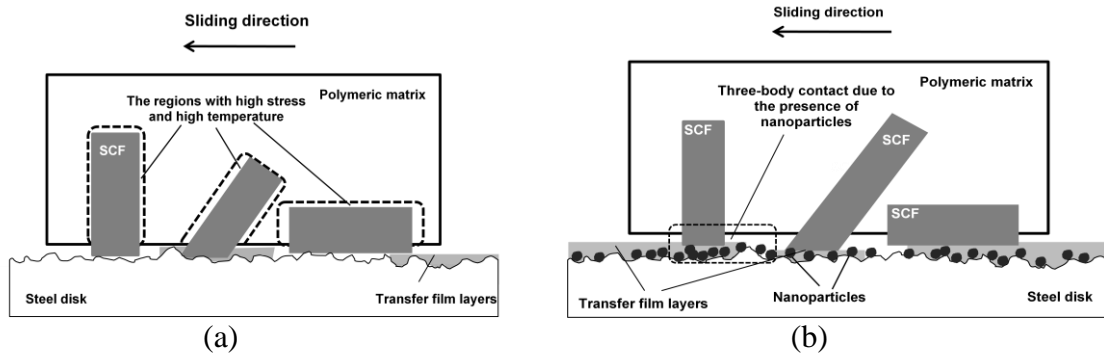
TFL could act as a thermal barrier, since the thermal conductivity of the steel (in the range of  $58 \text{ Wm}^{-1}\text{K}^{-1}$ ) is much higher than that of polymers (e.g. PA66 has a value of about  $0.25 \text{ Wm}^{-1}\text{K}^{-1}$ ). As a result, the local contact temperature in such a thick TFL region would be relatively high, resulting in strong adhesive wear between the polymer specimen and the TFL. Consequently, a back-transfer of compacted wear debris (CWD) could be observed on the worn surface of the polymer nanocomposite (cf. Figure 3f). Nevertheless, the presence of sufficient TFL could protect short fibers from severe fibre breakage or pulverization, and thus contributed to a relative stable wear performance of the polymeric specimen under different sliding conditions (Figure 1).



**Figure 4.** Specific wear rate and friction coefficient as functions of the transfer film efficiency factor,  $\lambda$ , as defined by Equation 2.

#### 4.3 Considerations of the contact mechanisms

On the basis of the experimental observations shown above, Figure 5 gives a schematic illustration of the failure mechanisms during sliding wear of SFRP composites without nanoparticles. Thin, discontinuous transfer film formed during the running-in stage can somewhat reduce the ‘direct contact’ of the composite with asperities of the hard metallic counterface. Meanwhile, 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. When the  $p\nu$  product is relatively low, fibers can undertake the load with a gradual removal process, resulting in relative smooth worn surfaces (cf. Figures 2a and 3a). However, under high  $p\nu$  conditions, the polymer composites may risk severe wear loss, as the short fibers are more likely pulverized and quickly removed. In particular, 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  $p\nu$  factor, failure of the material occurs firstly 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. Figure 2c), whereas thermal softening/melting was evident for the PA 66 based composites (cf. Figure 3c). When the matrix failed to support the short fibers, fast fiber removal could occur and thus a rapid increase in the composite’s wear rate. Finally, the material can no longer be employed.



**Figure 5.** Schematic illustration of the failure mechanisms for the sliding wear of (a) SFRP composites without nanoparticles and (b) polymeric hybrid nanocomposites (for better illustration purposes: fiber diameter too small relative to roughness of steel counterpart).

For the nanocomposites, a three-body contact condition was induced by the additional nanoparticles between the contact surfaces. Accordingly, a three-body contact mode was proposed for the sliding wear of hybrid nanocomposites, as illustrated in Figure 5b. It is known the hard particles tend to be embedded in the softer surface, thus scratching the harder one [9]. This was also proved by nano-grooves observed with SEM (Figures 2d, 2e and 3d), which in-turn, supported the presence of nanoparticles in contact regions. Based on the contact mode, the following beneficial effects of nanoparticles can be further proposed:

- 1) With the presence of nanoparticles, the distance between the steel and the composite material was also enhanced i.e. the particle acted as ‘spacers’. This could cause a reduction in the adhesion between the contacting surfaces, which explained the fact that the friction coefficient of the nanocomposites was always lower than that of the composites without nanoparticles (Figure 1).
- 2) As the nanoparticles were free to move, they tended to be dispersed uniformly over the transfer film during the wear process, which minimized 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 specific wear rate of the nanocomposites was stable, even under extreme loading conditions.
- 3) The rolling ability of nanoparticles could restrict the further increase of the friction force of the system, especially under extreme loading conditions. Accordingly, the temperature rise for the nanocomposites would be much less than that for the composites without nanoparticles. The rolling or tumbling behavior is evidenced by the discontinuous indents on the short fibers (cf. Figures 2f and 3f). Very recently, such friction reduction caused by rolling behavior of nanoparticles was also experimentally confirmed by Anantheshwara et al [10].
- 4) Finally, owing to the ‘spacers’ effect and rolling ability of nanoparticles, a low friction coefficient was achieved by nanocomposites, which also contributed to the formation of TFLs, especially under high  $pv$  conditions (Figure 4). Although earlier results had shown that the wear performance of the formed TFLs was little affected by nanoparticles under a relatively low  $pv$  condition e.g. 2MPa, 1m/s [11], a low friction status is generally helpful for the formation of TFLs on the steel counterparts, since wear debris could be more likely remained in the worn regions [7]. On the other hand, soft TFLs could hold the nanoparticles, as shown in Figure 5b. In this way, TFLs can partly cover the nanoparticles and minimize their abrasiveness. Such a synergistic action between the nanoparticles and TFLs is critical for an enhanced wear performance of the polymer hybrid nanocomposites.

## 5. Conclusions

Over the past few decades, interest has grown rapidly polymers and polymer composites for technical applications, in which low friction and low wear are essential. Nevertheless, new developments are still under way to explore other fields of application for these materials and to further enhance their properties for more extreme loading and environmental conditions. Nano-scale inorganic particles have recently come under consideration, which strongly suggests that this method promises new routes for the design of wear-resistant materials even at very low filler content. For example, the combinative effect of nanoparticles with short carbon fibres has exhibited a clear improvement in the wear resistance of both thermosetting and thermoplastic composites. In addition, this concept allowed the use of these materials under more extreme wear conditions, i.e. higher normal pressures and higher sliding velocities, suggesting a novel approach to design tribo-polymeric hybrid composites

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## References

- [1] Friedrich K., Zhang Z., Klein P., Wear of polymer composites, in Stachowiak G.W. (Ed.) *Wear - Materials, Mechanisms and Practice*, as part of "Handbook of Measuring System Design" edited by Sydenham P. and Thorn R., John Wiley & Sons (2005) pp. 269-290.
- [2] Cho M.H., Bahadur S., Study of the tribological synergistic effects in CuO-filled and fiber-reinforced polyphenylene sulfide composites, *Wear* 258 (2005) 835-845.
- [3] Lin G.M., Xie G.Y., Sui G.X., Yang R., Hybrid effect of nanoparticles with carbon fibers on the mechanical and wear properties of polymer composites, *Composites: Part B* 43 (2012) 44–49
- [4] Su F.H., Zhang Z.Z., Liu W.M., Mechanical and tribological properties of carbon fabric composites filled with several nano-particulates, *Wear* 260 (2006) 861–868.
- [5] Tewari U.S., Bijwe J., Recent development in tribology of fibre reinforced composites with thermoplastic and thermosetting matrices, in K. Friedrich (Ed.), *Advances in Composites Tribology*, Elsevier Science Publishers, B.V. (1993) pp.159-207.
- [6] Bahadur S., The development of transfer layers and their role in polymer tribology, *Wear* 245 (2000) 92–99.
- [7] Chang L., Friedrich K., Ye L., Study of transfer film layer in sliding contact between polymer composites and steel disks using nanoindentation, *Wear* (2012) submitted.
- [8] Tsui T.Y., Vlassak J., Nix W.D., Indentation plastic displacement field: Part I. The case of soft films on hard substrates, *Journal of Materials Research*, 14 (6) (1999) 2196-2203
- [9] Dwyer-Joyce RS, Sayles RS, Ioannides E, An investigation into the mechanisms of closed three-body abrasive wear, *Wear* 175 (1994) 133-142.
- [10] Anantheshwara K., Lockwood A.J., Mishra R.J., Inkson B.J., Bobji M.S., Dynamical evolution of wear particles in nanocontacts, *Tribology Letters* 45 (2012) 229–235
- [11] Chang L., Friedrich K., Enhancement effect of nanoparticles on the sliding wear of short fiber-reinforced polymer composites: A critical discussion of wear mechanisms, *Tribology International* 43(2010) 2355-2364