A Synergistic Effect of Nano-TiO$_2$ and Graphite on the Tribological Performance of Epoxy Matrix Composites

Guijun Xian,* Rolf Walter, Frank Haupert

Institut für Verbundwerkstoffe GmbH, Technical University of Kaiserslautern, 67663 Kaiserslautern, Germany

ABSTRACT: The influence of incorporated 300 nm TiO$_2$ (4 vol %), graphite (7 vol %), or combination of both fillers on the tribological performance of an epoxy resin was studied under various sliding load (10–40 N) and velocity conditions (0.2–3.0 m/s). Mechanical measurements indicated that the incorporation of TiO$_2$ significantly enhanced the flexural and impact strength of the neat epoxy and the graphite including epoxy. Tribological tests were conducted with a cylinder-on-flat testing rig. The incorporation of nano-TiO$_2$ significantly improved the wear resistance of the neat epoxy under mild sliding conditions; however, this effect was markedly diminished under severe sliding conditions (high velocity and normal load). Nano-TiO$_2$ reduced the coefficient of friction only under severe sliding conditions. Graphite showed a beneficial effect in reducing the wear rate and the coefficient of friction of the neat epoxy. Compared to the nano-TiO$_2$-filled epoxy, the graphite-filled epoxy showed more stable wear performance with the variation of the sliding conditions, especially the normal load. A synergistic effect was found for the combination of nano-TiO$_2$ and graphite, which led to the lowest wear rate and coefficient of friction under the whole investigated conditions. The synergistic effect was attributed to the effective transfer films formed on sliding pair surfaces and the reinforcing effect of the nanoparticles. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 2391–2400, 2006

Key words: nanocomposites; nanoparticles; films

INTRODUCTION

Epoxy and its matrix composites have found extensive applications in the tribological field, i.e., bearings, coatings, dental restoratives, etc.[1,2] To meet practical requirements of the wear performance, reinforcements (i.e., fibers, inorganic fillers, etc.) together with solid lubricants [graphite, polytetrafluoroethylene, etc.] are frequently incorporated into the epoxy.[1–10] The reinforcements increase the compressive and shear strength of the materials, thus enabling the application of higher normal loads and reducing the wear.[8,11] The lubricants help to form transfer films between the subsurfaces during sliding, thus decreasing the frictional forces and lowering the mechanical stress and wear of the polymer surface.[5,12] The combination of reinforcements and lubricants commonly endows a polymeric material with an improved wear characteristics, which cannot be realized with one component only.[1,2,5,13]

In recent years, nanometer-sized mineral particles have been widely introduced to the polymer matrix composites for tribological studies.[1,2,4,5,9,13] In comparison with the conventional microscale particles, nanoparticles proved to have some special advantages for tribological applications[1,2,4,9,14]: (1) lower abrasiveness due to its reduced angularity; (2) a remarkable reinforcing effect, i.e., the enhanced modulus, strength, and toughness simultaneously; (3) better adhesion between the nanoparticles and the matrix due to its higher specific areas; and (4) a lower content of filler needed.

Wetzel et al.[2] used 300 nm TiO$_2$ to modify the tribological and impact properties of an epoxy. It was found that TiO$_2$ (4–5 vol %) effectively improved the wear resistance and the impact strength. A low content of uniform sized silica particles (120 and 510 nm, 0.5–4 wt %) improves the wear resistance of an epoxy and shows that the smaller the particle is, the higher the wear resistance reaches.[4] Nano-Al$_2$O$_3$ with an average diameter of 3.8 nm proved to reduce the wear rate of polyphenylene sulfide significantly.[9] The optimum filler concentration was found to be 0.24 vol % for the best wear resistance. Besides neat polymeric materials, nanometer-sized particles were also applied to modify the wear behavior of polymer-based composites for tribological applications,[1,2,5,13] which include traditional reinforcements or lubricants. Note that the composites filled with only nanometer-sized particles still show a relatively high wear rate compared to the practical criterion (<10^{-6} mm^3/N m).[15]

As widely known, the wear behavior of a polymeric material is not an intrinsic material characteristic,[12,16] and varies with test conditions, ambient humidity, etc. It is generally important to understand the tribological

*Present address: Department of Structural Engineering, University of California, San Diego 9500, Gilman Drive, La Jolla, CA 92093-0085, USA.

Correspondence to: R. Walter (rolf.walter@ivw.uni-kl.de).

performance under various wear conditions before using a material for tribological applications. This is valid for the novel nanocomposites as well because the wear performance was mostly investigated under very mild (low sliding velocity and load) wear conditions in publications.[1,2,4,9,14] In the present study, 300 nm TiO$_2$ (4 vol %) and graphite (7 vol %) were incorporated into an epoxy material. Previous studies of the wear performance of nanoparticles filled epoxy systems[2] found an optimum nanoparticle of 4 vol % and graphite is well established as filler that offers a lubricating effect. The combination of both the nanoparticle and graphite is expected to exhibit a synergistic effect on the wear performance. The aim of the present study is to understand the effect of the nanometer-sized TiO$_2$ and graphite on the wear behavior of an epoxy material under a wide range of sliding velocity (0.2–3 m/s) and normal load (10–40 N) conditions. Finally, as known, a transfer film formed on the steel counterpart is generally a prerequisite for a good tribological behavior.[17] Our previous investigations reveal that a back transferred film is occasionally formed on composite sample surface.[18,19] Transfer films formed on the sliding pair are believed to separate the substrates (avoiding the ''direct contact''), and thus to reduce the force transferred from the hard counterpart to the composite materials.[16] Consequently, the tribological behavior is improved. In the present study, transfer films are analyzed for the epoxy or its composites under various sliding velocity and load conditions so that wear mechanisms can be clarified.

EXPERIMENTAL

Materials and mixing process

In the present study, commercially available epoxy resins (Araldite MY721 and LY564) were used as the matrix systems and were cured by polyamide hardeners (HY 2954 and XB 3403) at 140°C. Resins and hardeners are all purchased from Vantico GmbH. Three hundred nanometer TiO$_2$ (Kronos 2310, Kronos Titan GmbH and Co. OHG, Germany) and graphite (Superior 9039, Superior Graphite, USA) were selected as additives, which are shown in Figure 1(a, b), respectively. Epoxy-based composites containing 4 vol % of 300 nm TiO$_2$, 7 vol % of graphite or both were prepared for mechanical and tribological measurements. The contents of nanoparticles and graphite powders were set based on previous investigations.[2]

Before mixing, the resin and the fillers were dried at 70°C for more than 10 h, and the hardeners were dried at 70°C for about 2 h. To avoid agglomerates of the fillers, especially for the nanometer-sized TiO$_2$ particles, a dissolver (Dispermat®, VMA-Getzmann GmbH, Reichshof) under a vacuum atmosphere ($\sim 10^{-4}$ Pa) was used for the mixing process. For the preparation of TiO$_2$ containing samples, first, TiO$_2$ particles were slowly added into the epoxy resin at 60°C at a low disc rotation speed about 300 r/m. Then, the mixture was cooled down with water and the rotation speed of the dissolver disc was increased. Afterwards, the mixture was blended with graphite (if necessary) at slow disc rotation speed at 60°C. Finally, the hardener was introduced into the mixture (including TiO$_2$ or together with graphite) at 60°C, and the compound was cast into an open mold. The compositions were cured in an oven for 8 h at 80°C, followed by 8 h at 140°C. This mixing process proved to be effectively in distributing nanoparticles in the matrix,[5] which is the prerequisite for the unique features of a nanocomposite. For graphite/epoxy, the mixing process was done without high disc rotation speed.

HV=25 WD=31 X20000 ⊢ 2 µm ⊣
(a)

HV=25 WD=31 X3500 ⊢ 10 µm ⊣
(b)
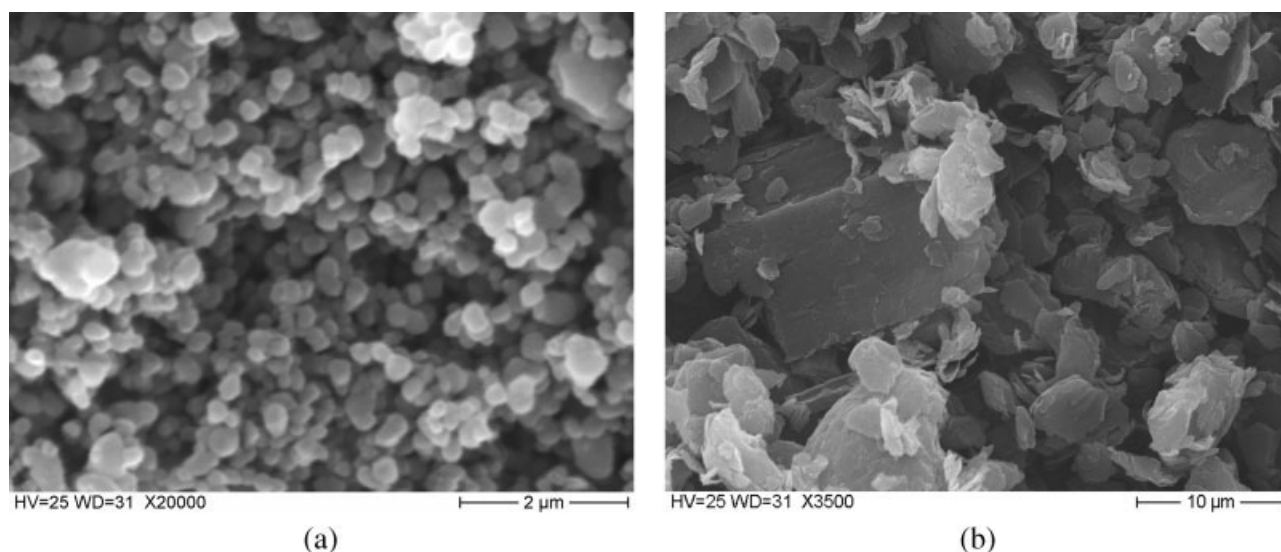
Figure 1 Scanning electron micrographes of nanometer-sized TiO$_2$ (a) and graphite (b).
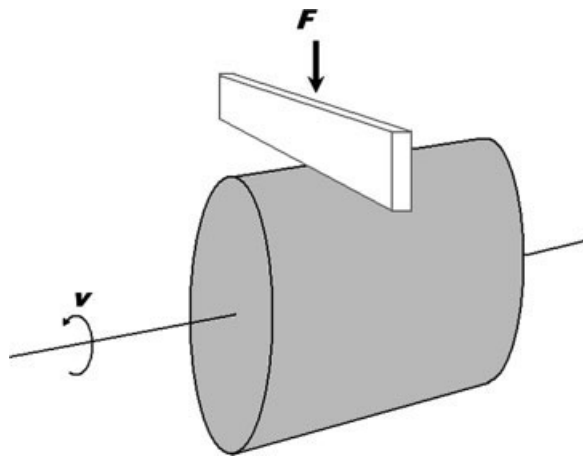
Figure 2 Sketch of a cylinder-on-flat testing rig and the sample dimensions.

Mechanical tests

Flexural properties were measured according to the ISO 178. The sample dimensions were 80 mm × 10 mm × 4 mm, and the crosshead speed was set as 2 mm/min. For each composition, the average result from at least five samples was determined.

Unnotched Charpy impact tests were performed by a pendulum ram impact testing machine using rectangular samples (80 mm × 10 mm × 4 mm), according to the ISO 179-1. The distance between the supports was 62 mm. All specimens were impacted at an impact velocity of 2.9 m/s, which led to impact energy of 4 J. For each composition, at least five samples were tested.

Wear tests

A cylinder-on-flat testing rig [Fig. 2(a)] was employed to evaluate the sliding wear behavior of samples

[Fig. 2(b)] of dimensions of 80 × 6 × 4 mm^3 under following experimental condition: normal load 10–40 N, sliding velocity 0.2–3 m/s, and sliding distance 3600 m at room temperature. Smooth and hardened 100 Cr6 steel rings (Ra 0.15 μm) served as counterpart. Since contact pressures continuously change during sliding, it makes little sense to write the sliding wear rates as specific wear rates in the unit of mm^3/Nm. In the present study, wear rates (w) were calculated based on the weight loss of the samples after sliding:

$$w = \Delta m/(l\rho)(\text{mm}^3/\text{m}) \tag{1}$$

where Δm is the measured mass loss in mg, l the sliding distance in m, and ρ the density of the composite in mg/mm^3. The presented wear rates are the averages over the total test course (3600 m sliding distance). The frictional force was measured to calculate the coefficient of friction (μ). The average μ at a steady state was considered in further presentation of data.

Scanning electron microscopy and optical microscopy

Sliding tracks on the steel counterparts were examined with an optical microscope (Aristomet, Leitz). A scanning electron microscope (SEM) (JSM-T330A, Jeol, Japan) was used to study the topography of the worn sample surfaces.

To detect if a tribo-layer[18] was formed on a worn sample surface, the sample was embedded in an epoxy resin, a cross section was polished and a microscopical observation after ultrasonic cleaning was carried out. Because of the loose characteristics, the transfer film will be removed through ultrasonic cleaning and leaves a gap between the composite and the embedding epoxy (Fig. 3). Thus, the
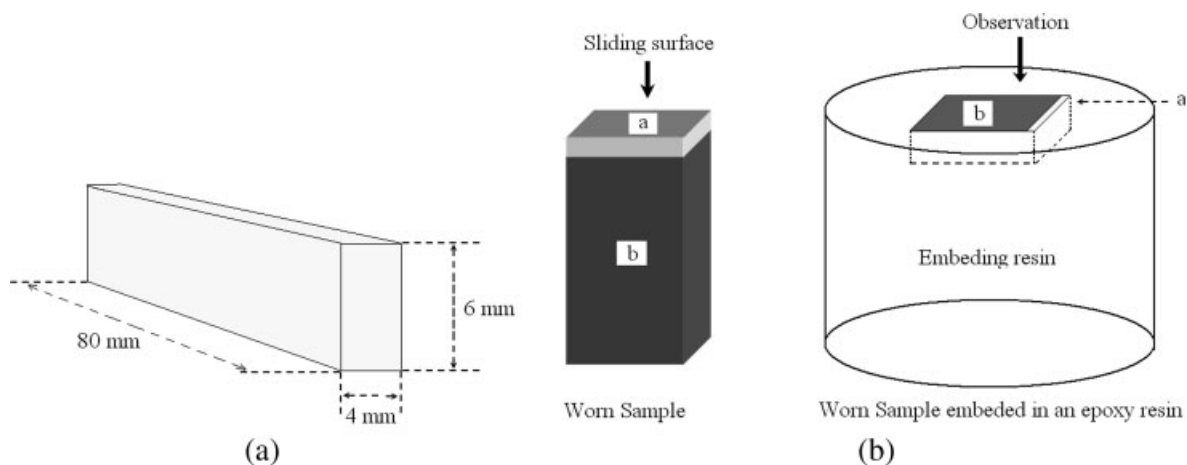
Figure 3 Observation of a back transfer film on the worn composite sample surface: (a) substrate of samples and (b) a tribo-layer formed on the worn surface of sample.
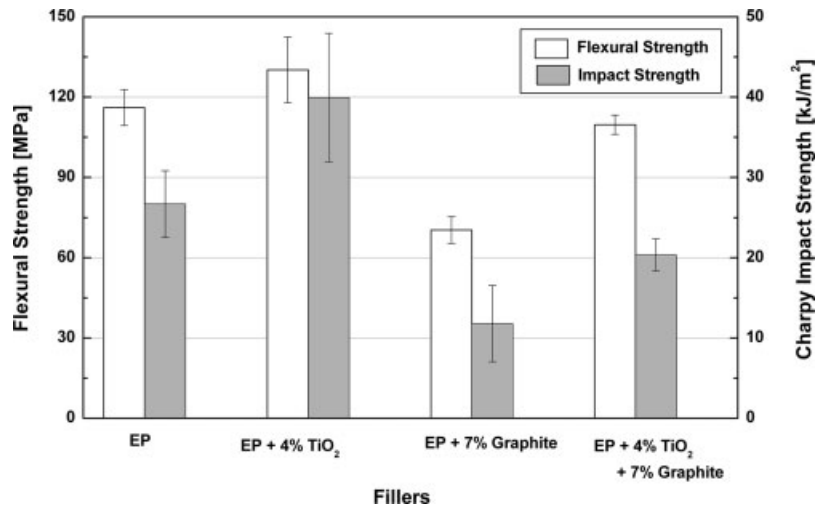
Figure 4 Flexural strength and unnotched Charpy impact strength of the epoxy resin and its composites.

existence of a transfer film can be detected by SEM observation.

RESULTS AND DISCUSSION

Mechanical properties

The flexural mechanical properties and unnotched Charpy impact strength were studied for the selected composites. Figure 4 illustrates the effect of TiO$_2$, graphite, or the combination of both fillers on the flexural strength and the impact strength. Addition of 4 vol % 300 nm TiO$_2$ enhanced both the flexural strength and the impact strength of the neat epoxy and the graphite-filled epoxy significantly. As indicated,[2,20] the nanometer-sized TiO$_2$ particles of low aspect ratio could lead to low stress concentration, and are able to block the propagation of cracks through

the polymer. This is assigned to the profound reinforcing effect of nano-TiO$_2$. The fractograph of TiO$_2$-filled epoxy after impact [Fig. 5(a)] illustrates crack deviation and crack blocking due to nano-TiO$_2$.

In contrast with TiO$_2$, addition of graphite deteriorated the flexural strength and the impact strength markedly (Fig. 4). The larger size of graphite is believed to cause higher stresses in the polymer matrix near the particles edges, which will facilitate failure under impact or flexural bending.[2,20] Besides, the poor adhesion between graphite and epoxy that is presented in Figure 5(b) may also be responsible for the impaired strength and impact properties.

Note that nano-TiO$_2$ also exhibits a reinforcing effect for graphite-filled epoxy (Fig. 4). The flexural strength increased from only 70 MPa of the graphite-filled epoxy to 110 MPa, which is close to the result for the neat epoxy. At the same time, the impact
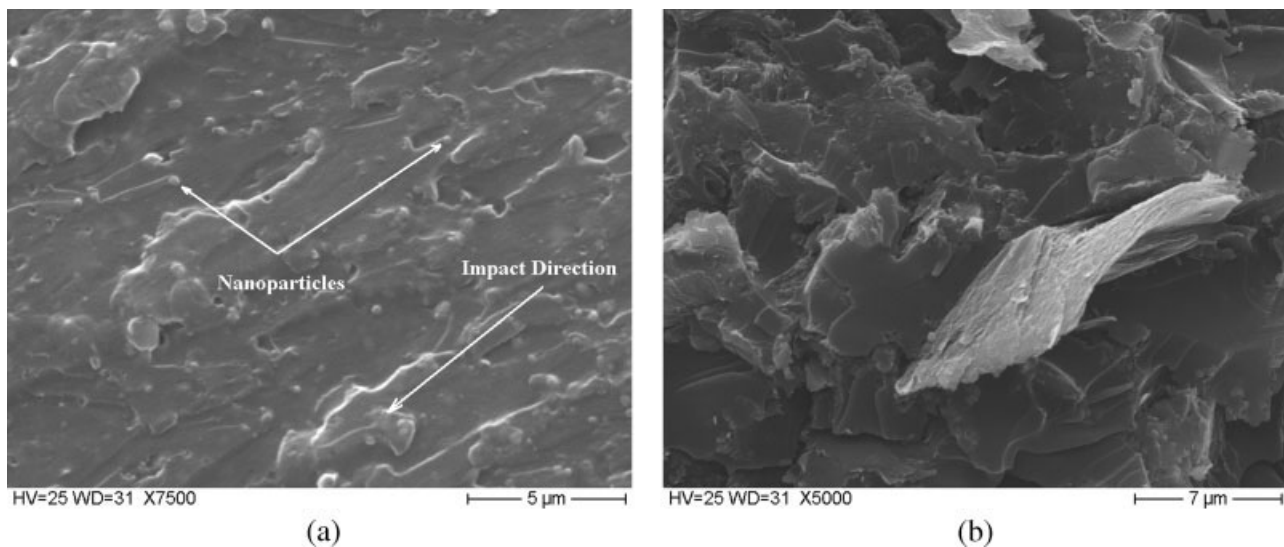
Figure 5 Fractographes of TiO$_2$ (a) and graphite (b) filled epoxy resin after impact.

TABLE I
Under the Constant Normal Force (10 N), Influence of Sliding Velocity on the
Variation of Wear Rate, Coefficient of Friction, and Formation of Transfer Films

Materials	Velocity (m/s)	Wear rate (10^{-3} mm^3/m)	μ	Transfer film on cylinder	Transfer film on sample
Epoxy	0.2	0.38	0.65	No	No
	0.6	0.53	0.72	/	/
	1	0.48	0.62	/	/
	2	0.40	0.79	Yes	Yes
	3	0.21	0.84	Yes	Yes
TiO$_2$/epoxy	0.2	0.09	0.98	Yes	Yes
	0.6	0.06	0.87	Yes	Yes
	1	0.07	0.83	Yes	Yes
	2	0.14	0.71	/	/
	3	0.26	0.60	No	No
Graphite/epoxy	0.2	0.05	0.50	No	No
	0.6	0.13	0.45	Yes	Yes
	1	0.24	0.46	Yes	Yes
	2	0.29	0.44	Yes	Yes
	3	0.16	0.46	Yes	Yes
Graphite/TiO$_2$/epoxy	0.2	0.05	0.56	No	No
	0.6	0.03	0.36	Yes	Yes
	1	0.02	0.35	Yes	Yes
	2	0.04	0.27	Yes	Yes
	3	0.08	0.39	Yes	Yes

''/'' means the transfer film is occasionally formed.

strength was enhanced from 12 to 20 kJ/m^2, indicating that the reinforcing effect of the nano-TiO$_2$ also acts in graphite/epoxy composite.

Friction and wear behavior

For all studied material samples, the wear rate, coefficient of friction, and the formation of the transfer films on the steel counterparts as well as the worn sample surfaces are summarized in Tables I and II.

The effect of the variation of the normal force and the sliding velocity is detailed below. The transfer films on both the steel cylinder and the worn sample surfaces were detected and applied to explain the tendency of the wear and friction behavior.

Load dependence of the wear performance

Figure 6(a) presents the specific wear rate against the applied normal load for the neat epoxy and its

TABLE II
Under the Constant Sliding Velocity (1 m/s), the Influence of the Normal
Force on the Variation of the Wear Rate, Coefficient of Friction,
and the Formation of Transfer Films

Materials	Force (N)	Wear rate (10^{-3} mm^3/m)	μ	Transfer film on cylinder	Transfer film on sample
Epoxy	10	0.48	0.62	No	No
	20	1.31	0.59	/	No
	30	2.11	0.58	/	No
	40	2.99	0.67	No	No
TiO$_2$/epoxy	10	0.07	0.83	Yes	/
	20	0.34	0.76	/	/
	30	1.79	0.51	No	No
	40	2.76	0.50	No	No
Graphite/epoxy	10	0.24	0.46	Yes	Yes
	20	0.36	0.40	Yes	Yes
	30	0.37	0.43	Yes	Yes
	40	0.52	0.39	Yes	Yes
Graphite/TiO$_2$/epoxy	10	0.02	0.35	Yes	Yes
	20	0.05	0.23	Yes	Yes
	30	0.08	0.25	Yes	Yes
	40	0.08	0.30	Yes	Yes

''/'' means the transfer film is occasionally formed.
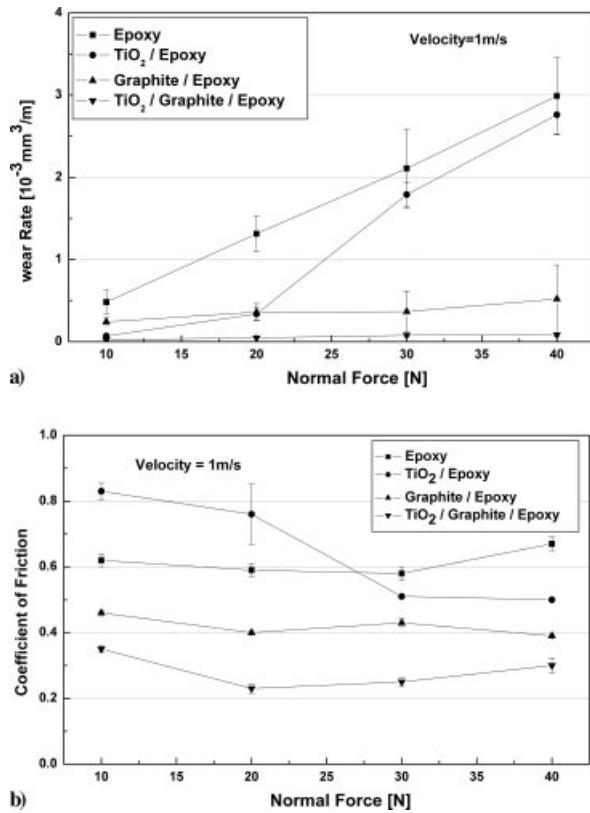
Figure 6 Variation of the specific wear rate (a) and coefficient of friction (b) with normal force for epoxy and its composites.

composites. As expected, nano-TiO$_2$, graphite, and the combination of both fillers improve the wear resistance of the neat epoxy matrix under the whole load range [Fig. 6(a)], but to a very different extent. Under lower load conditions, nanometer-sized TiO$_2$ (4 vol %) markedly enhances the wear resistance of the neat epoxy by about 10 times, in agreement with the result reported by Wetzel et al.[2] However, the wear reducing effect is significantly diminished as the normal load exceeds 20 N, where the wear resistance of the matrix is only increased by 8–10%. Graphite (7 vol %) particles as well prove to enhance the wear resistance of the neat epoxy significantly. It is worth to note that the graphite-filled epoxy shows a very stable wear rate (3×10^{-3}–5×10^{-3} mm^3/m) with the variation of the normal load, which is opposite to the case of the neat epoxy and the TiO$_2$-filled epoxy. The epoxy filled with nanometer-sized TiO$_2$ and graphite similar to the graphite-filled epoxy displays very insensitive to the normal load, while the wear rate is lowered by 6–10 times than that of the graphite-filled one. Although the wear reducing effect of nano-TiO$_2$ is reduced markedly under severe sliding conditions, the epoxy filled with both fillers still exhibits the lowest wear rate and does not fluctuate remarkably. Therefore, there exists a synergistic effect of the combination of nano-TiO$_2$ and graphite on the wear resistance.

Figure 6(b) shows the coefficient of friction as a function of the applied normal load for the neat epoxy and the composites. For the neat epoxy, the normal load does not affect the coefficient of friction (0.58–0.67) significantly. The minimum (0.58) is found at a normal load of 30 N.

Under lower normal load conditions (<20 N), the incorporation of TiO$_2$ increased the coefficient of friction to 0.76–0.83, higher than that of the neat epoxy. However, as the normal load exceeds 20 N, the coefficient of friction of the TiO$_2$-filled epoxy decreases to about 0.5, lower than that of the neat epoxy. In agreement to the expectation, the epoxy including graphite shows a coefficient of friction about 0.39–0.45, much lower than that of the neat epoxy. Surprisingly, a synergism in terms of the reduced coefficient of friction is found for the combination of the nanometer-sized TiO$_2$ and graphite. The coefficient of friction ranging from 0.27 to 0.35 cannot be reached with only one filler.

Velocity dependence of the wear performance

Figure 7(a) presents the influence of the sliding velocity (0.2–3 m/s) on the wear rate of the neat epoxy and its composites at a fixed load of 10 N. For the neat epoxy, a maximum wear rate (0.53×10^{-3} mm^3/m)
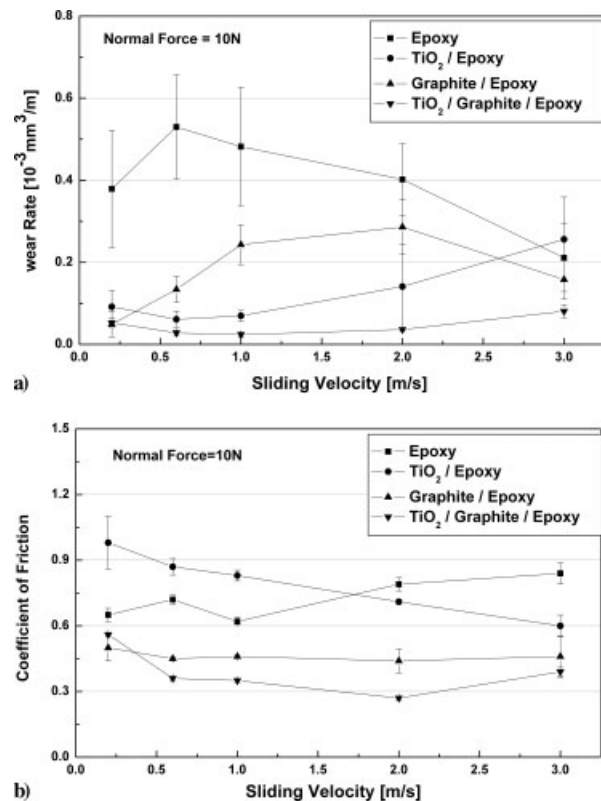
Figure 7 Variation of the specific wear rate (a) and coefficient of friction (b) with sliding velocity for the epoxy resin and its composites.

is found at the sliding velocity of 0.6 m/s. As the sliding velocity exceeds 0.6 m/s, the wear rate decreased to 0.2 × 10^{-3} mm^3/m linearly. At lower velocity (<2 m/s), the addition of nanometer-sized TiO$_2$ (4 vol %) alone leads the wear rate of the neat epoxy to be reduced significantly. Especially at intermediate sliding velocities (i.e., 0.6–1 m/s), the wear rate reached to the minimum (∼10 times lower than that of the neat epoxy). However, the further increase of the sliding velocity leads to a remarkable increase of the wear rate. At 3 m/s, the wear rate (0.25 × 10^{-3} mm^3/m) is even higher than that of the neat epoxy under the same conditions. The addition of graphite (7 vol %) reduces the wear rate of the epoxy under the whole velocity range. In contrast to the epoxy including TiO$_2$, the maximum wear rate (∼0.3 × 10^{-3} mm^3/m) of the graphite-filled epoxy is found at intermediate velocities (1–2 m/s). The further increase of the sliding velocity causes a decrease of the wear rate. Similarly, the incorporation of both nanometer-sized TiO$_2$ and graphite displays a synergistic effect in enhancing the wear resistance of the epoxy under the whole velocity range. The minimum wear rate is found in the range of 0.6–2 m/s, the decrease or increase of the sliding velocity causes a slight increase of the wear rate.

The variation of the coefficient of friction with the sliding velocity is shown in Figure 7(b). The coefficient of friction of the neat epoxy increases from 0.6 to 0.84 as the sliding velocity changes from 0.2 to 3 m/s. However, the coefficient of friction (0.98–0.6) of the nanometer-sized TiO$_2$-filled epoxy decreases almost linearly with increasing the sliding velocity. Only for sliding velocities higher than 2 m/s, the nanoparticles filled epoxy shows a lower coefficient of friction than the neat epoxy. Graphite-filled epoxy shows a coefficient of friction ranging from 0.44 to 0.5, insensitive to the sliding velocity. Epoxy filled with both TiO$_2$ and graphite exhibits the lowest coefficient of friction (0.27–0.56) except 0.2 m/s.

Transfer films

According to Bahadur,[12] the phenomenon of material transfer during sliding between polymer and metal is important from both the scientific and practical considerations because material transfer is the genesis of film development. The transfer film affects the friction and wear behavior of sliding pairs.[12] The role of transfer film in polymer-metal sliding contacts has long been realized as being responsible for the gradual transition from a transient wear behavior to steady state wear behavior.[12] In the present study, to reveal corresponding wear mechanisms, transfer films on either the composite sample surfaces or the steel counterparts were detected. It was found that the transfer film on the composites sliding surface was only formed for the graphite including composites (graphite-filled epoxy and graphite- and nano-TiO$_2$-filled epoxy) under some sliding conditions.

For the neat epoxy resin, high sliding velocity conditions (i.e., >2 m/s), however, lead to a patchy and discontinuous transfer film [Fig. 8(a)] formed on the steel counterpart. All the other sliding conditions show no transfer films [Fig. 8(b)] in agreement with a previous investigation.[5] The formation of the transfer film on the steel counterpart at high sliding velocity can be assigned to the increased temperature in the contact surfaces, which enhances the plastic deformation of the epoxy resin and thus the adhesion of the resin to the counterpart.[21] The transfer film, serving as a stress reducer,[12] is believed to contribute to the wear reduction at higher sliding velocities for the neat epoxy (>1 m/s) [Fig. 7(a)]. The increased
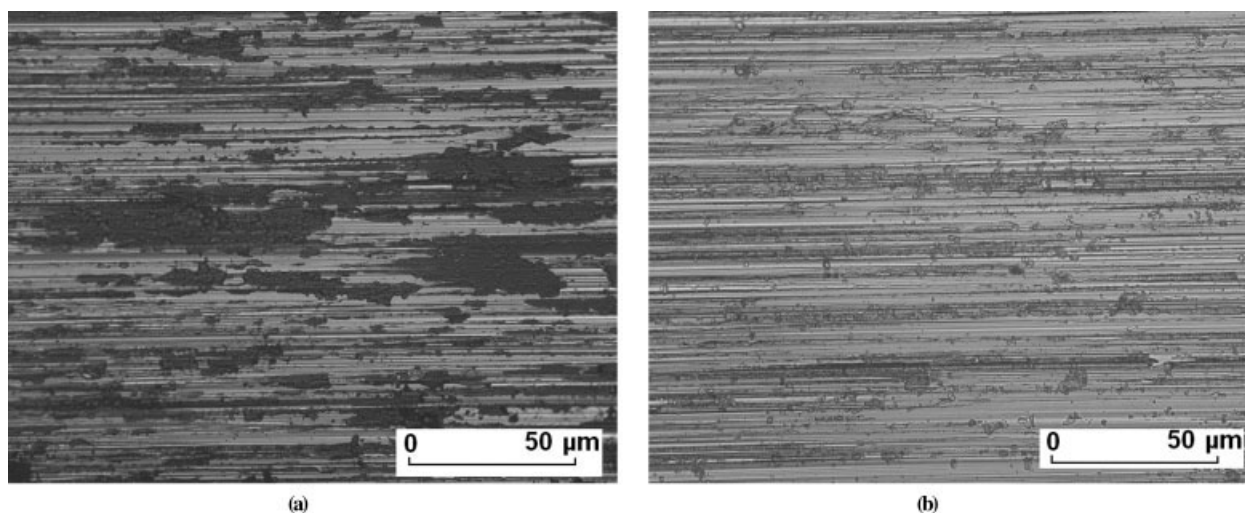
Figure 8 Light micrographes of the steel counterpart slid versus the neat epoxy at 3 m/s (a) or 0.2 m/s (b) with the applied load of 10 N.
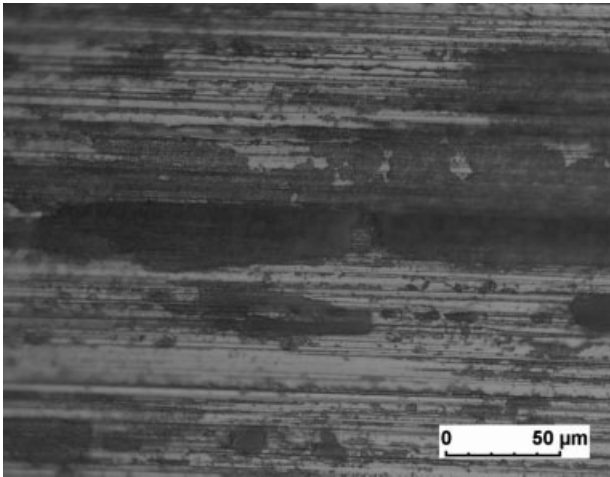
Figure 9 Micrographes of the steel counterpart slid by the TiO$_2$-filled epoxy at 0.2 m/s, 10 N.

normal load (i.e., >30 N), however, leads to much higher temperature, leading to a carbonization of the resin rather than plastic deformation. As we knew, the work (W) due to the friction is proportional to the normal force (F_N), sliding velocity (v), and μ:

$$W = \mu F_N V \text{ (Wall)} \tag{2}$$

Thus, the extreme high temperature is realized in the contact surfaces with the relative higher normal force and μ [Fig. 6(b)]. As a result, the transfer film cannot form. Because of the lack of the protection by a transfer film and reduced mechanical properties, the epoxy material is easily worn away, displaying the gradually increased wear rate with the normal load [Fig. 6(a)].

Although the incorporation of nanometer-sized TiO$_2$ into the neat epoxy does not lead to a transfer film on the composite sample surface, it supports the formation of a transfer film on the steel counterpart under almost all selected sliding conditions (Fig. 9) (except at high normal load, i.e., >30 N). Because of the nanometer size, TiO$_2$ can be blended with the resin uniformly in the wear debris, and can improve the adhesion strength of the transfer film to the counterpart.[22] At high normal load (i.e., >30 N), similar to the case of the neat epoxy, high temperatures cause a resin degradation. Thus, the transfer film cannot be formed. The collapse of the wear resistance of the nano-TiO$_2$-filled epoxy at high normal load conditions [Fig. 6(a)] is attributed to the reduction of the transfer film and the deterioration of the mechanical properties of the resin due to the high temperature. Consequently, the wear resistance is in the range of that of the unfilled resin [Fig. 6(a)].

Micrographs of sliding surfaces of composite materials under mild conditions illustrate that the reinforcing effect of the nano-TiO$_2$ can be responsible for the enhancement of the wear resistance. Figure 10(a, b) illustrates the worn surfaces of the neat epoxy and nano-TiO$_2$-filled epoxy, respectively. It is clearly visible that the crack formation on the worn surface is markedly reduced by the incorporation of TiO$_2$, which indicates the diminished fatigue wear.

In contrast with the neat epoxy and the nano-TiO$_2$ containing epoxy, graphite particles are able to form a transfer film on its sliding surface except at 0.2 m/s. The gap between the embedding resin and the composite sample indicates an example transfer film (Fig. 11). For the present selected sliding conditions (except at 0.2 m/s), graphite-filled epoxy formed a transfer film on the steel counterpart [Fig. 12(a)].
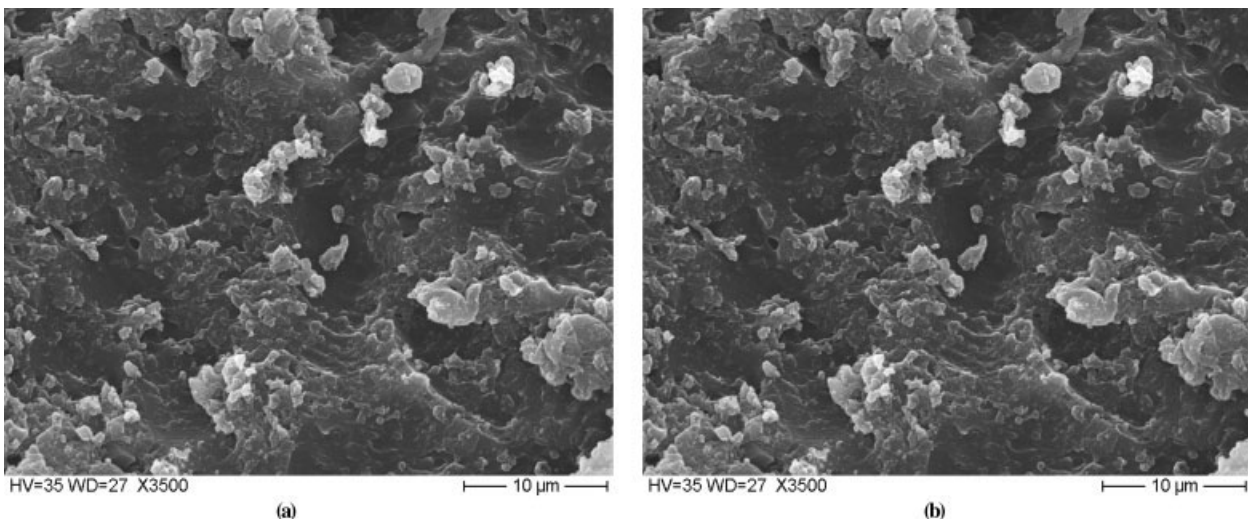
Figure 10 Scanning electron micrographes of the worn sample surfaces of the epoxy (a) and TiO$_2$-filled epoxy (b) at 1 m/s, 10 N.
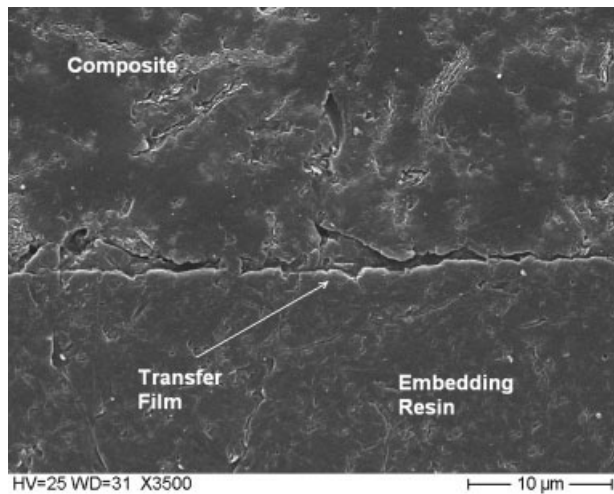
**Figure 11** Back transferred film on the composite (epoxy filled with graphite) sample at 1 m/s, 10 N.

Especially under higher normal load (i.e., >30 N), a more continuous and thicker transfer film was formed. As expected, the increased normal load improves the mechanical embedding of graphite flakes to grooves of the steel counterpart, thus facilitating the formation of a transfer film. The transfer films formed on both sliding pair surfaces endow the graphite-filled epoxy with the relative stable wear resistance and coefficient of friction (Figs. 5 and 6).

It is interesting to note that the steel counterpart was polished significantly by graphite-filled epoxy at 0.2 m/s [Fig. 12(b)]. This phenomenon indicates the composite possessing a severe abrasiveness. Note that this phenomenon is not found for nanometer-sized TiO$_2$-filled epoxy at the same sliding conditions (Fig. 9). As known, the larger the particle size, the higher the angularity of the particle can be.[13] Therefore,

the micrometer-sized graphite shows higher abrasiveness than nanometer-sized TiO$_2$. Because of lack of transfer films on both sliding surfaces, graphite may directly impact the asperity of the steel counterpart, and polish the surface. Under the other sliding conditions, transfer films prevent the above direct contact, and abrasiveness does not occur. In addition, the orientation of graphite flakes in the sliding direction is proposed to be responsible for the lubricating effect.[19] Therefore, it is supposed that the graphite flakes cannot orient in the sliding direction at such low velocity (0.2 m/s), and thus the lubricating effect of graphite flakes is diminished.

Also for the epoxy filled with nanometer-sized TiO$_2$ and graphite, transfer films were formed on both the steel counterpart and composite sample surfaces, except at 0.2 m/s. Compared to the graphite only filled epoxy, the transfer films on the steel counterface seems to be more continuous and uniform (Fig. 13) under the same sliding conditions. The mechanical properties of the transfer films, containing nanoparticles, graphite flakes, and epoxy resins, were improved in analogy to the bulk materials (Fig. 3). As a result, the protecting effect for the substrates of the composite sample is increased. Furthermore, the reinforcing effect of the nanoparticles on the toughness diminishes the occurrence of microcracks on the composite samples surface and enhances load- and velocity-carrying capacities.

In summary, nano-TiO$_2$ possesses reinforcing effect and promotes the formation of the transfer film on the steel counterpart, while graphite helps the formation of transfer films on both sliding pair surfaces but deteriorates the mechanical properties of the bulk materials. The combination of both fillers leads to an effective transfer film on both sliding pair surfaces and improved mechanical properties. This is assigned to
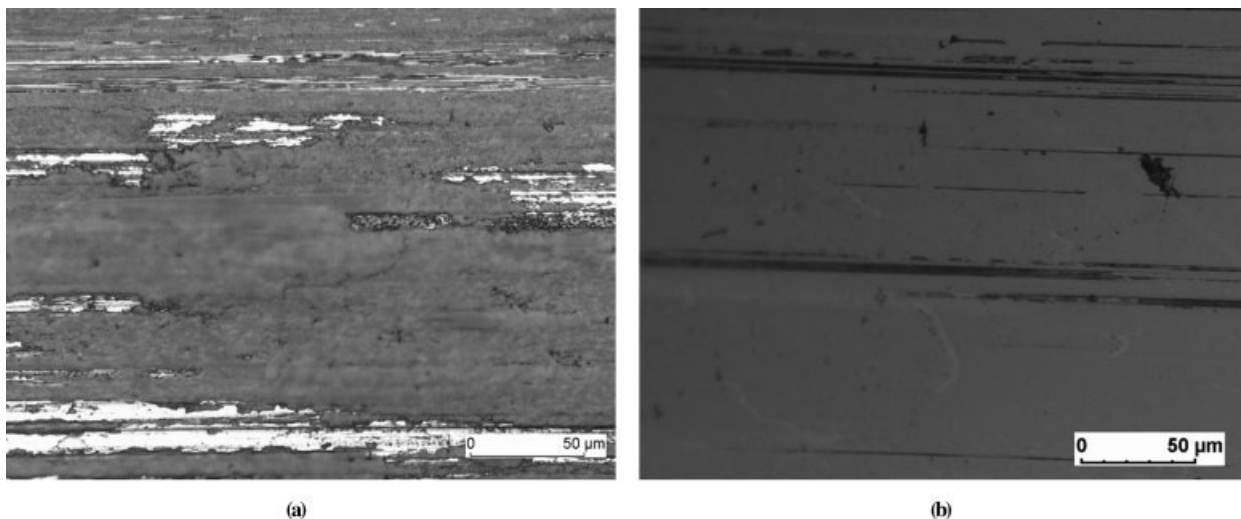
Figure 12 Micrographes of the steed counterpart slid by the graphite-filled epoxy at 1 m/s, 40 N (a) and 0.2 m/s, 10 N (b).
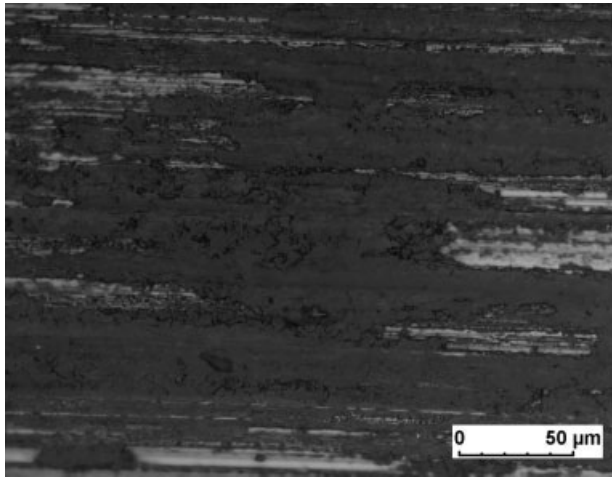
Figure 13 Micrographs of the steel counterpart slid by the graphite and TiO₂-filled epoxy at 1 m/s, 40 N.

the synergistic effect in reducing the wear rate and the coefficient of friction under the investigated sliding conditions.

CONCLUSIONS

1. The nanometer-sized TiO₂ particles of low aspect ratio leads to low stress concentration and is able to block the propagation of cracks through the polymer. As a result, a low content of nanometer-sized TiO₂ effectively improved the flexural strength and the impact strength of the neat epoxy or graphite-filled epoxy.
2. Under mild sliding conditions (i.e., low sliding velocity and load), the incorporation of nanometer-sized TiO₂ enhanced the wear resistance significantly, but led to a higher coefficient of friction than that of the neat epoxy. Under severe sliding conditions, the wear rate reducing effect of nano-TiO₂ markedly diminished, while the coefficient of friction was lower than that of the neat epoxy. The reinforcing effect and the formation of transfer films due to the corp. of the nanoparticles were assigned to the variation of the tribological behavior.
3. A synergistic effect was found for the combination of both TiO₂ and graphite on the wear performance of the neat epoxy. The corresponding composite exhibited the lowest wear rate and coefficient of friction under the investigated sliding conditions. The synergistic effect attributed to effective transfer films formed on sliding pair surfaces and the reinforcing effect of the nanoparticles.
4. SEM micrographs show that the incorporation of nanometer-sized TiO₂ to the graphite-filled epoxy benefited the formation of transfer films on both contact surfaces. In combination with improved mechanical properties of the transferred material different wear mechanisms can take place, which are attributed to the synergism in term of the improved wear resistance and reduced coefficient of friction.

References

1. Xian, G. J.; Walter, R.; Haupert, F. J Synth Lubrication 2005, 21, 269.
2. Wetzel, B.; Haupert, F.; Friedrich, K.; Zhang, M. Q.; Rong, M. Z. Polym Eng Sci 2002, 42, 1919.
3. Kishore, P.; Sampathkumaran, S.; Seetharamu, S.; Vynatheya, A.; Kumar, M. R. K. Wear 2000, 237, 20.
4. Xing X. S.; Li, R. K. Y. Wear 2004, 256, 21.
5. Xian, G.; Walter, R.; Haupert, F. Materialwissenschaft Und Werkstofftechnik 2004, 35, 670.
6. Schon, J. Wear 2004, 257, 395.
7. Pihtili, H.; Tosun, N. Wear 2002, 252, 979.
8. Jacobs, O.; Jaskulka, R.; Yang, F.; Wu, W. Wear 2004, 256, 9.
9. Shi, G.; Zhang, M. Q.; Rong, M. Z.; Wetzel B.; Friedrich, K. Wear 2004, 256, 1072.
10. Wetzel, B.; Haupert, F.; Zhang, M. Q. Compos Sci Technol 2003, 63, 2055.
11. Xian G. J.; Zhang, Z. Wear 2005, 258, 776.
12. Bahadur, S. Wear 2000, 245, 92.
13. Cho, M. H.; Bahadur, S. Wear 2005, 258, 835.
14. Schwartz, C. J.; Bahadur, S. Wear 2000, 237, 261.
15. Czichos, H.; Klaffke, D.; Santner, E.; Woydt, M. Wear 1995, 190, 155.
16. Friedrich, K.; Flöck, J.; Varadi K.; Neder, Z. Wear 2001, 251, 1202.
17. Palabiyik, M.; Bahadur, S. Wear 2002, 253, 369.
18. Walter, R.; Xian, G.; Haupert, F. Tribologie und Schmierungstechnik 2005, 52, 32.
19. Xian, G. J.; Zhang, Z. Wear 2005, 258, 783.
20. Riley, A. M.; Paynter, C. D.; McGenity P. M.; Adams, J. M. Plast Rubber Process Appl 1990, 14, 85.
21. Bassani, R.; Levita, G.; Meozzi, M.; Palla, G. Wear 2001, 247, 125.
22. Bahadur, S.; Sunkara, C. Wear 2005, 258, 1411.