The preparation and the friction and wear behaviours of TiO$_2$/CNT/PI composite film

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Recently, the tribological properties of polyimide composites filled with TiO$_2$ nanoparticles and short pitch-based carbon nanotubes (CNTs) were investigated. Sliding tests were performed on a co-rotating twin-screw extruder under different temperatures and regular pressure and speed. It was found that the composite with 4 wt% TiO$_2$ and 6 wt% CNT could reduce the frictional coefficient and wear rate in the most effective way. Compared to the conventional hybrid composites up to now, the above composite was characterised by relatively lower filler content, which would reduce the manufacturing cost. Therefore, it could be largely processed in practice. Increased surface hardness, lubricating effect of the sheet-like wear debris reinforced by TiO$_2$ and rapidly formed transfer film were believed to be the key issues accounting for the obvious wear-resisting and friction-reducing behaviours.

Keywords: frictional coefficient; sliding wear; tribological performance; TiO$_2$ nanoparticles; hybrid composites

1. Introduction

With the continuous development of industry, polymer composites have been increasingly used as structural materials, owing to their good strength and stiffness, high load-carrying capacity, self-lubrication and superior cleanliness.[1–3] The features that make polymer composites so promising for industrial applications are opportunities to tailor their properties with special fillers. More recently, with the booming of nano-phased materials, nano-sized particles have also come under consideration. Numerous of attempts have been made to develop polymer-based nanocomposites for tribological applications.[4,5] Compared with the conventional micrometre-sized fillers, nanoparticles are believed to have the following advantages when considering the composites’ tribological performance: (1) the nanofillers possess decreased angularity, and thus they are less abrasive; (2) the transferred film can be strengthened; and (3) in contrast to conventional composites, because of the increased number density of nanoparticles, the relative volume fraction of interfacial material to bulk is drastically increased as the size becomes smaller.[6–8]

Polyimide (PI), i.e. nylon 66, is selected as an important thermoplastic and is widely used in injection moulded components, with excellent mechanical performances and strong commercial advantages of lower manufacturing cost. Many experiments show that additional fillers, e.g., inorganic compounds and graphite, have greatly improved
Mechanical performances of composites. Effects of fillers on the mechanical performances of composites strongly depend on their property, shape, dimension, size and aggregate degree, surface characteristics and concentration. In view of this, various researchers have concluded that mechanical properties of polymer composites filled with smaller particles are superior to those with larger ones at micron level, which were deeply investigated in rubber particle toughened polyamide (PA). In the past few decades, the research on nanoparticle-filled polymer composites has been growing exponentially with the aim of developing the materials, and has been mainly focusing on the effect on the mechanical properties of these nanocomposites.

Recent studies indicate that thermoplastics filled with rigid particulates reported a significant increase in toughness and strength compared to the neat polymers. It has been shown that dramatic improvements in fracture toughness can be achieved by incorporating of a few weight percentages (wt%) of rigid inorganic particles. Many possible toughening mechanisms have been proposed. Generally speaking, two categories can be mainly considered, i.e. the crack front bowing and the cavitation mechanisms. With the development of science and technology, it is easy for us to see that the size of particles that are studied varies from microscale to nanometre scale. However, compared with the toughening mechanisms of micro-composites, that of nanocomposites are obviously different, which is likely due to the huge particle–matrix interface introduced by the nanofillers.

Due to the lack of research on the toughness of rigid nanoparticle-filled polymers this deserves a new approach. Toughening mechanisms induced by nanoparticles is not yet well understood. Lots of factors (particle size, shape, distribution, type, aspect ratio, interface, particle concentration, dispersion, etc.) may strongly affect the toughening efficiency of nanoparticles. To our knowledge, nanoparticles with a high aspect ratio, e.g. clay, often bring negative toughening effects, because under external load the large aspect ratio will generate significantly high stress concentrations at the end of the particles, which lead to earlier crack initiation and propagation, and finally are adverse to material toughness.

Our research indicates that the huge interfacial area between filler and matrix is a special feature of nanocomposite materials, which can dramatically reach up to 1000 m²/g filler and is considered as a key factor to be able to intensely improve the mechanical properties of a polymer matrix. Due to this reason, rubber particles, with fairly large aspect ratios, have been widely researched in recent years. Many attractive enhancements were obtained in physical and mechanical performances of polymer/clay nanocomposites; however, the addition of rubber particles usually results in the decrease in yield stress that may limit the application of the material in some instances. Consequently, various kinds of spherical nanoparticles, such as glass fibre, silica, titanium oxide and calcium carbonate, have been used in the attempt to prepare nanocomposites. However, any studies on fracture toughness of polymer nanocomposites were scarcely found in the literatures.

According to the authors’ knowledge, no study is available in the literature on TiO₂ nanoparticles and short carbon nanotubes’ (CNTs) abrasive wear behaviour of PI/polypropylene (PP) blends and their composites. In view of the above, the goal of the present investigation is to study the mechanical and TiO₂ nanoparticles and short CNTs’ abrasive wear behaviour of PI blend in order to understand the wear performance and the dominant wear mechanisms of these composites. The measured wear volume loss increases with the increase in abrading distance and abrasive particle size. However, the specific wear rate decreases with the increase in abrading distance and the decrease in abrasive particle size.
2. Experimental

2.1. Material preparation

TiO$_2$ nanoparticles (Degussa P25) were applied as nanofillers with a density of 4 g/cm$^3$ and a mean diameter of 21 nm. The volume contents were in the range of 1%–6%. CNT with diameter of 5–15 nm, length ≤10 μm, purity >95 wt%, bulk density of 0.02–0.04 g/cm$^3$.

2.1. Fabrication of the samples

PI hybrid films were prepared by using in situ polymerisation; modified nano-TiO$_2$, methyl-cyclopentadienyl-manganese-tricarbonyl (MMT) and N,N-dimethylacetamide (DMAC) were added into a three-opening round-bottomed flask with a stirrer and the flask was placed in an ultrasonic bath. The mechanical stirrer and ultrasonic wave were simultaneously utilised until a stable suspension was obtained. Then, 4,4′-oxy dianiline (ODA) was added into the flask and dissolved in the suspension (the mixture of nano-TiO$_2$, MMT particles and pyromellitic dianhydride (PMDA) in the flask exposed in ultrasonic bath for 2 h in DMAC solvent). Finally, the PMDA was divided into five portions and one portion was added into the suspension at one time to ensure the complete dissolution of the portion before adding another one, until all five portions were added. Then, polyamic acid (PAA) suspension is stirred for 4 h at this viscosity until the suspension turns to yellow. Hybrid films were obtained after forming, heat treatments and imidisation. The films are light yellow and transparent with thicknesses about 30 μm.

2.2. Friction and wear tests

Friction and wear tests were carried out with an M-200 model block-on-wheel friction and wear tester under dry sliding conditions. GCr15 bearing steel wheel, whose composition is C 0.95–1.05 wt%, Si 0.15–0.35 wt%, Mn 0.20–0.40 wt%, Cr 1.30–1.65 wt%, and Fe balance with a bulk hardness of HRC65±5 was used as the counterpart. The sizes of specimen and steel wheel are 10 × 10 × 14 mm and Φ 40 × 10 mm, respectively.

3. Results and discussion

3.1. Characteristic of film

The chemical structures of the PI/TiO$_2$, monolayer and PI films with 5 wt% doping were characterised using Fourier transform infrared spectroscopy (FTIR) technique, as shown in Figure 1. Since the energy range (with wavenumber from 400 to 3500 cm$^{-1}$) of FTIR only covers molecular vibration bands, the similarity of all FTIR spectra of nanocomposite films tested in Figure 1 indicates that similar organic molecular structures of PI and inorganic doping of one and components in all nanocomposite films do not alter PI molecular matrix significantly in PI/TiO$_2$ manufacturing processes.

The peaks between 1000–1050 and 469 cm$^{-1}$ are the characteristic absorption bands of the Ti–O from the TiO$_2$. Three characteristic bands at 3694, 3664, and 3649 cm$^{-1}$ for inner-surface hydroxyl stretching are found, which shift to 3692, 3662, and 3646 cm$^{-1}$ in sample due to the influence of interlamellar modifications. Two additional bands at 1418 and 1604 cm$^{-1}$ which attributed to the vibration peaks of symmetric and antisymmetric
stretch vibrations of CH$_3$ COO$^-$ have, respectively, appeared in the spectra of sample. The couplings of C–O vibration and O–H deformation are marked by the new band at 1346 cm$^{-1}$. The band at 3606 cm$^{-1}$ provides the interaction between the inner surface O–H and the hydrogen bond of CH$_3$ COO$^-$. The surfaces of the PI/Ti and PI/Ti/CNT hybrid films were investigated by atomic force microscope (AFM), and the cross-sectional two-dimensional (2D) images are shown in Figure 1.
Figure 2. The small peaks have a light appearance in the 2D images signalling a higher modulus, which are corresponding to the particles. The film containing TiO$_2$ was characterised by a higher root-mean-square (RMS) (2.830 nm) than that containing CNT, indicating a much higher surface roughness for the PI hybrid films. This is ascribed to the more serious enrichment of CNT on the film surface.
3.2. Friction and wear performance

Figures 3 and 4 summarise the friction coefficients and specific wear rate test results of the TiO$_2$-reinforced PI and the pure polymer 66, when the sliding speed reaches 0.42 and 0.84 m/s. It was found from these figures that a slight increase in the friction coefficient was observed for increasing sliding speed and specific wear rate obviously increased by $1 \times 10^{-6}$ mm$^3$/Nm with the improvement of sliding speed. In comparison with the pure PI, the addition of TiO$_2$ particles obviously reduced the friction coefficient and wear loss of the polymer composites in the same conditions. Therefore, it can be inferred that TiO$_2$ particle is helpful to improve the mechanical properties of PI composites.

During containing different contents of TiO$_2$, the differences in the friction and wear behaviours of PI and TiO$_2$/PI nanocomposites are possibly related to their worn surface morphologies, transfer film characteristics and wear debris features. Solid lubricant, which is the property of TiO$_2$, has an effect on the worn composite and transfer film surfaces so that the high mass fractions of TiO$_2$ can reduce the friction coefficient and wear.

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**Figure 3.** Variations of friction coefficients with sliding speed for the TiO$_2$/PI composites.

**Figure 4.** Variations of specific wear rate with sliding speed for the TiO$_2$/PI composites.
In order to investigate the effect of the addition of TiO$_2$ nanoparticles on the friction coefficient and wear performance of TiO$_2$/PI nanocomposites, we can observe the morphologies of the nanocomposite worn surfaces by scanning electron microscopy (SEM). In accordance with an earlier finding, the neat polymer (Figure 5(a)) cannot form a transfer film on the steel counterpart. However, Figure 5(b) and 5(c) showed that PI filled with nano-TiO$_2$ formed a patchy and thick transfer film on the counterpart. The worn surface of pure PI (Figure 5(a)) showed signs of scuffing and adhesion. It perhaps indicated that the wear

![Figure 5](image_url)

Figure 5. The morphologies of the nanocomposite worn surfaces: (a) PI, (b) 3 vol% TiO$_2$/PI, (c) 6 vol% TiO$_2$/PI.
mechanisms may be fatigue. However, the worn surface of 3 vol% TiO₂/PI (Figure 5(b)) and that of 6 vol% TiO₂/PI (Figure 5(c)) showed signs of abrasives and mild abrasive wear, which accounted for the increased wear of the nanocomposite with high mass fraction of nanometre TiO₂.

The variation in the specific wear rate with abrading distance at the content of 3 vol% TiO₂ and 6 vol% TiO₂ for PI-based nanocomposites has been studied. When too much TiO₂ were incorporated, the worn morphology of the composites (Figure 5(c)) became

Figure 6. Typical time dependences of friction coefficient of the materials: (a) PI, (b) TiO₂-reinforced PI.
obviously coarse. Crack initiation, growth and coalescence take place in the sub-layer of the worn surface. And, when the composites were filled with CNT, the detached fibre debris could act as a third body abrasive, which leads to higher wear rate and friction coefficient; in that a major share of normal load was supported by the fibres. However, it was worth noting that the number of the cavities left by detachment of CNT was reduced after the incorporation of TiO$_2$ (Figure 5(b)).

Figure 6 compared the friction coefficient of PI composites without and with TiO$_2$ nanoparticles for the last 30 minutes. As shown in Figure 6(a), for the PI without TiO$_2$ nanoparticles, the friction coefficient obviously decreased and suddenly appeared a sharp increase at the time of 20 minutes, but the friction coefficient kept on 0.19. With the addition of TiO$_2$ nanoparticles (Figure 6(b)), the friction coefficient kept stable from the beginning to the end as a function of the formation of the continuous transfer film, and the friction coefficient was obvious smaller than that of pure PI, which was 0.18. Hence, the friction coefficient reduction for nanocomposites was mainly caused by a change in the contact mechanisms due to the presence of TiO$_2$ nanoparticles.

Experiments showed that the decrease of the friction coefficient and the wear rates of unreinforced PI and of the TiO$_2$-reinforced material in its initial stages mainly depended on their remarkable load-carrying capability. Of course, the addition of TiO$_2$ particles has positive improved the tribological properties of PI composites to some extent. Also, the tribological programme of composites, which incorporated two types of additives, were investigated (Figure 7). It was showed from the figure that the synergetic effect of 4 vol% TiO$_2$ and 6 vol% CNT had the lowest friction coefficient and specific wear rate. Although TiO$_2$ is less effective in reducing wear rate and friction coefficient than short CNT, a combination of TiO$_2$ and short CNT can get much better outcomes. It was a pleasure result.

![Figure 7. The synergetic effect of CNT and TiO$_2$.](image-url)
4. Conclusions
In the present paper, tribological properties of TiO$_2$-filled PI matrix composites, incorporated additionally with short CNT, were systematically studied under different sliding conditions. It was found that nano-TiO$_2$ could effectively reduce the frictional coefficient and wear rate. In order to promote this effort, the current study concentrated on the thermoplastic PI matrix composites. PI was selected as an important thermoplastic and being widely used in injection moulded components, with strong commercial advantages of lower manufacturing cost. From the experiments and figure analysis, we could draw the following conclusions:

(1) The addition of TiO$_2$ and short CNT into PI was able to have a positive synergetic effect on the tribological performance. Pure PI containing 4 wt% TiO$_2$ and 6 wt% short CNT exhibited significantly lower wear rate and friction coefficient than those filled with either TiO$_2$ or short CNT;

(2) With the further investigation of the synergetic effect, it was observed that CNT mainly improved surface hardness, and sheet-like wear debris reinforced by TiO$_2$ acted as lubricant.

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