

THE ENHANCEMENT OF THE TRIBOLOGICAL PROPERTIES OF FIBRE-REINFORCED POLYAMIDE 6,6 BY TiO₂ NANOPARTICLES

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ABSTRACT

The tribological properties of polyamide 6,6 (PA6,6) composites, filled with TiO₂ nanoparticles, short carbon fibres (SCF), and graphite flakes, were investigated. Sliding tests were performed on a pin-on-disk apparatus under different contact pressures, p , and sliding velocities, v . It was found that nano-TiO₂ could effectively reduce the frictional coefficient and the contact temperature, consequently the wear rate, especially under higher pv (the product of p and v) conditions. Based on SEM observations, the wear mechanisms were discussed.

1. INTRODUCTION

Over the past decades, polymer composites have been increasingly applied as structural materials in aerospace, automotive and chemical industries, providing lower weight alternatives to traditional metallic materials. A number of these applications are concentrated on tribological components, such as gears, cams, bearings and seals etc., where the self-lubrication of polymers was of special advantages. The features that make composites so promising in industrial applications are opportunities to tailor their properties with special fillers. For instance, short fibre reinforcements, such as carbon and glass fibres, have been successfully used to improve the strength and therefore the load carrying capacity of polymer composites [1-3]. Solid lubricants, e.g. PTFE and graphite, were proved to be generally helpful on developing a continuous transfer film between the two counterparts and normally reduce the frictional coefficient [4-6]. Nano-scale inorganic particles are recently under consideration, which gives special hints that this method is promising for new routes of wear resistant materials even at very low filler content (about 1~4vol.%) [7,8].

Though most polymers can provide low frictional coefficient and specific wear rate, its applications are generally limited to low contact temperature and consequently lower pv conditions [9]. For instance, as shown in Fig.1, the T_g of PA6,6 is around 80°C and the material become very soften when temperature reaches up to above 50°C, which could possibly happen in dry sliding wear depending on pv conditions. Correspondingly, the wear rate of material would be seriously increased with the degraded mechanical properties [3]. In order to evaluate the durability of materials under different loading conditions, the time-related depth wear rate, W_t , was frequently applied,

$$W_t = k^* \cdot pv = \frac{\Delta h}{t} \quad [m/s] \quad (1)$$

in which k^* is called the basic wear factor of the material, p is the normal pressure, v is the sliding velocity, t is the test time and Δh is the height reduction of the specimen. In this equation, the wear factor, k^* is supposed to be a material parameter, which can also be dependent on alterations of the external loading conditions p and v . Based on Equation 1, the pv factor could be considered as a tribological criterion of the load-carrying capacity for bearing materials, which results in two evaluation parameters [1]: (i) the basic wear factor k^* , which keeps nearly constant in a certain range of the pv product, and (ii) the “limiting pv ”, above which the increase of the wear rate of materials is too rapid, so that the material cannot be used any more. To reduce the basic wear factor k^* and to enhance the “limiting pv ” value are the general targets of the design of wear resistant polymer composites.

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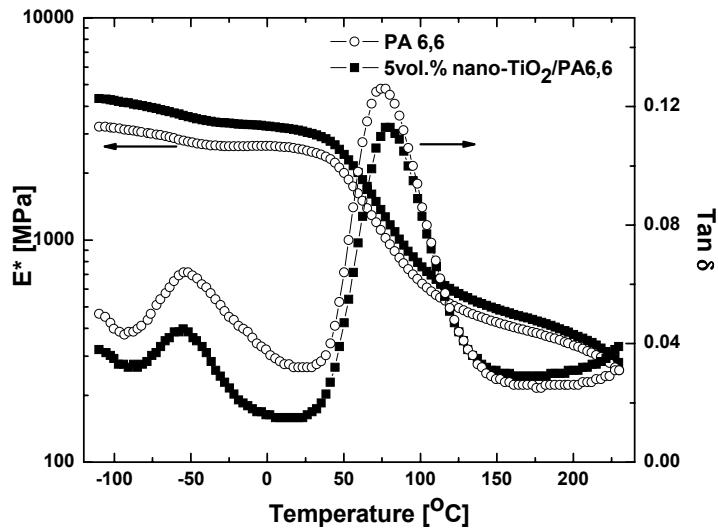


Fig.1. Dynamic mechanical properties of the neat PA6,6 and PA6,6-based nanocomposite with 5vol.% nano-TiO₂ for the temperature range -110 to 230°C.”

In our recent studies, wear behaviours of epoxy-based nanocomposites were investigated under different load pressures and sliding velocities [10,11]. It was found that the addition of nano-TiO₂ could apparently reduce both the frictional coefficient and the wear rate, especially under high *pv* conditions. To promote the effort, this work concentrated on the polyamide 6,6 (PA6,6) matrix composites. This matrix material was selected as an important thermoplastic and being widely used in injection moulded components [12-15], which were strong commercial advantages for their lower manufacturing cost. The tribological influence of the addition of nano-TiO₂ to the PA6,6-based composite, containing short carbon fibre (SCF) and graphite flakes, was investigated under different sliding conditions. It was expected that the work could be helpful towards a further understanding to the tribological role of nano-TiO₂ on polymer composites.

2. EXPERIMENTAL

2.1 Materials

A commercially available PA6,6 (Zytel 101L) was considered as matrix material in this study. Pitch-based short carbon fibres (Kureha M-2007S) and graphite flakes (Superior 9039) were selected as conventional reinforcements. The average diameter of short carbon fibres was approximately 14.5µm with an average fibre length of about 90µm. The particle size of graphite was about 20µm. TiO₂ (Kronos 2310) with an average diameter of 300 nm was applied as an additional reinforcement. The mixture of PA6,6 with different fillers was achieved by twin-screw-extruders at 292°C with standard configurations. Thereafter, the wear specimens were produced using an Arburg Allrounder injection moulding machine with an injection pressure of 500bar. The screw speed was set at 80cm/s and the mould temperature at 70°C. Two compositions were involved in this work, i.e. one is 5vol.%graphite+15vol.% SCF/PA6,6 and another one with additional 5vol.% of TiO₂ particles.

2.2 Wear tests and equations

The wear test was performed on a Wazau pin-on-disc apparatus according to ASTM D3702. The specimen pin ($4 \times 4 \times 12\text{mm}^3$) was rotated against a polished steel disc with the initial surface roughness of ~220 nm. The tests were conducted for 20 hours each in a wide range of wear conditions, i.e. the nominal pressure ranged from 1 to 8 MPa and the sliding velocity from 1 to 3 m/s. During the test, the temperature of the disc was monitored by an iron-constantan thermocouple contacted to the edge of the disc. The frictional coefficient was recorded and calculated by a ratio between the tangential force and normal load. The mass

loss of the specimen was measured in order to calculate the specific wear rate by the following equation, which is the same as the wear factor k^* mentioned in equation 1,

$$W_s = \frac{\Delta m}{\rho F_N L} \quad \left[\frac{mm^3}{N \cdot m} \right] \quad (2)$$

in which F_N is the normal load applied on the specimen during sliding, Δm is the specimen's mass loss, ρ is the density of the specimen, and L is the total sliding distance. All the test results were summarized in Table 1. Both the frictional coefficient and the contact temperature given in the table were mean values during the steady state of the sliding process. After wear tests, the worn surfaces of specimens were examined by a JEOL-5400 scanning electron microscopy (SEM).

3. RESULTS

3.1 Observation under a standard wear condition: 1MPa and 1m/s

Fig. 2 shows the typical variations of the frictional coefficient and contact temperature against sliding time of neat PA 6,6 and other two composites. It was distinct that the two parameters were closely correlated and the tendencies were well coincided, which has been reported as well in an earlier study [11]. As shown in the figure, the stable frictional coefficient of unfilled PA 6,6 was even higher than 1.0, which occurred in certain wear conditions because of the high contact temperature [12,16]. This value was significantly reduced by the conventional fillers, i.e. SCF and graphite, which conduced to the development of polymer transfer film on the counterpart and produced adhesive mechanism. Correspondingly, the contact temperature was apparently reduced, thus preformed an improved wear resistance (Table 1). With the addition of nano-TiO₂, the frictional coefficient was further reduced to a mean value of about 0.4 after the initial wear stage (Fig. 2). This reduction could be explained by the assumption of the rolling effect of the nanoparticles between the contact pairs [10,11]. On the other hand, hard nanoparticles could act as the third bodies inducing mild abrasive wear [9], which in some extent, counteract the reduction effect on wear loss by the lower friction. As a result, the specific wear rates of the composites with and without nanoparticles were similar with each other.

“Table 1. Tribological properties of PA6,6 and PA6,6 matrix composites under various wear conditions”

Composition	<i>p</i> v factors	Frictional Coefficient	Contact Temperature [°C]	Specific Wear Rate [$10^{-6}mm^3/Nm$]
neat PA6,6	1MPa, 1m/s	1.16	45.09	6.70
graphite+SCF/PA6,6	1MPa, 1m/s	0.60	30.57	0.53
	2MPa, 1m/s	0.57	46.07	0.80
	4MPa, 1m/s	0.69	94.98	2.92
	8MPa, 1m/s	0.35	97.37	16.93
	2MPa, 2m/s	0.78	97.67	4.87
	2MPa, 3m/s	0.62	115.80	5.73
nano-TiO ₂ +graphite +SCF/PA6,6	1MPa, 1m/s	0.44	26.66	0.50
	2MPa, 1m/s	0.34	33.21	0.72
	4MPa, 1m/s	0.26	45.55	0.80
	8MPa, 1m/s	0.22	64.69	3.26
	2Mpa, 2m/s	0.34	45.94	0.63
	2Mpa, 3m/s	0.38	62.36	3.35

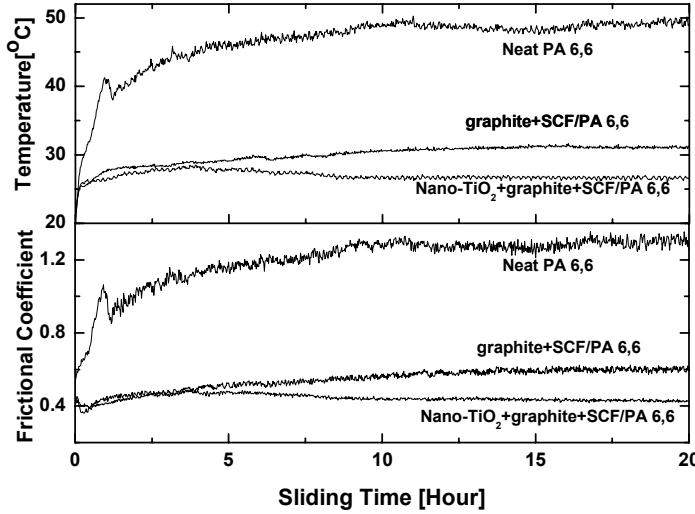


Fig.2. The typical sliding process curves of frictional coefficient and contact temperature against sliding time of neat PA6,6 and without and with nano-TiO₂ under a standard wear condition of 1MPa and 1m/s.”

The worn surface of neat PA6,6 is given in Fig.3. Grooves paralleled to the sliding direction are clearly observed and suggest the abrasive wear mechanism. This was greatly influenced by the original roughness of harder counterface and the contact pressure [13, 17]. With a magnified view, viscous flow of material was observed in a micron scale due to the relatively high contact temperature. As a result, the soft PA6,6 was rapidly removed by the hard asperities of the metallic counterface, which exhibited a weak load carrying capacity.

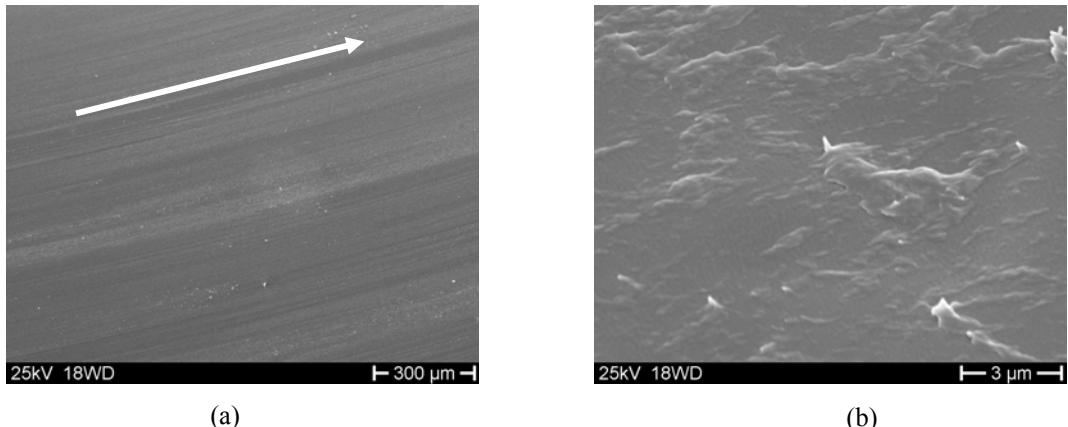


Fig. 3. (a) SEM micrographs of the worn surfaces of neat PA 6,6 measured at 1MPa and 1m/s, and (b) the magnified view of viscous flow.”

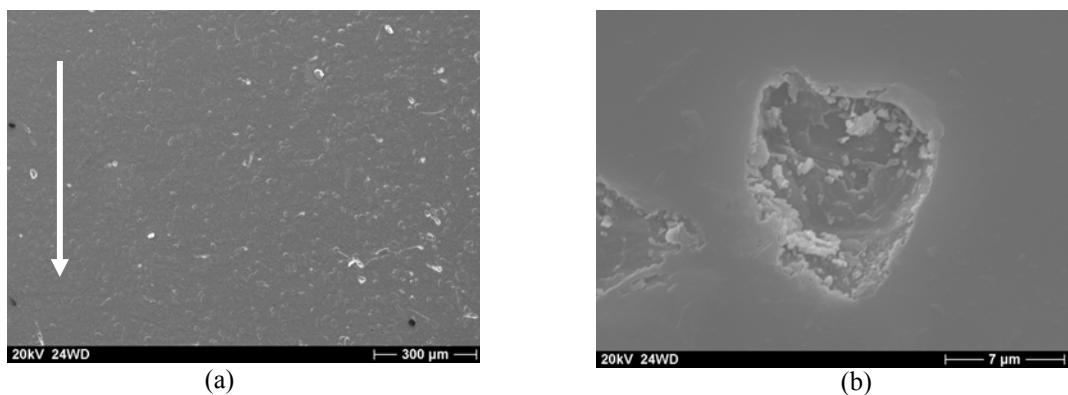


Fig. 4. (a) SEM micrographs of the worn surfaces of the composition without nanoparticles at 1MPa and 1m/s, and (b) the magnified view of matrix ploughing damage.”

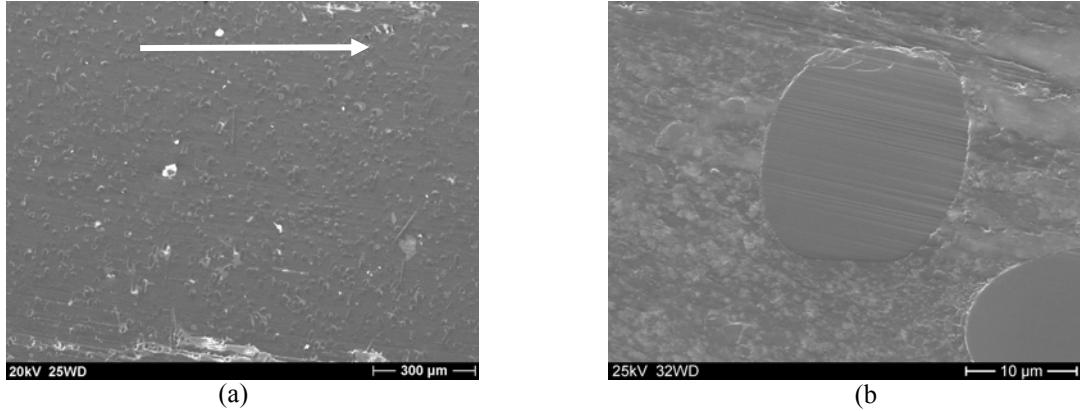


Fig. 5. (a) SEM micrographs of the worn surfaces of the composite nano-TiO₂+graphite+SCF/PA6,6 with nanoparticles at 1MPa and 1m/s, and (b) the magnified view of nano grooves on the fibre.”

Figs. 4 and 5 present the worn surface of two composites without and with nano-TiO₂, respectively. It is clear that the surfaces of both the composites were quite smooth with some micro-cracks (Fig. 4b) caused by the “fatigue wear” of adhesive contact [9]. For the nanocomposite, nano-grooves were observed on the carbon fibres (Fig. 5b), which also occurred for the epoxy-based nanocomposites and inferred a combinative effect of carbon fibres and nanoparticles [18]. This effect was assumed to reduce the frictional coefficient and protect fibre from serious removal.

3.2 Wear under high *pv* products

With the improvement on the load-carrying capacity by fillers, the composites could be subjected at much higher *pv* conditions compared to the neat PA6,6. Fig.6 presents the sliding processes of the two composites under a contact pressure of 4MPa and a sliding velocity of 1m/s. In comparison to Fig. 2, it can be seen that the duration of running-in stages of both composites was apparently reduced, which corresponded to the more rapid formation of the stable transfer films under a higher contact pressure. This was probably resulted by the accelerated generation of wear debris and easier formation of transfer film. After the running-in stage, the frictional coefficient of the composite without nano-TiO₂ became stable and obtained a high contact temperature. As a result, the wear rate of the material was badly increased. However, the frictional coefficient for nanocomposite was sharply decreased and achieved a relatively low value, even lower than that obtained under 1MPa and 1m/s. As a whole, the wear resistance of nanocomposite was remarkably enhanced under this condition.

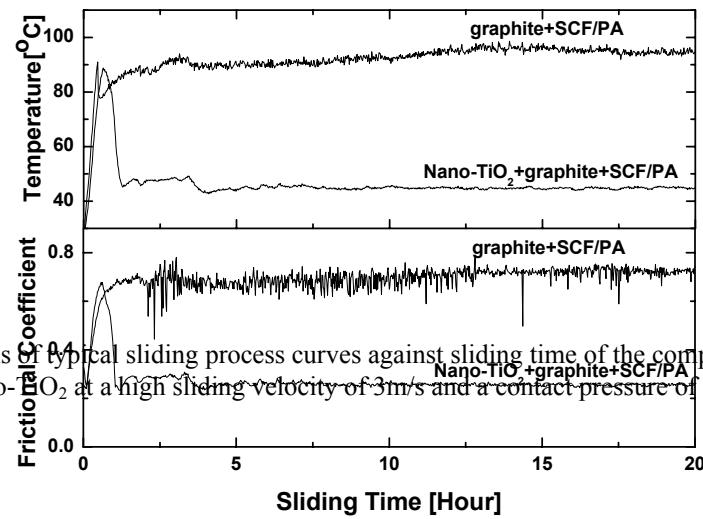


Fig. 6. Comparisons of typical sliding process curves against sliding time of the composites without and with nano-TiO₂ at a high sliding velocity of 3m/s and a contact pressure of 2MPa.”

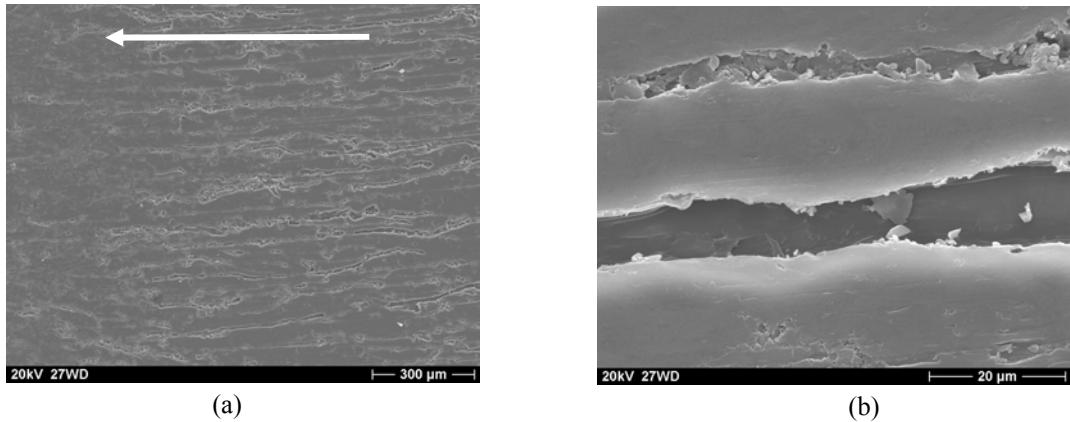


Fig. 7. (a) SEM micrographs of the worn surfaces of the composition without nanoparticles at 4MPa and 1m/s, and (b) the magnified view of fibre removal.”

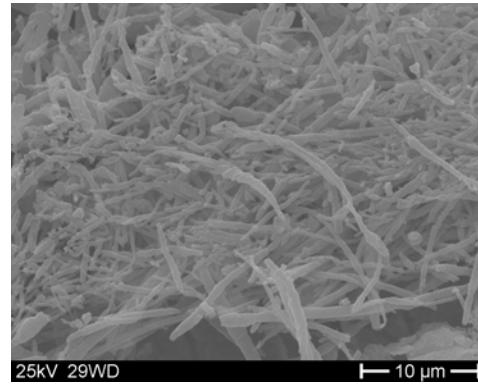


Fig.8. SEM micrographs of roll debris on the metallic counterpart surface.”

Fig. 7 shows the SEM micrographic of worn surface of the composition without nano-TiO₂ at 4MPa and 1m/s. Due to the high contact temperature during sliding, the fibre removal was seriously aggravated since the soft PA6,6 matrix could not effectively protected SCF from peeling off, associated with the increase of friction. However, it was noticed that the breakage in interfacial region of SCF/PA6,6 was much limited in comparison to that of brittle epoxy composite. This was caused by the ductile of the polyamide, which deformed through elongation rather than breakage and thus a roll formation of debris. Additionally, Fig.8 shows the typical roll debris on the counterpart surface formed by the composite. The worn surface of the nanocomposite was given in Fig. 9. With the protective nano-rolling effect on the SCF by nanoparticles, the fibres effectively undergo the load and were gradually removed within a normal process, i.e. fibre thinning, fibre fracture, and finally fibre peeling-off [18].

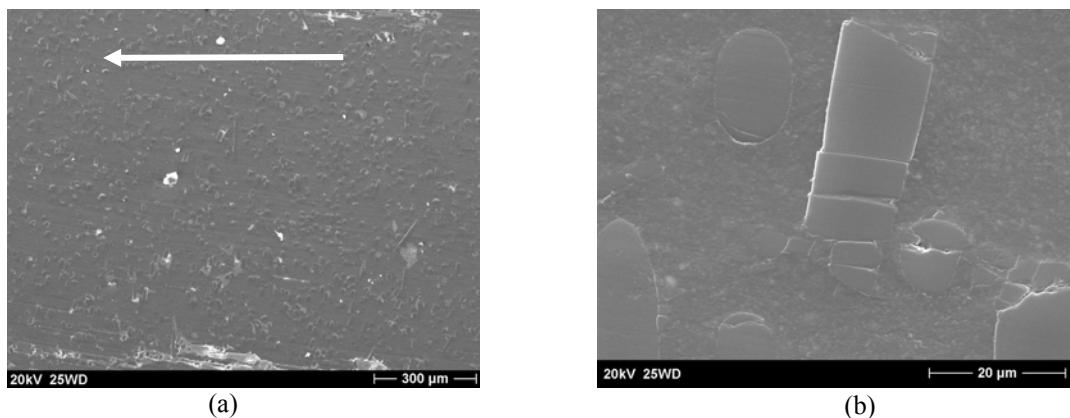
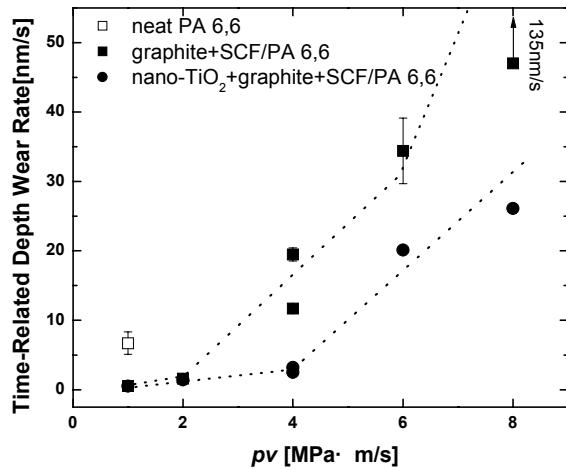


Fig. 9. (a) SEM micrographs of the worn surfaces of the composition with nanoparticles at 4MPa and 1m/s, and (b) the magnified view of fibre fracture.”



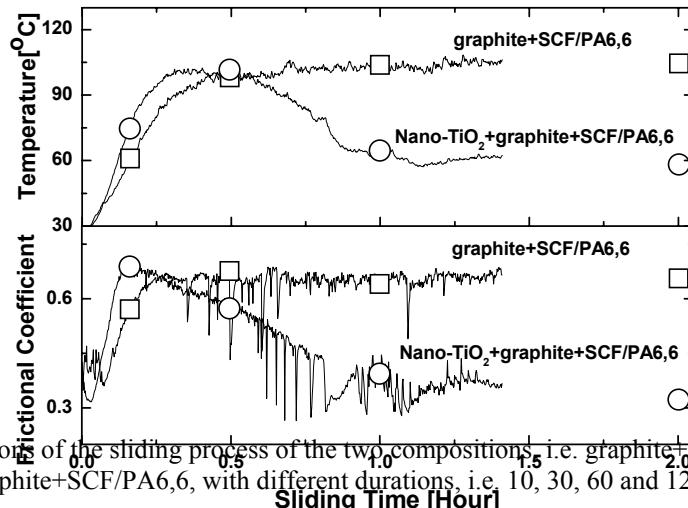
“Fig.10.The time-related depth wear rate of the composites filled with and without nano-TiO₂ as a function of pV factor.”

3.3 Time-related depth wear rate

The time-related depth wear rates calculated by Equation 1 are given in Fig. 11 as a function of the pV factor. It is clear that the basic wear factors, k^* , of the two composites at 1 MPa and 1 m/s were very close to each other. However, for the composite without nanoparticles, the slope change occurred between 2 and 4 MPa·m/s, whereas for the nanocomposite it occurred between 4 and 6 MPa·m/s. It was noticed that the slope change, i.e. “ pV limiting”, for both composites occurred when the contact temperature was around 60°C, which was in the glassy region of the PA 6,6 matrix. Therefore, even though the addition of nanoparticles little affects the value of the T_g of PA6,6 (Fig.1), the nanocomposite could be used for higher duties with lower heat generation due to the remarkable reduction of the frictional coefficient.

4. DISCUSSIONS

In order to further understand the contribution of the nano-TiO₂ during sliding process, the running-in stages of two composites were compared at various sliding durations, i.e. 10, 30, 60 and 120 minutes. Fig. 11 gives the dependence of the frictional coefficient and the contact temperature on sliding time. And the correlated worn surfaces are given in Fig. 12.



“Fig. 11. Comparison of the sliding process of the two compositions i.e. graphite+SCF/PA6,6 and nano-TiO₂+graphite+SCF/PA6,6, with different durations, i.e. 10, 30, 60 and 120 minutes.”

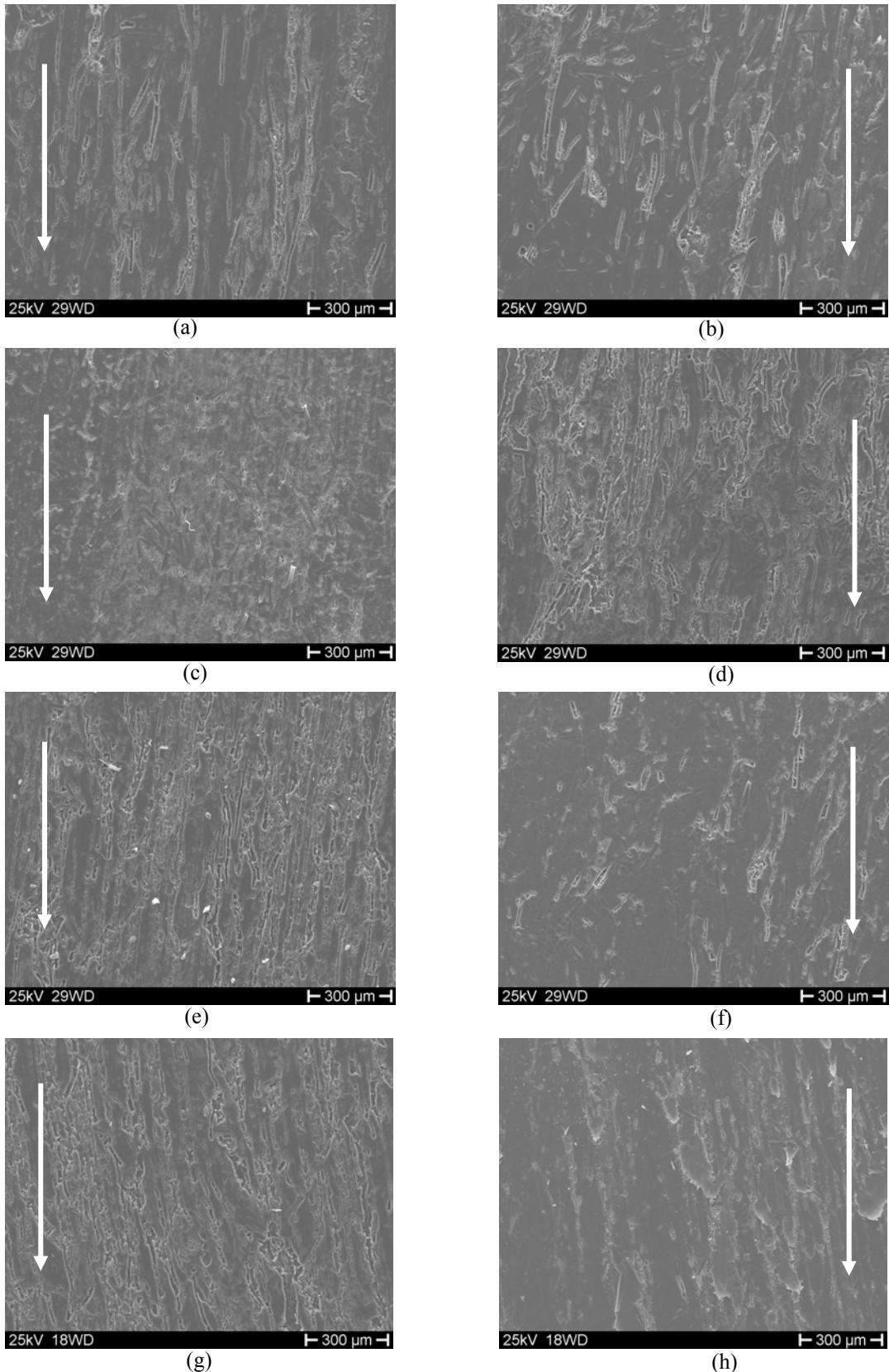


Fig. 12. Comparisons of (a) the worn surfaces of graphite+SCF/PA6,6 after 10minutes (c) 30 minutes, (e) 60 minutes (g) 120 minutes, and (b) that of graphite+SCF/PA6,6 after 10minutes (d) 30 minutes (f) 60 minutes (h) 120 minutes”

As shown in Fig. 12, the patterns of the surface damages were very well agreed to the performances of the frictional coefficient in Fig. 11 for both compositions. Both compositions

performed a similar frictional coefficient and contact temperature during first 10 minutes. Accordingly the worn surfaces are also very similar (Figs. 12a and b). After 30 minutes, both compositions reached almost the highest contact temperature. Serious fibre removals were observed consequently (Figs. 12c and d). Thereafter, the sliding process of the composition without nano-TiO₂ became stable and serious fibre removal remained (Figs. 12e and g). However, for the composition with nanoparticles, the surface became much smoother with reduced fibre broken and removal (Figs. 12f and h) due to the reduction of the frictional coefficient and the contact temperature, once the nanoparticles commenced to function.

According to the sliding processes of the two composites under various conditions (Figs. 2, 6, and 11), it can be found the reduction of friction by nanoparticles occur always after the initial wear stage, in which the stable transfer films were developed and produced adhesive mechanism. The two composites performed very similar in the running-in stages. Two possible mechanisms were assumed to account for the reduction. One is that nanoparticles were gathered and distributed on the counterpart surface during initial wear stage and then observed reduced the friction with the rolling effect combined with SCF [18]. Another assumption is that nanoparticles reduce the cohesive force by the reduction of real contact area with the presence of adhesive wear. In this case, the friction of adhesion equals the product of the real contact area and the shear strength of the plastic material depending on contact temperature [13]. With addition of nanoparticles, the real contact area was greatly reduced by three bodies contact instead of surface contact and thus resulted in a lower frictional coefficient. As a whole, the reduction of the frictional coefficient by nano-TiO₂ effectively restricts the elevation of the contact temperature, especially under extreme high *pv* conditions. This effect consequently enhances the load carrying capacity of the composite.

5. CONCLUSIONS

In the present paper, the tribological properties of nano-TiO₂ filled PA6,6 based composites, incorporated additionally with short carbon fibres and graphite flakes, were systematically studied under different sliding conditions. The following conclusions can be drawn:

1. It was found that the conventional fillers, e.g. SCF and graphite, could effectively reduce the frictional coefficient and wear rate of PA6,6 at lower *pv* condition, e.g. 1MPa and 1m/s.
2. The serious fibre removal and rapid increase of wear rate were occurred at the contact temperature increased up to the *T_g* of matrix. In comparison with short fibre reinforced epoxy composites, the wear damage in the interfacial region of fibre/PA6,6 was slight due to the ductile nature of the matrix material.
3. With the addition of nano-TiO₂, the frictional coefficient and contact temperature of the composite were further decreased, especially with very high *pv* products. As a result, the “limiting *pv*” of nanocomposite was doubly improved, although the basic wear factor *k** was little changed.
4. With further investigations at the running-in stage, it was found the fibre removal was correspondingly changed with the change of frictional coefficient. The increase of frictional coefficient caused the aggravated fibre removal and thus resulted in a higher specific wear rate.

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