JOURNAL OF MATERIALS SCIENCE **40** (2005) 2815–2821

Wear and mechanical properties of epoxy/SiO_2-TiO_2 composites

SHAO-RONG LU
College of Chemistry Xiangtan University, Xiangtan, Hunan 410005, People's Republic of China; Key Laboratory of Nonferrous Metal Materials and New Processing Technology (Institute of Guilin Technology), Ministry of Education, Guilin, Guangxi 541004, People's Republic of China
E-mail: lushaor@163.com

JING- HONGYU
Key Laboratory of Nonferrous Metal Materials and New Processing Technology (Institute of Guilin Technology), Ministry of Education, Guilin, Guangxi 541004,
People's Republic of China

HAI-LIANG ZHANG, XIA-YU WANG
College of Chemistry Xiangtan University, Xiangtan, Hunan 410005,
People's Republic of China

Preparation of epoxy/SiO_2-TiO_2 composites is investigated in this paper. The products are characterized by FT-IR spectroscopy. Results of FT-IR spectroscopy and atom force microscope (AFM) demonstrated that epoxy chains have been covalently bonded to the surface of the SiO_2-TiO_2 particles. The particles sized of SiO_2-TiO_2 are about 20–50 nm, which characterized by AFM. The properties of composites such as impact strength, flexural strength, tensile strength and ring-on-block wear are also investigated. Dry sliding wear tests showed that the SiO_2-TiO_2 particles could improve the wear resistance of the epoxy matrix even though the content of the SiO_2-TiO_2 particles was at a relatively low level (1.95–2.65 wt%). This makes it possible to develop novel type of epoxy-based materials with improved wear resistance for various applications. The worn surface was observed by scanning electron microscopy (SEM), and mechanisms for the improvement are discussed in this paper *© 2005 Springer Science + Business Media, Inc.*

1. Introduction

Epoxy resin (EP) is a thermoset resin with good thermal and environmental stability, high strength and wear resistance .In recent years, method of using nanoparticles as fillers in epoxy matrix composites to improve the tribological performance of the materials has attracted a great deal of attention from materials scientists, technologists and industrialists. Ng *et al.* dispersed TiO_2 nanoparticles in epoxy. The resultant composites not only appear to be tougher than the traditional microparticle filled epoxy but also possess higher scratch resistance [1]. Rong *et al.* also conducted tribological experiments on nano-TiO_2/epoxy composites and found that the wear performance significantly depended on the dispersion state and microstructural homogeneity of the fillers [2]. Guang *et al.* studied the sliding wear performance of epoxy composites filled with nanosized Al_2O_3 particles, which were pretreated by either silane coupling agent or graft polymerization. The experimental results indicated that the frictional coefficient and wear rate of epoxy could be reduced rather low concentration of nano-Al_2O_3. And the flexural modulus and flexural strength of epoxy were increased by the incorporation of nano-Al_2O_3particles [3]. Zhang *et al.* also investigated PAAM grafted nano-SiO_2 modifying epoxy matrix. The testing results demonstrated that grafted nano-SiO_2 reinforced composites have lower frictional property and higher wear resistance than that of the microsized silica and untreated nanosilica[4]. Through analyzing above the literature, we can see that the wear characteristic of nanocomposites is over than that of microcomposites lying in that it acquired at relative low concentration. This is beneficial to the mechanical properties, tribological application, processability and aesthetic appearance of the end-products.

However, these nanoparticles are very difficult to be uniformly dispersed in polymers because of the strong attraction between the particles and the limited shear force during compounding. Consequently, nanoparticles filled polymers usually contain a number of loosed clusters of particles, which may lead to extensive material loss as a result of disintegration and crubling of the particle agglometrates under tribological conditions. Therefore, it is necessary to explore a new method to break down nanoparticle agglometrates and to promote nanoparticle uniformly dispersed in polymers.

Based on the above analyses, SiO_2-TiO_2 nanoparticles were introduced into the epoxy matrix by grafted via sol-gel process, and the agglomerated nanoparticles are further separated. This is beneficial for enhancing filler/matrix adhesion by chemical bonding between the SiO_2-TiO_2 nanoparticles and the epoxy matrix. It is believed that SiO_2-TiO_2 nanoparticles would be tightly attached to the epoxy matrix as a result, bringing the wear resisting and friction reducing features of the SiO_2-TiO_2 nanoparticles to play.

The present paper focuses on investigating the mechanical and tribological properties of the EP/SiO_2-TiO_2 composites. The friction and wear tests using ring-block tester were carried out and the wear mechanisms were studied by scanning electron microscope (SEM) observations. The wear mechanisms were discussed basing on the obtained results. It was believed that this work would be helpful for understanding the nanoparticle filled epoxy matrix composites and for providing guidance to the tribological application of epoxy nanocomposites.

2. Experimental

2.1. Materials and measurements

Epoxy resin (diglycidyl ether of bisphenol A DGEBA(E-51),Wep = 196, purchased from Yueyang Chemical Plant, China, without further purification); 4,4′-diaminodi-phenylsulphone (DDS), from Shanghai Chemical Reagent Company, China),with a molecular mass of 248.31 and purity $> 96\%$ according to the supplier. Tetraethoxysilane (TEOS) and Tetrabutyltitanate (TBT) (Both chemical reagent grade) were ordered from Xilong Chemical Fractory, Guang dong, China).Tetraisopropyl titanate (TPT) was obtained from Dupont Co., Distilled water was used to induce the hydrolysis of the alkoxysilane or tetrabutyltitanate components using HCl as catalyst.

The impact strength was measured on a tester of type XJJ-5, with no notch in the specimen. The flexural strength and tensile strength were examined on an electron omnipotence tester RGT-5, with the flexural rate 2 $mm{\cdot}min^{-1}$, and the tensile rate 10 $mm{\cdot}min^{-1}$. All the presented results are average of five specimens. UV-Vis Spectra were measured on a shimadzu UV-265 spectrophotometer. The friction and wear tests were conducted on a ring block tester MRH-5A. The experimental parameters were rotation speed 200 $r{\cdot}min^{-1}$, load 196N and test time 2 h. All tests were carried out in dry friction state and at room temperature. The friction coefficient,μ, was calculated by the formula

$$\mathrm{II} = \frac{9.45(B + R)}{10(A + C) - 2.5(B + R)}$$

where $A = 19.6$ N, $C = 7.8$ N, B is the weight of weights exerted by the pole friction force, R is the scale reading of the free weights. The abrasion characteristic was assessed by the weight loss, W, which was calculated by the following relationship

$$W = W_1 - W_2$$

where W_1 and W_2 are respectively the weight of a sample before and after its test. They are also recorded accurately using an electronic balance after cleaning with acetone. The morphologies of the worn surfaces were observed by a JSM5610LV scanning electron microscope, which were sputter coated with a thin conducting layer of gold. Atomic force microscopy (AFM) was carried out using AJ-IIIa (Shanghai AJ Nano-Science Development Co. Ltd.). The scan rate is 2.00061 Hz, scan size 5.00061,number of sample 256.

2.2. Preparation of EP/SiO_2-TiO_2 materials precursor

About 100 g epoxy resin, 0.5 wt% 0.35 g TPT and the desired amount of TEOS were added to 250 ml three-neck, round-bottom flask equipped with a reflux condenser, a Teflon-coated magnetic stirring bar. The mixture was carried out at 130°C for 2 h, followed by addition of distilled water. The molar ratio of water to TEOS was 2:1 in all formulations. Then the reaction system was hydrolyzed and polymerized at 60–65°C for 3 h. After that, the solution was cooled to room temperature, an appropriate amount of TBT and distilled tetrahydrofuran (THF) were added by vigorous stirring for 1 h, the mixture became homogeneous. Then amount of 1 M HCl was added and the reaction was stirred continually for 1 h. And the solution was transferred into a glass mold, which was partially covered with parafilm to avoid too rapid evaporation of the solvent during the hydrolysis and sol-gel reactions. The yellow viscous liquid was obtained after one week. The recipe for the EP/SiO_2-TiO_2 hybrids sample is listed in Table I and Its chemical structure is shown in Scheme 1.

2.3. Curing procedure

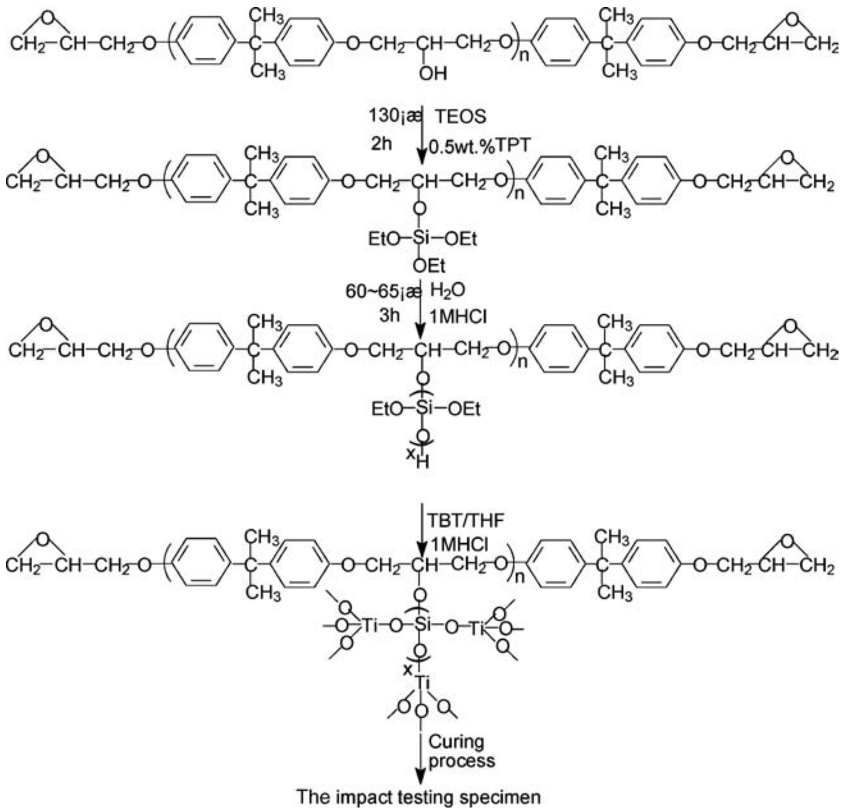
A mixture of EP/SiO_2-TiO_2 materials precursor and a stoichiometric amount of DDS (30 g per 100 g of epoxy resin) was degassed in vacuum at 130°C for about 30 min. The resulting mixture was then cast into a preheat mold coated with silicone resin. All samples were cured at 130°C for 2 h, 170°C for 2 h and 190°C for 2 h.

TABLE I Preparation recipe for the EP/SiO_2-TiO_2 Hybrids[a].

Sample	EP/g	$Si(OC_2H_5)_4$/g	$Ti(OC_4H_9)_4$/g	SiO_2-TiO_2^b/wt%
0	100	0	0	0
1	100	1.34	1.3	0.65
2	100	2.67	2.6	1.30
3	100	4.0	3.9	1.95
4	100	5.34	5.2	2.65
5	100	6.67	6.5	3.25

[a] Preparation condition: $[H_2O] + [\ Si(OC_2H_5)_4 + Ti(OC_4H_9)_4] = 1{:}1$ $[HCl] + [\ Si(OC_2H_5)_4 + Ti(OC_4H_9)_4] = 0.05$ (mol.rate).

[b] Silica and titania contents were calculated theoretically.



Scheme 1 Preparation and curing process of EP/SiO_2-TiO_2 composites.

3. Results and discussion

3.1. TT-IR analysis

Fig. 1 is the FT-IR spetra of EP, TEOS grafted EP and EP/SiO_2-TiO_2hybrid material. From Fig. 1a, we can see that the hydroxyl-stretching band of epoxy resin appears at 3507 cm^{-1} and oxirane absorption at 915 cm^{-1}. Fig. 1b showed in the case when TEOS grafted epoxy resin, hydroxyl-absorption peak of epoxy disappeared. In Fig. 1c there is the absorption peak at 3402 cm^{-1}(characteristic of –OH stretching, which is the unreactive Ti—OH or Si—OH groups in inorganic networks) and 1108 cm^{-1}(Si—O—C). And there also was the broad absorption at lower wavenumber region. Especially 1100–920 cm^{-1}(characteristic of Si—O—Si and Si—O—Ti networks) at 900–450 cm^{-1} due to Ti—O—Ti linkage in the titania matrix. The peak at 952 cm^{-1} is attributed to Si—O—Ti bonds [5].

3.2. Optical behavior of the EP/ SiO_2-TiO_2 composites films

The appearances of the EP/ SiO_2-TiO_2 composites films with different EP/SiO_2-TiO_2 contents are shown in Fig. 2. It can be seen that the transparency of the EP/ SiO_2-TiO_2 composites films are almost unchanged by the addition of the TEOS and TBT. This is because TEOS and TBT hydrolyzed to form Si—OH and Ti—OH groups that can polycondense with the hydroxyl groups of epoxy, which leads to increased compatibility with epoxy. This factor leads to smaller SiO_2-TiO_2 particles size and well dispersion of the SiO_2 and TiO_2 in the epoxy matrix.

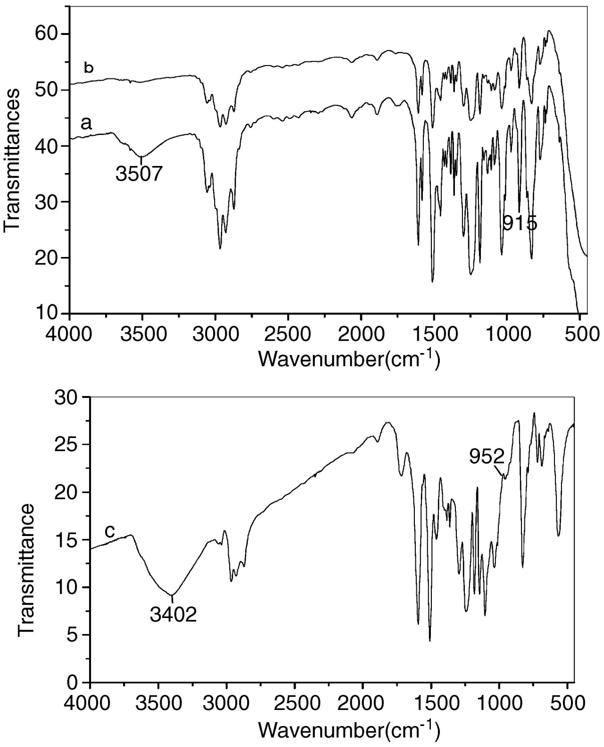


Figure 1 FT-IR spectra of EP/SiO_2—TiO_2hybrid material.

3.3. Mechanical properties and interfacial interaction

Fig. 3 shows the effect of SiO_2-TiO_2content on impact resistance of the EP/ SiO_2-TiO_2composites. It can be seen that the impact resistance increased at first and then decreased with the increase of SiO_2-TiO_2content. It reached the maximum when the SiO_2-TiO_2 content

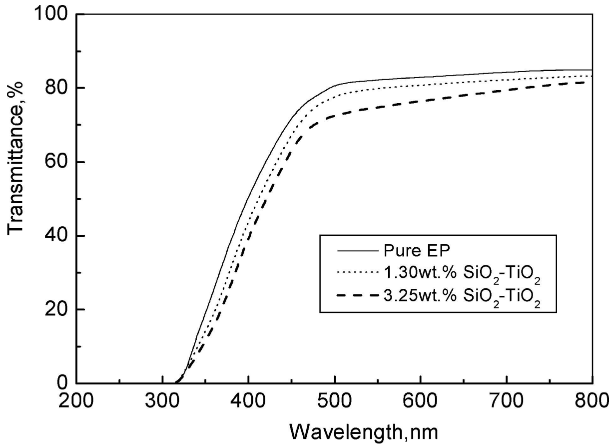


Figure 2 The transparency curves of the pure EP and EP/ SiO_2-TiO_2 composite films.

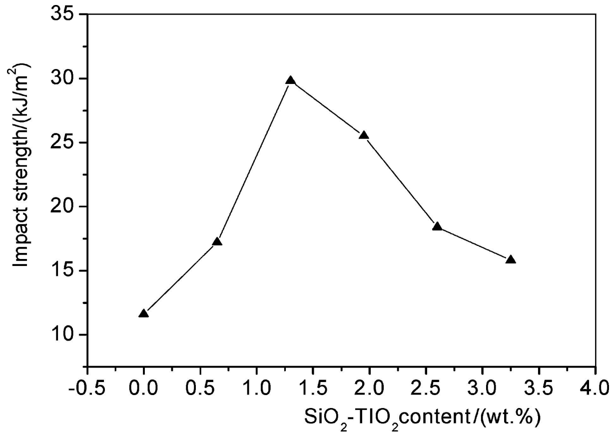


Figure 3 The relation between SiO_2-TiO_2contents and impact strengths.

was about 1.3 wt%. Since impact strength reflects the energy consumed before fracture, the results given in Fig. 3 demonstrated that the nanoparticles in the composites were able to induce plastic deformation of the surrounding matrix polymer to a certain extent under the condition of high strain rate.

The flexural strength of microparticle filled composites is known to be reduced with rising of filler content, for the bonding between the filler particles and the matrix is poor [6, 7]. If the bonding between fillers and matrix is strong enough, the yield strength of a particulate composite can be higher than that of the matrix polymer [8]. From Fig. 4, it may be seen that both flexural strength and modulus increase with SiO_2-TiO_2 content increasing. That means the interaction between nanoparticles SiO_2-TiO_2 and epoxy matrix is so strong that the nanoparticles are able to carry the applied load. The results of experiment indicated that when the SiO_2-TiO_2 content is 1.95 wt%, the flexural strength (106.2 MPa) and modulus (2.30 GPa) of the composite were 24.6 percent higher than that of epoxy resin(85.3 MPa) and 69.1 percent higher than that of the epoxy resin (1.36 GPa), respectively.

Fig. 5 shows the relation between SiO_2-TiO_2 nanoparticle content and tensile strength and modulus. The results of experiment indicated that the tensile strength curves are somewhat analogous with that of flexural strength, for the same maxima content of SiO_2-TiO_2. When SiO_2-TiO_2 content is up to 1.95 wt%, the tensile strength is almost two times as much as that of the neat epoxy resin. This is because when the material is subjected to a tensile test, the EP/SiO_2-TiO_2 hybrid materials have generated micro-phase separated for introducing of the SiO_2-TiO_2particles, which may induce epoxy matrix yielding deformation and resistance to crack propagation [9]. For this reason, the tensile energy of the epoxy matrix is expected to decrease significantly as SiO_2-TiO_2 particles are introduced, and resulted in toughening of the EP/SiO_2-TiO_2 hybrid materials enhancing.

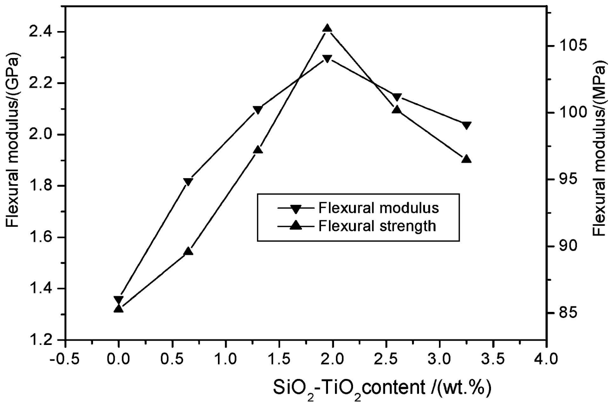


Figure 4 The relation between SiO_2-TiO_2 contents and flexural strengths, flexural modulus.

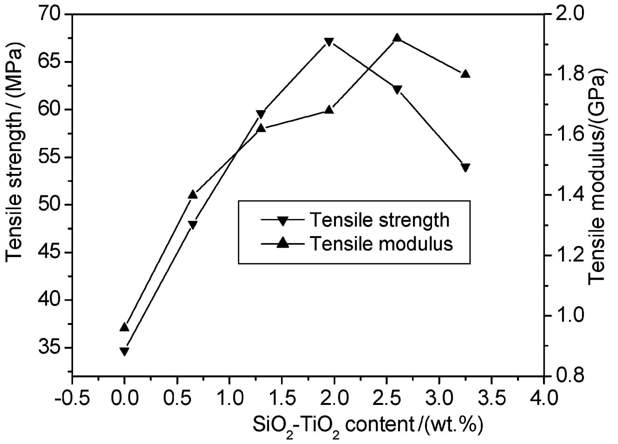


Figure 5 The relation between SiO_2-TiO_2contents and tensile strength, tensile modulus.

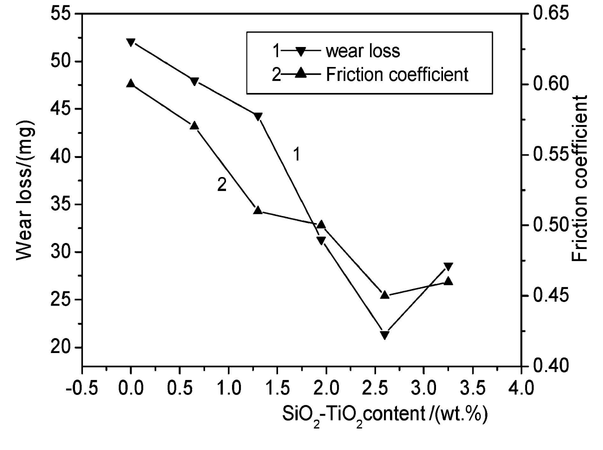


Figure 6 Effect of SiO_2-TiO_2contents on the friction coefficient and wear loss.

3.4. Friction and wear performance

Fig. 6 line1 shows the relationship between the wear loss and the SiO_2-TiO_2 content of the EP/ SiO_2-TiO_2composites. It can be seen the wear loss decreases with the increasing of the SiO_2-TiO_2 contents. It is lower by 58 percent than that of neat epoxy when SiO_2-TiO_2 content is 2.65 percent. This phenomenon indicates that the improvement of wear resistance of epoxy on the one hand grafting polymers are able to increase the interfacial interaction between nanoparticle and matrix. On the other hand, the matrix enhancement act as a result of the particles incorporation. Such reinforcing effect is strongly related with the bonding TEOS grafted epoxy and titania nanoparticles. The relationships between the friction coefficient and SiO_2-TiO_2 content are shown in Fig. 6 line 2, the trend is almost the same as that of the wear loss to the SiO_2-TiO_2 content. This may be explained by the following reasons. (1) With the incorporation of uniform sized SiO_2-TiO_2 nanoparticles into the epoxy matrix, the propagation of the cracks into the epoxy matrix was hindered to a certain degree by the SiO_2-TiO_2 nanoparticles. Furthermore, hard filler particles in a polymer matrix would reduce the wear rate in case of the applied stress less than a critical value. Both of these could contribute to reduction of the wear rate of epoxy matrix. (2) As the fillers were uniform sized SiO_2-TiO_2 nanoparticles, the greater the number of the particles on the worn surface, the larger the contact area between the particles and the wear pin, and hence the better the wear resistance offered by the SiO_2-TiO_2 nanoparticles.That might be a reason for explaining the better improvement of the wear resistance by using smaller paticles (sized 20–50 nm). (3) Under lower particle contents, the dispersion of the particles in the epoxy matrix was good enough so that the friction

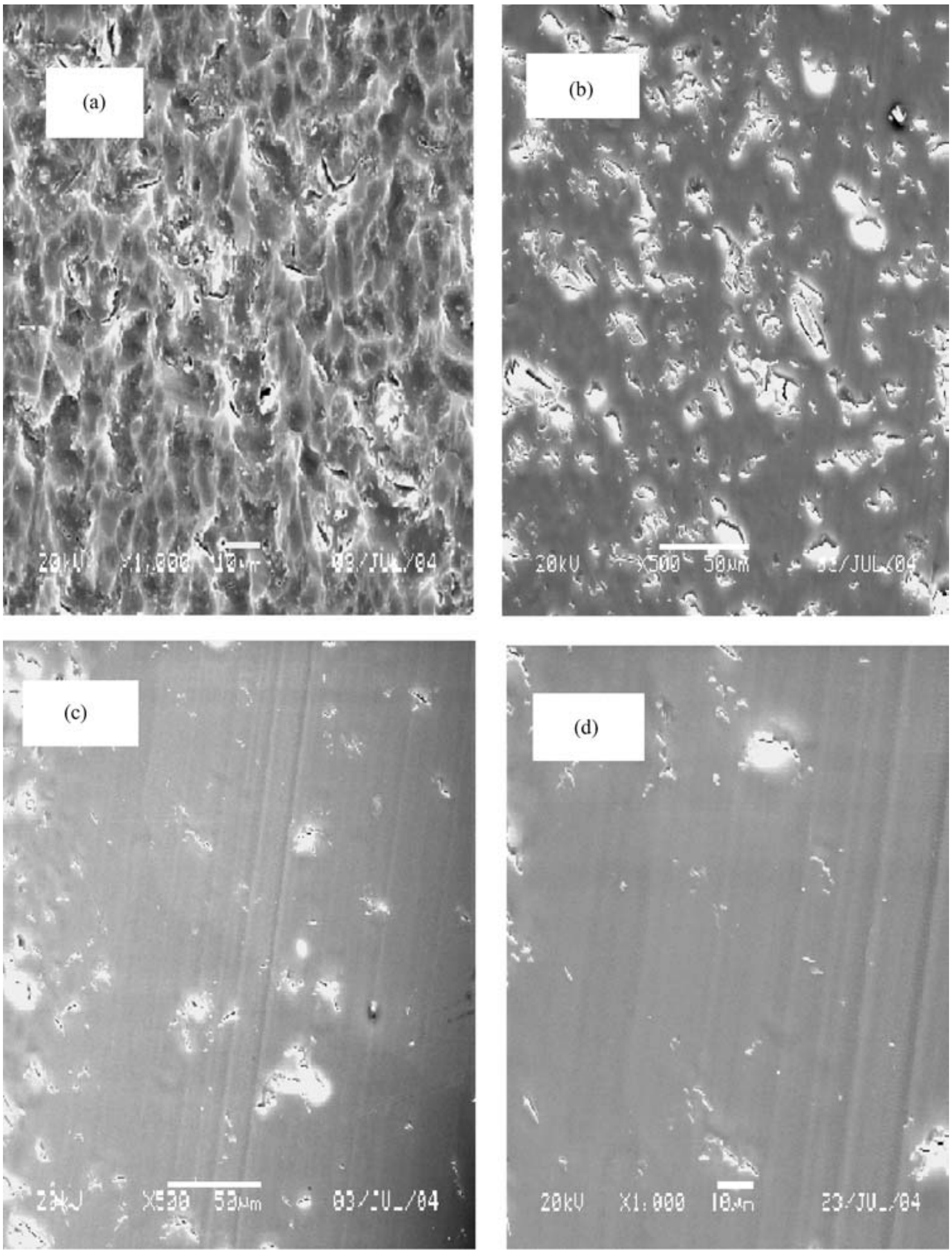


Figure 7 SEM morphology of the worn surface of (a) Pure epoxy, (b) EP/SiO_2-TiO_2 composites (1.30 wt.%), (c) EP/SiO_2-TiO_2 composites (1.95 wt.%), (d) EP/SiO_2-TiO_2 composites (2.65 wt.%).

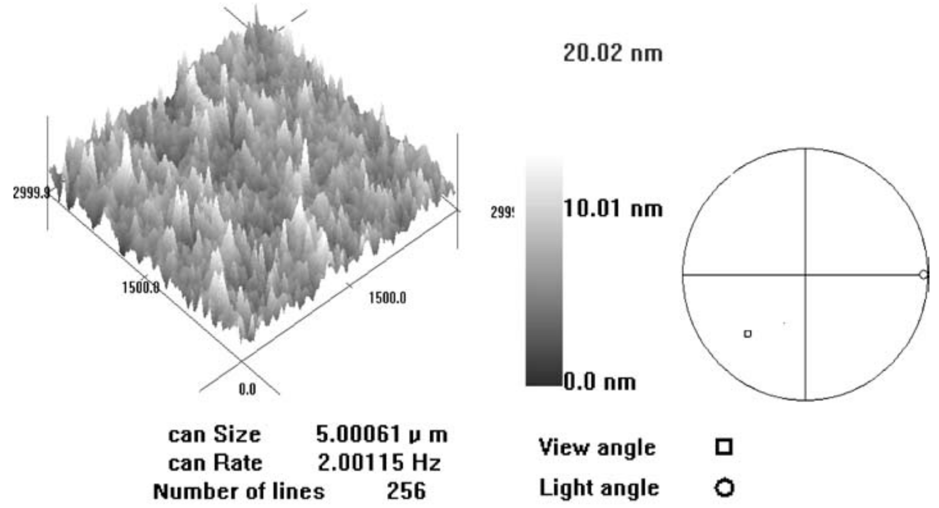


Figure 8 AFM surface images of the SiO_2-TiO_2 composite specimen,The scan area is 3 μm × 3 μm.

coefficient decreased as increasing of the particle content.

The SEM morphology of the worn surface of neat epoxy and composites are compared in Fig. 7a–d. From Fig. 7a, it can be seen that severe wear associated with the detachment of bulk material and left the traction of the harder asperity′s hole on the frictional surface. This phenomenon reflects that adhesive wear has been regarded as a main mechanism for neat epoxy. In the case of filled nanocomposites, the appearances are completely different and become rather smooth. Many small craters are quite shallow on the composites with containing of 1.30 wt% SiO_2-TiO_2 content (Fig. 7b). The reasons for the nano-fillers pulled out of the matrix, and then further moved across the surface by scratching and rolling. The resulting wear mechanism should be described as a mild abrasive wear and accompanied by fatigue wear. It is noted that some cracks across the wear tracks are perceivable on the composites'worn surface (Fig. 7c and d). They might be nuleated at subsurface layer as a result of shear deformation induced by the traction of the harder asperities. The fleet cracks damage patterns resulting from the coalescence of the cracks imply that the effect of fatigue-delamination[10] is the main wear mechanism.It can be concluded that the adhesive wear of unfilled epoxy is replaced by fatigue wear when SiO_2-TiO_2 nanoparticles are introduced. So a conclusion can be draw from the above that the wear and friction performance of nanocomposites have been greatly improved with the addition of the SiO_2-TiO_2 nanoparticles.

3.5. AFM surface image of hybrid material

The surface topography structure of the hybrid film (2.65 wt%SiO_2-TiO_2 content) is characterized by AFM (Fig. 8). The film thickness is about 20 nm, the scan area is 3 μm × 3 μm. From the micrograph, it can be seen that the SiO_2-TiO_2 particle size is about 20–50 nm, this indicates that SiO_2-TiO_2 "composite" particles is homogeneously and well disperse in the hybrid material matrix.

4. Conclusions

SiO_2-TiO_2nanoparticles can significantly improve mechanical properties of the composites, which contains an optimum amount of nanoparticles (1.3–2.6 wt%). The impact strength and tensile strength are almost 2–3 times as much as that of the pure epoxy resin.The mechanism for this improvement is ascribed to increase the interfacial strength between nanoparticles and epoxy matrix through chemical bonding. When the material is subjected to an impact test, the epoxy/SiO_2-TiO_2 composites have generated microphase separated for introducing of the SiO_2-TiO_2 particles, which may induce to crack propagation, and resulted in the performance of the epoxy/SiO_2-TiO_2 composites improved. It proves to be an effective way in lowering frictional coefficient and wear rate of epoxy composites. The results of experiment indicate that the wear mechanism of the composites changed from the adhesive wear to mild abrasive wear plus fatigue wear with the increase of the SiO_2-TiO_2content, the wear and friction performance of composites have been greatly improved with the addition of SiO_2-TiO_2nanoparticles.

Acknowledgements

Financial supports from the Natural Science Foundation of China (No.20374042), Natural Science Foundation of GuangXi province (No.0447053) are gratefully acknowledged.

References

1. C. B. NG, L. S. SCHADLER and R. W. SIEGEL, *Nanost. Mater.* **12** (1999) 507.
2. M. Z. RONG, M. Q. ZHANG, H. LIU, H. M. ZENG, B. WETZEL and K. FRIEDRICH, *Lubr Tribol.* **2** (2001) 72.
3. GUANG SHI, MING QIU ZHANG, MIN ZHI RONG, BERND WETZEL and KLAUS FRIEDRICH, *Wear* **256** (2004) 1072.
4. MING QIU ZHANG, MIN ZHIRONG, SHULIYU., BERND WETZEL and KLAUS FRIEDRICH, *Wear* **253** (2002) 1086.
5. Inorganics IR Grating Spetra, Vols, 1-2, Y249k, Sadlter Research Laboratories, Philadaphia, Sadlter, 1965.

6. L. NICOLAIS and M. NARKIS, *Polym. Eng . Sci.* **11** (1971) 194.
7. A. AHMED and F. R. JONES (Chapman & Hall, New York, 1995) pp. 1–71.
8. C. L. WU, M. Q. ZHANG, M. Z. RONG and K. FRIEDRICH, *Comp. Sci. Tech.* **62** (2002) 1357.
9. BERND WETZEL, FRANK HAUPERT and MING QIU ZHANG, *Comp. Sci. and Techn.* **63** (2003) 2055.
10. N. P. SUH, *Wear* **25** (1973) 111.

Received 17 December 2004
and accepted 25 January 2005