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Inorganic whiskers reinforced bismaleimide composites

Part II *The tribological behavior of BMI/potassium titanate composites*

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The whisker-reinforced polymer composites have good friction and wear properties and widely used in many fields. Potassium titanate ($K_2Ti_6O_{13}$) whiskers have good properties, lower prices and show good foreground in whisker-reinforced polymer matrix composites. The surface properties of the whisker are vital for the performance of the reinforced composites. In this paper, the friction and wear properties of potassium titanate whiskers reinforced bismaleimide copmposites and the surfaces of whiskers treated by coupling agents were studied. Two coupling agents, a silane compound (KH550) and a titanate (NDZ311) were selected to treat the surface of $K_2Ti_6O_{13}$ whiskers, respectively. Three whisker-reinforced BMI composites, $K_2Ti_6O_{13}$/BMI, $K_2Ti_6O_{13}$ (KH550)/BMI and $K_2Ti_6O_{13}$ (NDZ311)/BMI, were prepared and their tribological behaviors were investigated. Results show that the wear-resistance of the matrix improved by the incorporation of whiskers into the matrix, while the improvement efficiency is depended on the nature of the surface of whiskers and whisker content. The composite containing KH550 treated whiskers has the best wear-resistance, and that containing untreated whiskers has the poorest wear-resistance among the three composites. Experiment results were explained from the point of the interfacial adhesion between the matrix and whiskers as well as the surface morphologies of worn surface and wear particles of the matrix and composites.

1. Introduction

Nowadays, there are an increasing number of applications in which friction and wear are critical issues [1]. Polymer composites containing different fillers and/or reinforcements are frequently used for these purposes [2–5]. And it is now widely recognized that friction and wear properties of some polymers may be significantly improved by filling them with inorganic compounds.

For designing the composites of wear-resistant polymer composites, the matrix should possess a high temperature resistance and have a high cohesive strength [1]. Epoxy, polyester and phenolic resins have been used as the matrix to prepare friction and wear materials for many years. However, in order to further increase wear-resistance, the matrix with high thermal resistance is needed. Bismaleimide (BMI) is one of most important high performance thermosets that have been widely used in many related industries where high performance properties are required [7–9]. Well, pure BMI is brittle and has poor processing characteristics, so many modified BMI systems have been developed. A system made up of 4,4′-bismaleimidodiphenyl methane (BDM) and o, o′-diallyl bisphenol A (DBA), BDM/DBA, has been proved to be a good matrix for advanced composites [10, 11], therefore, the system was chosen as the base matrix in this paper.

Recently, inorganic whiskers reinforced polymer composites have attracted considerable attention of many investigators because whiskers exhibit high stiffness and strength, and they are nearly free from internal flaws owing to their small diameter, hence the yield strength of whiskers tends to approach the maximum

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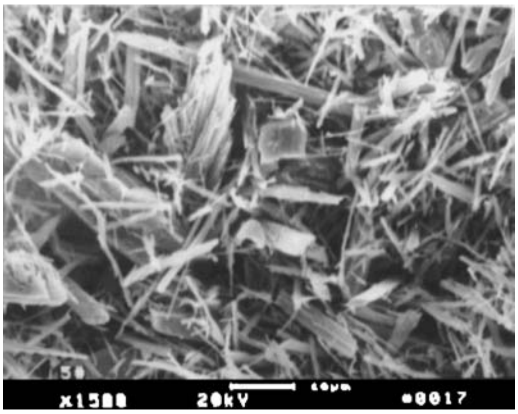


Figure 1 SEM micrograph of the $K_2Ti_6O_{13}$ whisker.

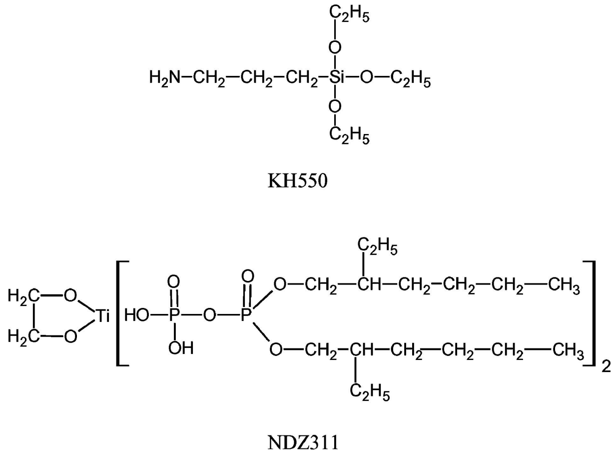


Figure 2 The chemical formulae of KH550 and NDZ311.

theoretical value expected from the theory of elasticity [12–15]. Potassium titanate ($K_2Ti_6O_{13}$) whiskers have been an ingredient of great interest during past decades due to its thermal stability and good compatibility with binder resins. The $K_2Ti_6O_{13}$ whiskers consist of fine ceramic poly-crystalline whiskers and have tunneling structures with relatively high modulus and strength. These whiskers are white acicular in appearance and have the chemical formula of $K_2O{\cdot}6TiO_2$, and their diameter and length are 0.8–1.2 μm and 30–50 μm in average, respectively. The SEM micrograph of $K_2Ti_6O_{13}$ whiskers is showed in Fig. 1. Furthermore, $K_2Ti_6O_{13}$ whiskers have outstanding friction and wear properties as well as self∼lubrication [16]. One of most important features is that $K_2Ti_6O_{13}$ whiskers are the only whiskers that have achieved breakthrough in commercial use [17].

The surface treatments of whisker are important for the properties of the whisker-reinforced polymer composites. Two coupling agents, a silane compound (KH550) and a titanate (NDZ311) were selected to treat the surface of $K_2Ti_6O_{13}$ whiskers in this paper, and one whisker-reinforced BMI composite and two treated whisker-reinforced BMI composites were prepared and the tribological behaviors of these composites were investigated.

2. Experimental

2.1. Materials

4,4′-bismaleimidodiphenyl methane (BDM) (mp156–158°C) is provided by Northwestern Chemical Engineering Institute (China), o,o′-diallyl bisphenol A (DBA) is purchased from Sichuan Jiangyou Chemical Factory (China). $K_2Ti_6O_{13}$ whiskers were kindly supplied by Qihai Haixing Science and Technology Development Ltd. (China). A silane compound KH 550 and titanate (NDZ311) were bought from Nanjing Shuguang Chemical Factory (China), and the chemical formulae of these two coupling agents are showed in Fig. 2. Acetone was bought from Xi'an Chemical Factory (China). All the materials involved in this work are of industrial grades and used as received without any further purification.

2.2. Surface treatment of whiskers

$K_2Ti_6O_{13}$ whiskers were dried at 105–110°C, then added into appreciated quantities of acetone solution of KH550 or NDZ311 with thoroughly stirring to form homogenous whisker solution. After that evaporated the solvent at room temperature for 8 h, subsequently dried at 80–90°C for 2 h, the resultant whiskers were coded as $K_2Ti_6O_{13}$ (KH550) or $K_2Ti_6O_{13}$ (NDZ311), respectively.

2.3. Preparation of neat BMI resin (the matrix)

100 g BDM and 80 g DBA were placed in a flask equipped with a mechanical stirrer and thermometer. The mixture was heated to 110–130°C for 20 min, and then was degassed in a vacuum oven at 120°C for 15 min. After that, the mixture was cast into the glass mould for curing and postcuring per following procedures:

$$\text{Curing: } 145^\circ\text{C}/2\text{ h} + 160^\circ\text{C}/2\text{ h} + 180^\circ\text{C}/2\text{ h} + 200^\circ\text{C}/2\text{ h}$$

$$\text{Postcuring: } 220^\circ\text{C}/8\text{ h.}$$

2.4. Preparation of BMI/ $K_2Ti_6O_{13}$ composites

100 g BDM and 80 g DBA were placed in a flask equipped with a mechanical stirrer and thermometer. The mixture was heated to 110–130°C for 20 min, then pre-weighted $K_2Ti_6O_{13}$ whiskers were added into the mixture with thoroughly stirring. Thereafter the mixture was degassed in a vacuum oven at 120°C for 15 min and cast into the glass mould for curing and postcuring per the procedures described above. The obtained composite was coded as BMI/$K_2Ti_6O_{13}$. The SEM micrograph of the composite is showed in Fig. 3, from which we can see the distribution of the whisker in the matrix instead of the whisker agglomerate together.

Other two kinds composites were prepared by similar method described above except the employed whiskers were $K_2Ti_6O_{13}$ (KH550) or $K_2Ti_6O_{13}$ (NDZ311), respectively, then the resultant composites were

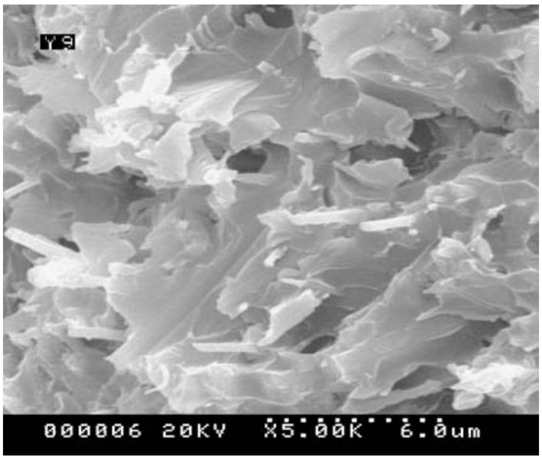


Figure 3 The SEM micrograph of $BMI/K_2Ti_6O_{13}$ composite.

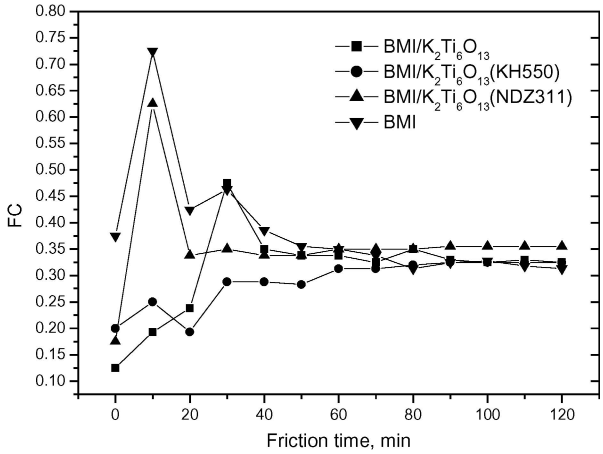


Figure 4 Dependence of friction coefficient (FC) of three BMI/ $K_2Ti_6O_{13}$ composites and the matrix on friction time.

designed as $BMI/K_2Ti_6O_{13}$ (KH550) or $BMI/K_2Ti_6O_{13}$ (NDZ311), respectively.

2.5. Measurements

Tribologiacl properties were tested by Chinese standard of GB3960-83 "Test method for friction and wear of plastics by sliding". Pin-on-disk sliding wear test and "MM-200" machine were used in the test. The accuracy of the machine can achieve 5% in measuring the frictional force and wear loss.

The couple is 45# steel and has the outer and inner diameters are 45 and 16 mm, respectively. The length of the couple is 10 mm. The outer surface of the couple was polished by silicon carbide and obtains surface roughness of 0.08–0.12 μm before the test.

The dimension of the specimen was $30 \times 7 \times 6\ mm^3$ and the surface was washed by acetone and also polished by silicon carbide and obtained the same surface roughness as that of the couple.

During the test, the upper rotate axis is keeping still and the lower rotate axis has the rotate speed of 0.24 m/s. The applied load is about 196 N, and the wear test is keeping for 2 hrs.

HITACHI S-570 SEM (Japan) was used to observe the worn surfaces and wear particles of the matrix and composites. The microstructure of the whisker-reinforced BMI composites was also observed.

3. Results and discussion

3.1. Effects of coupling agents

The stable friction coefficient is strongly dependent on the initial surface roughness of both sliding pairs. Before the test, all the surfaces of the matrix and the three BMI/ $K_2Ti_6O_{13}$ composites are polished by silicon carbide and obtained almost the similar roughness. The surface of the counterpart is finished according to the requirement of test standard.

Fig. 4 shows the dependence of friction coefficient (FC) of the matrix and three BMI/ $K_2Ti_6O_{13}$ composites on friction time. Apparently, all composites have better friction stability than the matrix. $BMI/K_2Ti_6O_{13}$ (NDZ311) has the best friction stability among the three composites, which has the shortest sliding time (20 min) to achieve stable FC. The time of friction stability of $BMI/K_2Ti_6O_{13}$ (KH550), $BMI/K_2Ti_6O_{13}$ and the matrix are 60, 70, and 80 min, respectively. Note that although $BMI/K_2Ti_6O_{13}$ (NDZ311) has the shortest sliding time to reach friction stability, but it has highest stable FC, and $BMI/K_2Ti_6O_{13}$ (KH550) has the lowest stable FC, so $BMI//K_2Ti_6O_{13}$ (KH550) has the best wear-resistance. Results from Fig. 4 suggest that the surface treatment of whiskers influences the tribological behavior of BMI/ $K_2Ti_6O_{13}$ composites, which could be further seen from other friction characteristics such as wear width and wear rate as shown in Table I. For all composites, they have much narrower wear width and smaller wear rate than the matrix, indicating that the addition of whiskers into the matrix effectively improve the wear-resistance of the matrix. For example, the wear rate of the matrix is $4.39 \times 10^{-6}\ mm^3/Nm^{-1}$, and those of $BMI/K_2Ti_6O_{13}$ (KH550), $BMI/K_2Ti_6O_{13}$ (NDZ311), and $BMI/K_2Ti_6O_{13}$ are 1.03, 1.40, and 1.62, respectively, which are about 23.5, 31.9, and 35.9% of that of the matrix, respectively.

The effect of different surface treatments for whiskers on the tribologcal properties of composites is due to the difference of interfacial adhesion between whiskers and the matrix. In case of KH550, it has $-NH_2$ groups, which can be reacted with imide groups in BMI resin. Meanwhile, $-OC_2H_5$ groups in KH550 molecular can react with $-OH$ groups in whiskers [18]. For NDZ311, no active groups exist in its molecular structure, its interaction with BMI resin only results from the physical tangle of hydrocarbon links of them, while the interaction of NDZ311 with whiskers comes from the physical absorption of titanium atoms in both NDZ311 and whiskers. Obviously, the interactions of KH550

TABLE I Friction properties of composites containing 5 wt% whiskers

Sample	FC	Wear width (mm)	Wear rate $\times 10^{-6} mm^3 (N \cdot m)^{-1}$
Matrix	0.322	4.51	4.39
$BMI/K_2Ti_6O_{13}$ (KH550)	0.322	2.76	1.03
$BMI/K_2Ti_6O_{13}$ (NDZ311)	0.351	3.06	1.40
$BMI/K_2Ti_6O_{13}$	0.331	3.19	1.62

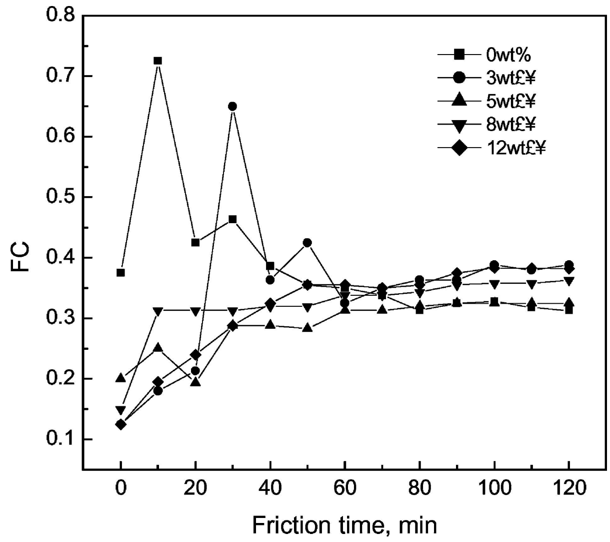


Figure 5 Variation of FC with whiskers content for BMI/ $K_2Ti_6O_{13}$ (KH550) composites.

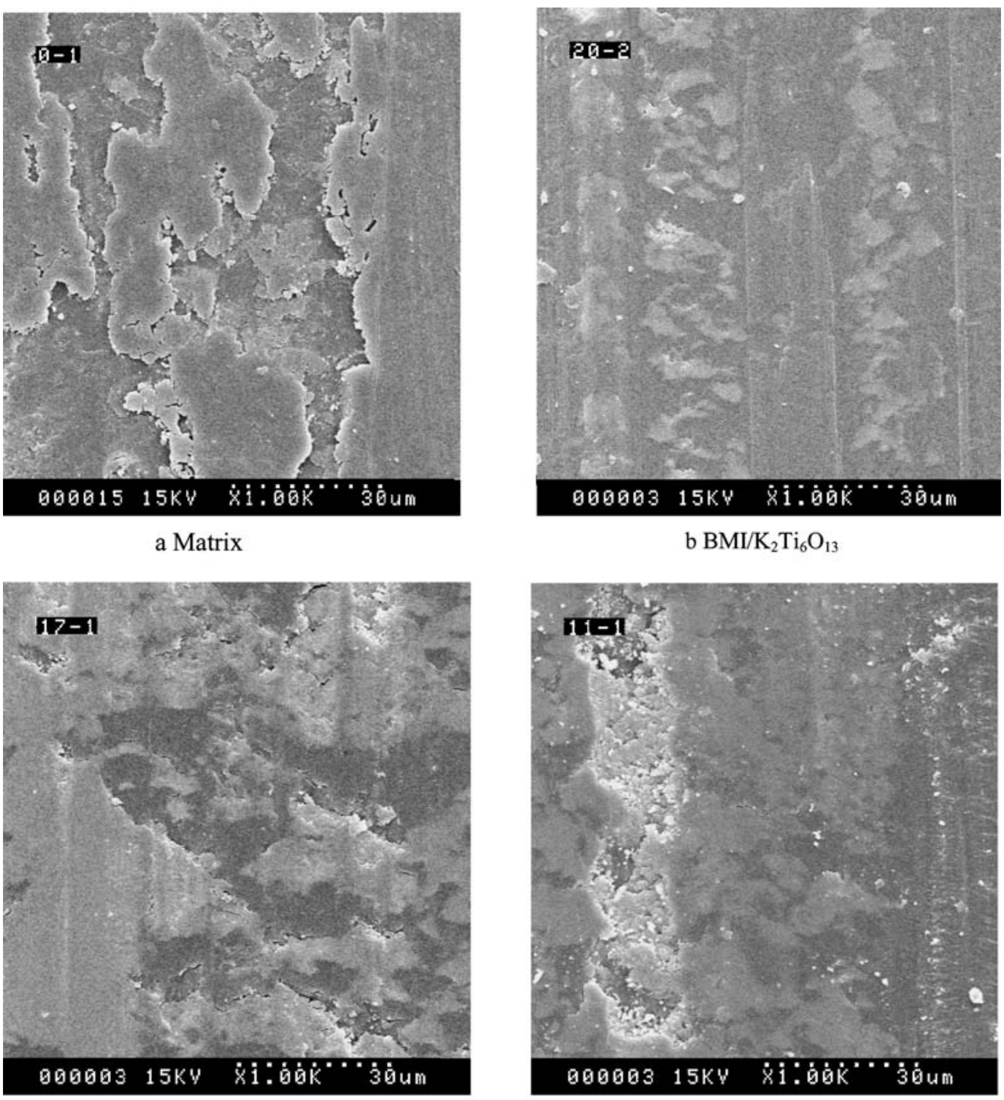
with the matrix and whiskers are stronger than that of NDZ311 with the matrix and whiskers. Good interfacial adhesion is beneficial to form well-developed durable friction film, which in turn improve the wear-resistance of composites. Further discussion on this point is done in the later part of the paper.

TABLE II $K_2Ti_6O_{13}$ (KH550) whisker content on friction properties of BMI/ $K_2Ti_6O_{13}$ (KH550) composites

Whisker content (wt%)	FC	Wear width (mm)	Wear rate $\times 10^{-6}$ mm^3 (N · m)$^{-1}$
0	0.322	4.51	4.39
3	0.372	3.37	1.77
5	0.322	2.76	1.03
8	0.352	2.83	1.10
12	0.382	2.82	1.08

3.2. Effect of whisker content on friction property of composites

Fig. 5 shows the variation of FC with whiskers content for BMI/$K_2Ti_6O_{13}$ (KH550) composites, it also can be seen that composites have better friction stability than the matrix. Moreover, small whiskers content (3 wt%) could greatly improve the friction stability of the matrix, which could also be concluded from other typical friction properties summarized in Table II. Table II



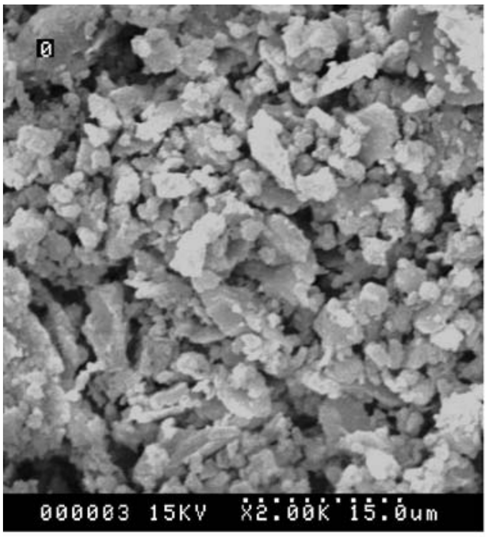
a Matrix

b BMI/$K_2Ti_6O_{13}$

c BMI/$K_2Ti_6O_{13}$ (KH550)

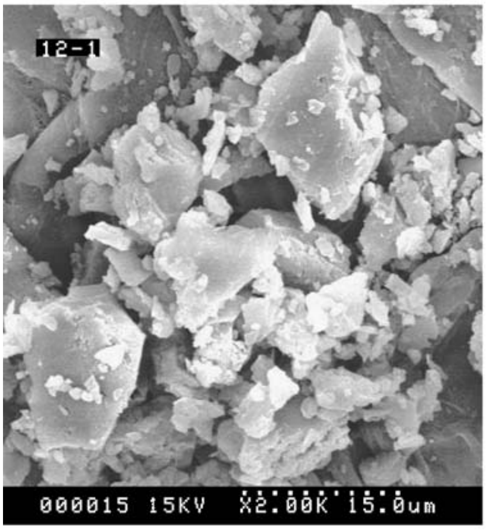
d BMI/$K_2Ti_6O_{13}$ (NDZ311)

Figure 6 Worn surface of the matrix and composites containing 5 wt% whiskers.

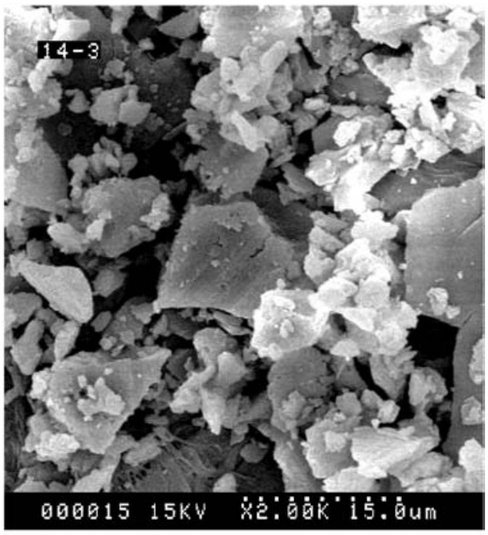


a matrix

b BMI/$K_2Ti_6O_{13}$



c BMI/$K_2Ti_6O_{13}$ (NDZ311)



d BMI/$K_2Ti_6O_{13}$ (KH550)

Figure 7 SEM micrographs of wear particles (each composite contains 5 wt% whiskers).

also suggested that there exists an optimum whiskers content to get the optimum friction properties. For example, the wear rate of composites with 3 wt%, 5 wt% whiskers are 40.3%, 23.3% of that of the matrix, respectively. Further increases the whisker content up to 8 wt% or 12 wt%, the wear rate slightly increases and nearly remains constant.

3.3. Surface morphology

Fig. 6 shows worn surfaces of the matrix and composites after friction test. The incorporation of whiskers into the matrix tends to smoothen friction surface, indicating that the importance of whiskers for building durable friction films, which resulting in lower frictional force and higher wear resistance. Fig. 4 shows that composites have better steady FC than the matrix because the well-developed friction films provided improved mechanical strength to the friction film, resulting in a steady FC during sliding tests. The rubbing surface of the matrix showed small wearing particles. On the other hand, some larger wear debris in the shape of plates might appear in all composites. Above expectation from surface morphology of the rubbing surfaces could be proved by the scanning electron microscope (SEM) micrographs of wear particles collected during the friction tests, as shown in Fig. 7.

4. Conclusion

One $K_2Ti_6O_{13}$ whiskers reinforced BMI composite and two surface treated $K_2Ti_6O_{13}$ whiskers reinforced BMI composites were prepared, and their typical tribological properties were investigated. Results show that the incorporation of whiskers into the matrix effectively improves wear-resistance of the matrix, and the improvement efficiency depends on the nature of the surface of the whiskers contained in the composites, $K_2Ti_6O_{13}$ (KH550) whiskers are more effective in the improvement of wear-resistance than $K_2Ti_6O_{13}$ (NDZ311) whiskers, and the latter is better than untreated $K_2Ti_6O_{13}$ whiskers. The positive effect from whiskers is attributed to the stable and durable friction film, and the improvement in efficiency in wear-resistance is based on the interfacial adhesion between the matrix and whiskers.

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References
1. K. FRIEDRICH, R. REINICKE and Z. ZHANG, in Proceedings of the Institution of Mechanical Engineers, Part J: *Journal of Engineering Tribology* **21** (2002) 415.
2. S. BAHADUR and DELI GONG, *Wear Mater.: Intern. Conf. Wear Mater.* **1** (1991) 177.
3. C. J. SCHWARTZ and S. BAHADUR, *Wear* **250/251** (2001) 1532.
4. T. C. OVAERT, *Tribol. Trans.* **38** (1995) 27.
5. J. HANCHI and N. S. JR. EISS, *Wear* **203/204** (1997) 380.
6. H. D. STENZENBERGER, W. ROMER, M. HERZOG, P. KONIG and K. FEAR, in "Materials and Processing-Move into the 90's," edited by S. Benson, T. Cook, E. Trewin and R. M. Turner (Elsevier Science Publishers B.V., Amsterdam, 1989) p. 277.
7. GUOZHENG LIANG and AIJUAN GU, in "Bismaleimides" (Chemical Industry Press, Beijing, 1997) p. 12.
8. AIJUAN GU and GUOZHENG LIANG, *Polym. Comp.* **18** (1997) 151.
9. TAKAO IIJIMA, HIDEHIKO SHIONO, WAKICHI FUKUDA and MASAO TOMOI, *J. Appl. Polym. Sci.* **65** (1997) 1349.
10. M. CHAUDHARI, T. GALVIN and J. KING, *National SAMPE Symp. Exhibit.* (Proceedings) **30** (1985) 735.
11. L GUOZHENG, G. AIJUAN and L. LIWEN, *J. Adv. Mater.* **27** (1996) 61.
12. T. H. COURTNEY, in "Mechanical Behavior of Materials" (McGraw Hill, Newyork, 1990) p. 83.
13. LIQUN ZHANG, SHEMAO WU, YUXING FENG, WEI FENG, HONGYI YANG and AN LI, *Hecheng Xiangjiao Gongye/China Synthetic Rubber Industry* **21** (1998) 261 (in Chinese).
14. Y. XU, D. D. L. CHUNG and C. MROZ, *Comp.—Part A: Appl. Sci. Manuf.* **32** (2001) 1749.
15. L. P. ANDERS and B. HANS, *Polymer* **39** (1998) 4183.
16. X. FEBG and JZ. LV, "Application of Potassium Titanate Whisker in Composite," *ACTA Materiae Compositae Sinica* **16** (1999) 1 (in Chinese).
17. JIAZHEN LU and XIAOHUA LU, *J. Appl. Polym. Sci.* **82** (2001) 368.
18. TJ LV and XL. WEI *Engng. Plast. Appl.* **23** (1995) 5 (in Chinese).

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