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Tribological Properties of Porous PPS/PTFE Composite Filled with Mesopore Titanium Oxide Whisker

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ABSTRACT: Nano-micro hierarchical porous polyphenylene sulfide/polytetrafluoroethylene (PPS/PTFE) composites were prepared by mold-leaching and vacuum melting process under high temperature condition. The tribological behaviors of porous PPS/PTFE composites and the synergism as a result of incorporation of both micro-porogen (NaCl) and mesoporous TiO_2 whiskers were investigated. The effects of mesoporous TiO_2 whiskers and nonperforated TiO_2 whiskers on the friction and wear properties of PPS/PTFE composites were comparatively studied, respectively. Results indicated that the wear rate of porous PPS/PTFE composites with 30 wt % NaCl and 7 wt % mesoporous TiO_2 whiskers obtained the lowest values under the load of 100 N. Compared with pure PPS, the wear resistance of nano-micro porous PPS/PTFE composite was enhanced by 6.45×10^3 times, showing outstanding wear resistance. During sliding condition, grease could be squeezed through the nano-micro pores under the coupling effect of load and friction heat, and formed a lubricanting layer on friction surface, providing self-lubricating effect and high wear resistance. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 129: 2321–2327, 2013

KEYWORDS: composites; friction; wear and lubrication; porous

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INTRODUCTION

Polyphenylene sulfide (PPS) is an attractive engineering thermoplastic that is widely used in practice due to its excellent properties such as chemical resistance, dimensional stability, and outstanding mechanical properties.[1–3] However, owing to its high friction coefficient and wear rate, pure PPS and it's composites are rarely used for tribo-materials in industry. Therefore, many attempting researches on the enhancement of tribological properties of PPS has been reported with the addition of various inorganic fillers.[4–6]

Among the numerous inorganic fillers, whiskers have been widely used as promising reinforcement and tribological improvement of polymer.[7,8] Titanium oxide (TiO_2) whisker as a sort of needle like form with TiO_2 element, were studied in many fields, such as used as reinforcement for the ceramics, biomedical realms, and catalyst supports.[9–11] Mesoporous TiO_2 whiskers can offer large surface areas and proper nano-scale channels which are able to absorb significant volumes of the liquid. However, to the best of our knowledge, no study has been carried out on hierarchical porous PPS for tribological applications by far. Therefore, it may be a feasible way to compound mesoporous TiO_2 whiskers into porous PPS composite to achieve synergistic improvement in tribological properties.

In this study, an attempt has been made to develop an effective processing technique and evaluate the feasibility of using NaCl, mesoporous titanium oxide whisker or nonperforated titanium oxide whisker as fillers for porous PPS/polytetrafluoroethylene (PTFE) composites. The aim of this work is to develop a preparation method for a new self-lubricating material—hierarchical porous PPS/PTFE material impregnated with lithium-base grease and to study their tribological properties.

MATERIALS AND DETAILS

Materials and Preparation of the Porous PPS Composites

In this article, PTFE was used as a solid lubricant in PPS matrix, owning to its characteristic of low friction coefficient, to improve the tribological properties of PPS composites.[12] The fraction of PTFE (commercial product of Dupont) was set as 10 wt %. PPS powder in 150-mesh size (supplied by Yuyao Degao Plastic Technology, Zhejiang, China), was used as the polymer matrix. Sodium chloride (NaCl) was seived, which plays the role of micro-scale pore-forming agent, the fraction of NaCl (140 mesh) was set as 30 wt %. Mesopore titanium oxide whisker (M-TiO_2-W) and nonperforated titanium oxide whisker (N-TiO_2-W) were used as nano-scale porogen for PPS, which are supported by Nanjing University of Technology (Nanjing, China).

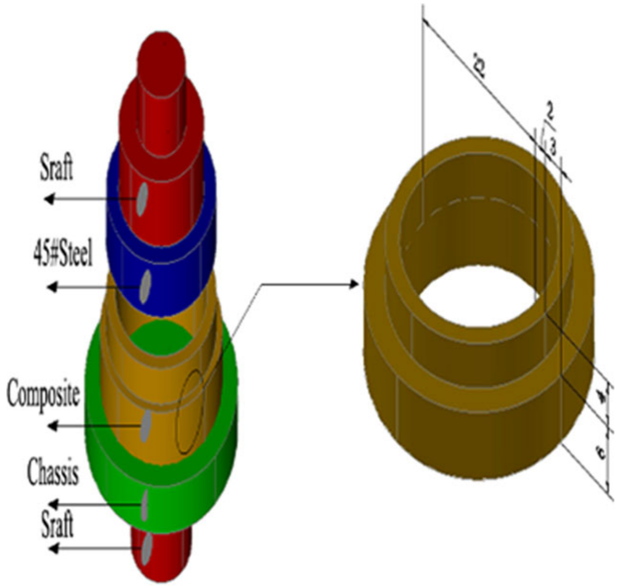

Figure 1. The schematic diagram of the wear tester and sample structure. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The PPS powder, NaCl and TiO_2 whiskers were dried at 120°C for 4 h, and then mixed mechanically. The samples were produced by cold molding in a press mold, then sintering. Finally, the samples were cut into a shape with an external diameter of 32 mm, an inner diameter of 22 mm, and a shoulder height of 2.5–4 mm. The samples were immersed in water bath maintained at 80°C for 2 h, and then NaCl was dissolved by deionized water. Washing times were determined by weight loss before and after washing until there was no further decrease. The leaching out of the NaCl from the polymer material leads to the creation of pores and channels. After leaching, the porous samples were dried by maintaining them at 100°C in a oven for about 8 h. Finally, the porous structure composite was filled with lithium-base grease at 120°C for 2 h under vacuum condition of 0.01–0.2 bar.

Friction and Wear Tests

The friction and wear tests were carried out on an MPX-2000 friction and wear tester (Xuanhua Testing Factory, Hebei, China). Sliding experiments were performed in the ring-on-ring configuration, shown in Figure 1. The tests were conducted under ambient conditions with sliding speeds of 1.40 m/s and normal loads of 100 N and 200 N. The friction duration was 120 min. Before each test, the specimen and counterpart ring were polished to an average roughness of 0.15–0.3 μm with 1000-grit SiC abrasive paper and cleaned with acetone. The samples were put into an oven at 135°C for 8 h before they were weighed. The computer recorded the frictional torque data once a second, and the friction coefficient was taken as the average value of the last 60 min. The specific wear rate [Wr (m^3/Nm)] was calculated with the following equation:

$$\mathrm{Wr} = \frac{\Delta m}{L \cdot \rho \cdot F_N} \tag{1}$$

where Δm is the mass loss (g), L is the sliding distance (m), ρ is the density of the composite (g/cm^3), and F_N is the normal load (N).

In this work, friction and wear tests were repeated three times to minimize data scattering, and the average value was reported. The microstructure of the cross-section, worn surface, and counterpart surface were investigated with a Quanta 200 scanning electron microscope (SEM; FEI, Eindhoven, Netherlands).

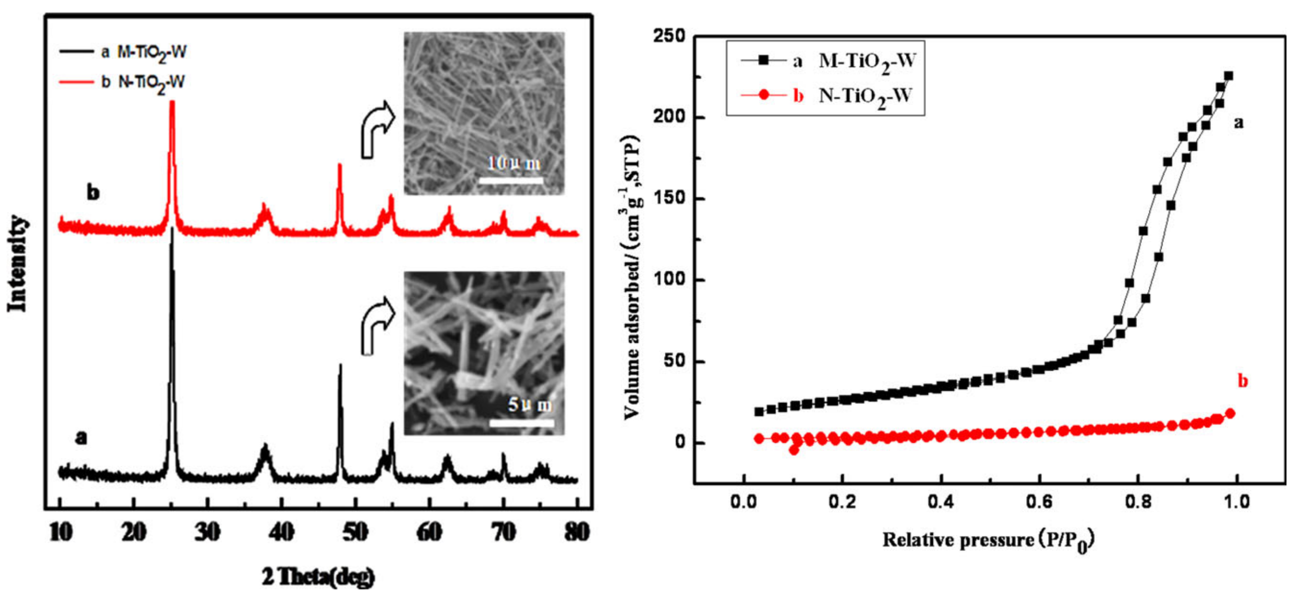

Figure 2. XRD, BET results of two types of TiO_2 whiskers, inset is SEM micrograph. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table I. Specific Surface Area and Average Pore Size of TiO_2 Whiskers

Samples	Specific surface area (m^2/g)	Pore volume (m^3/g)	Pore diameter (nm)
N-TiO_2-W	13	0.02	-
M-TiO_2-W	96	0.35	11.2

Temperatures in the friction zone were measured by infrared digital thermometer.

RESULTS AND DISSCUSSION

The Properties of TiO_2 Whiskers

Figure 2 shows the X-ray diffraction pattern, BET results and SEM micrographs of the two TiO_2 whiskers. It can be seen that the diffraction peaks of TiO_2 whiskers are completely consistent with the characteristic diffraction peaks of anatase TiO_2.[13] Meanwhile there is no diffraction peaks of other crystalline TiO_2 or other substances. Therefore, the mesoporous titania whiskers (M-TiO_2-W) and nonporous titanium whiskers (N-TiO_2-W) are mainly anatase TiO_2. It also can be seen that the two whiskers exhibit well-defined separated fibrous morphology.[14]

As listed in Table I, the pore structure parameters of the samples such as the surface area, pore size and pore volume are determined from BET results [Figure 2(b)]. M-TiO_2-W showed typical IUPAC(II) type adsorption characteristics, with a significant hysteresis loop. This proved that the obtained M-TiO_2-W is a mesoporous material. The average diameter of pores is 11.2 nm.

The Tribological Properties of Porous PPS/PTFE Composites

The Effect of Different TiO_2 Whiskers on the Friction and Wear Properties of Porous PPS/PTFE Composites. Figures 3 and 4 show the effect of different whiskers on the tribological properties of porous PPS/PTFE composite filled with mesoporous and nonperforated TiO_2 whiskers under the load of 100 N. It is clear that the wear rates decrease first and then increase with the increasing content of TiO_2 whisker. The wear rate of porous PPS/PTFE composites filled with M-TiO_2-W is lower than that of N-TiO_2-W. These nano-micro multiscale pores can store grease as lubricant. Table III also indicates that the porosity and grease adsorption of M-TiO_2-W filled porous PPS/PTFE composite are higher than those of N-TiO_2-W filled composite. Therefore, higher three-dimensional connected network may be formed inside the M-TiO_2-W filled porous PPS/PTFE composite.

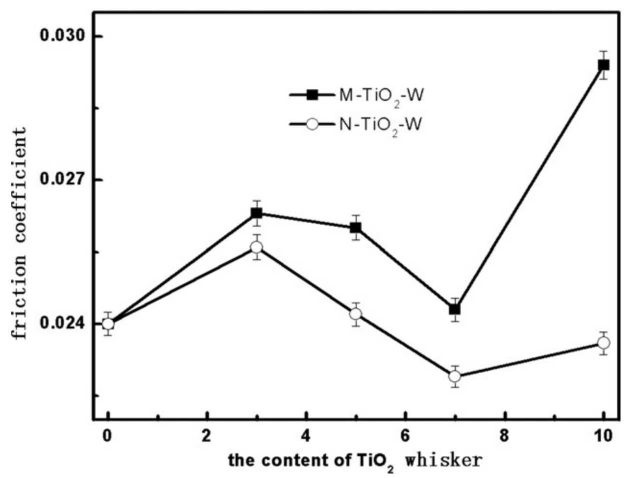

Figure 3. Effect of different whiskers on friction coefficient of porous PPS/PTFE composites (load: 100 N; Sliding velocity: 1.4 m/s).

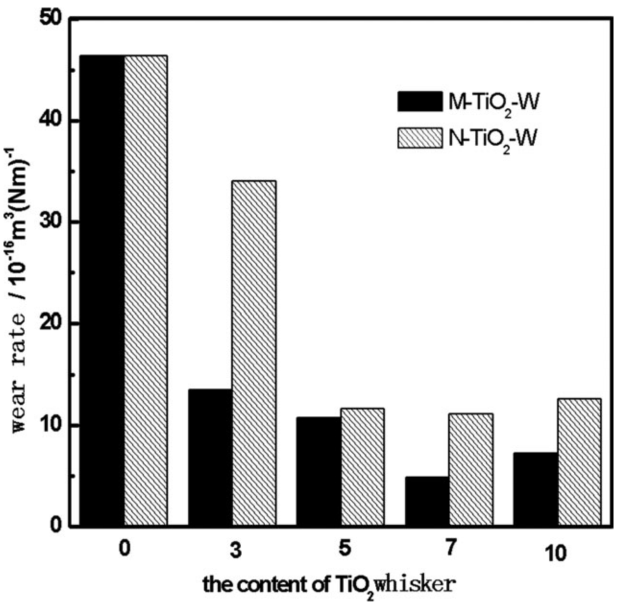

Figure 4. Effect of different whiskers on wear rate of porous PPS/PTFE composites (load: 100 N; Sliding velocity: 1.4 m/s).

During the friction process, grease can be exuded continuously through connected nano-micro pores under the coupling effects of the load and friction heat forming a stable lubricant layer on worn surfaces. As a result, it could solve the problems of sever heat-accumulation and poor heat transiting of pure PPS in practical application. Therefore, this nano-micro porous PPS composites with good self-lubrication and wear-resistant have potential uses in high temperature, vacuum, corrosion and other special circumstances.

Figures 5 and 6 show the tribological performances of porous PPS/PTFE composite with various mounts of mesopore and nonperforated TiO_2 whisker under higher load of 200 N sliding

Table II. The Comparative Tribological Performances of Several PPS Composites

Samples (mass fraction)	Friction coefficient		Wear rate ($10^{-16}m^3/Nm$)	
	100N	200N	100N	200N
PPS (dry condition)	0.29	–	31,500	–
30NaCl/10PTFE/PPS	0.024	0.024	14.0	46.4
3M-TiO_2-W/30 NaCl/10PTFE/PPS	0.0243	0.019	4.88	9.27

Note: '–' means failure.

Table III. The Weight of Grease Absorbed by Porous Composites

Materials	Porosity of composites	Grease adsorption, wt% of composite
7wt% N-TiO_2-W/PPS/ PTFE composite	27.4%	18.1%
7wt% M-TiO_2-W/PPS/ PTFE composite	37.5%	28.7%

condition. The addition of two TiO_2 whiskers decreases obviously the friction coefficient and wear rate of the PPS/PTFE composites. The friction coefficient and wear rate decrease first and then increase with increasing the content of TiO_2 whiskers. In addition, it indicates that the friction coefficient and wear rate of porous PPS/PTFE composites filled with M-TiO_2-W is lower than N-TiO_2-W. The lowest friction coefficient and wear rate are obtained with 3 wt % M-TiO_2-W under 200 N case. However, with the content of TiO_2 whisker farther increasing, the agglomerates and unevenly dispersion of TiO_2 whiskers particles in PPS composites would take place which leads to the degradation of wear resistance of porous PPS composites.

It is evident that when the load is light, the grease layer detaches the two contact surfaces and results in a lower friction coefficient. With the load increase the contact area increases and more grease is extruded out on the friction surface; and, under this situation it seems that the "boundary lubrication effect" may appear. Therefore, the nano-micro porous structure plays an important role on improving the performances of self-lubrication and wear resistance of porous PPS.

The Effect of M-TiO_2-W Content on the Friction and Wear Properties of Porous PPS/PTFE Composite. The results of tribological performances and counterpart surface temperature of porous PPS/PTFE composites filled with various amounts of mesopore TiO_2 whisker under 100 N are presented in Figure 7. It can be seen that the tribological performances and counterpart surface temperature of porous PPS self-lubricating composites decrease at first and then increase with the content of M-TiO_2-W increase. It shows that the nano-micro porous PPS/PTFE composite filled with 7 wt % M-TiO_2-W obtains the highest wear resistance.

Relationship between the tribological properties and mesopore TiO_2 whisker content and counterpart surface temperature of

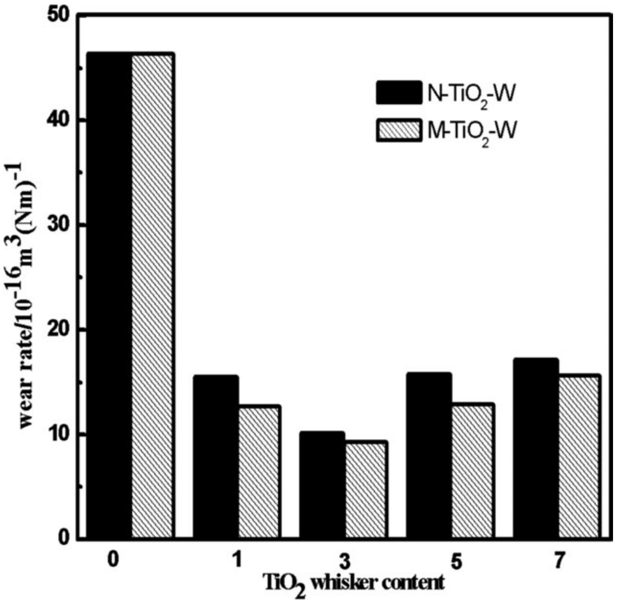

Figure 6. Effect of different whiskers on wear rate of porous PPS/PTFE composites (load: 200 N; Sliding velocity: 1.4 m/s).

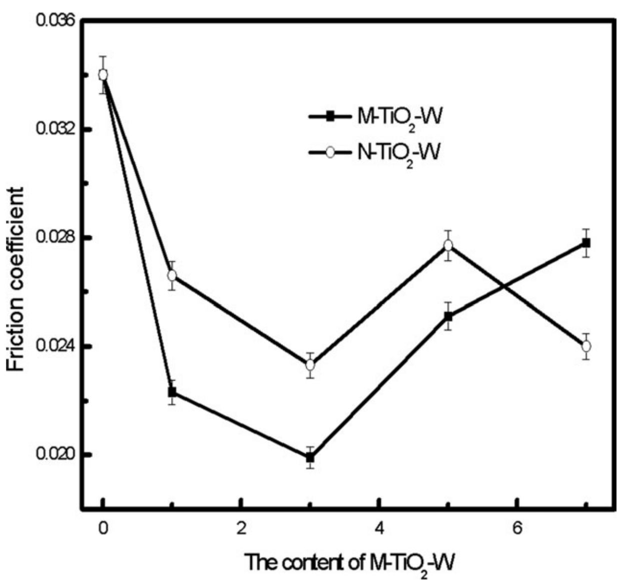

Figure 5. Effect of different whiskers on friction coefficient of porous PPS/PTFE composites (load: 200 N; Sliding velocity: 1.4 m/s).

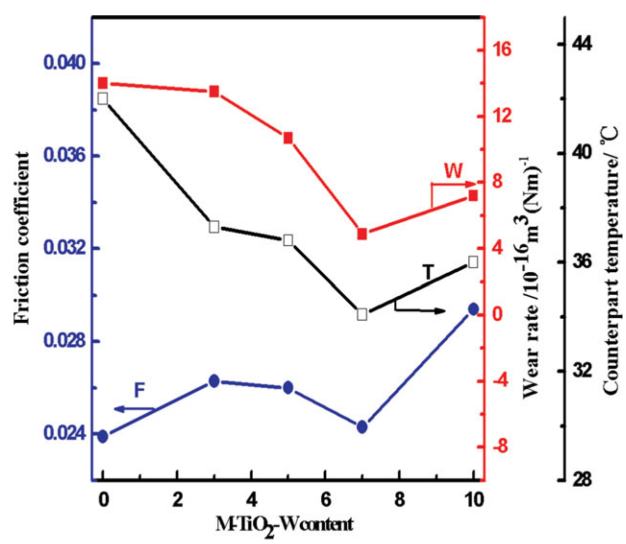

Figure 7. Effect of mesopore TiO_2 whisker's content on tribological properties and counterpart temperature of porous PPS/PTFE composite (load: 100 N; Sliding velocity: 1.4 m/s). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

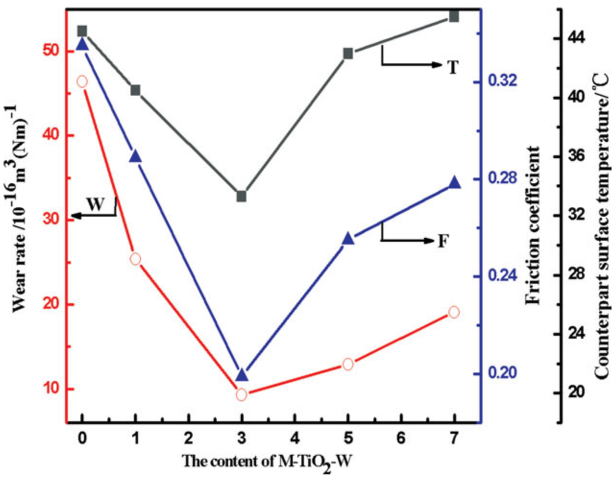

Figure 8. Effect of mesopore TiO_2 whisker's content on tribological properties and counterpart temperature and porous PPS/PTFE composite (load: 200 N; sliding velocity: 1.40 m/s). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

porous PPS/PTFE composite under 200 N are shown in Figure 8. It is obvious that the tribological performance and counterpart surface temperature of porous PPS/PTFE composites decrease first and then increase with the increasing content of M-TiO_2-W. When the content of M-TiO_2-W is 3 wt %, the friction coefficient of composite reaches the lowest value (only 0.019). At this concentration, nano-micro connected channels may be formed in the porous PPS/PTFE composites, which is capable of releasing lubricating grease uniformly and continuously to the worn surface. Therefore, the self-lubricating effect of grease ultimately decreases the friction coefficient and wear rate of porous PPS/PTFE composites.

Meanwhile, M-TiO_2-W can enhance the micro-reinforcement of porous PPS/PTFE composites (can be see in Figure 9). In addition, these micro-scale pores can collect and store partly debrises, and contribute to the decrease of abrasive wear of PPS composites. Therefore, under the coupling effect of load and temperature, grease can be uniformly squeezed from the nano-micro pores. In this case, it can solve the problems of poor lubrication and low wear resistance of PPS.

Self-lubrication of the porous composites based on two preconditions.[15] One is that the lubricants in pores can reach the sliding surface during friction. The other is that the lubricants have a good lubricating effect. As we know, both the two preconditions are closely related to frictional temperature. The counterpart surface temperature was examined to reflect frictional heat generated during the sliding. The tribological results are consistent with the temperatures on the counterpart ring under 100 N and 200 N, as shown in Figures 7 and 8, respectively.

The increase of real friction temperature (obviously higher than the counterpart surface temperature we tested) on the friction surface can make the viscosity of grease decrease. Under this condition, grease can be easily squeezed from composites' pores forming continuous lubricating layer on the friction surface, which ensures long-lasting self-lubricating effect. However, when the temperature is high, owing to leakage and volatility of grease, it is difficult to form continuous grease layer on the friction surface. Thereby, it leads to higher friction coefficient and poorer wear resistance of the porous PPS/PTFE composites filled with higher constant whiskers.

The Friction and Wear Properties of Several PPS Composites. From Table II, it indicates that wear rate of porous PPS/PTFE composites filled with 7 wt % M-TiO_2-W attains the lowest value under 100 N. Compared with pure PPS under dry sliding condition, the wear resistance is enhanced by a factor of 6.45 × 10,[3] showing outstanding wear resistance. Moreover, the wear resistance has increased by 65 times higher than that of porous PPS/10PTFE composite filled with 30% micro-porogen.

Pure PPS can not endure the sliding condition of 200 N. Although the tribological property of porous PPS/PTFE composite is enhanced largely than pure PPS. With 3 wt % M-TiO_2-W incorporation, the wear resistance can be further improved with five times higher than that of the porous PPS/PTFE composite filled with 30% micro-porogen. Consequently, it shows obviously synergistic effect on improving the wear resistance of porous PPS.

Microstructure of Nano-Micro Porous PPS/PTFE Composites
Figure 9 shows the SEM micrographs of the cross-section of porous PPS/PTFE composite filled with 3 wt % M-TiO_2-W and 7

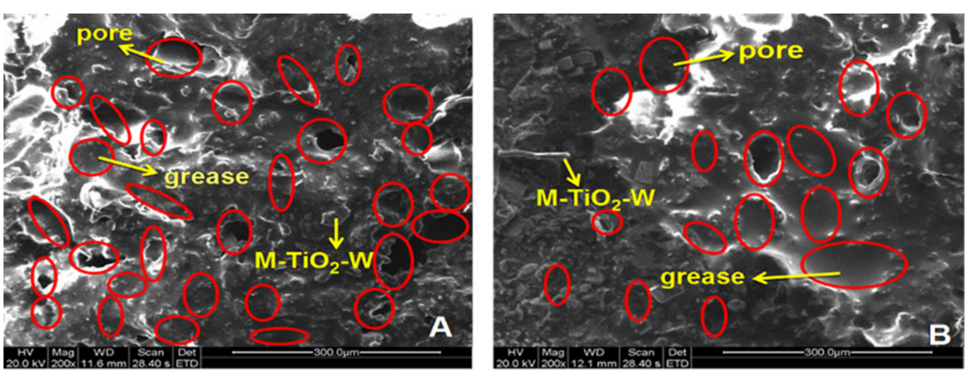

Figure 9. The cross-section of nano-micro porous PPS/PTFE composite (×200). A: PPS/10 PTFE/3 M-TiO_2-W/30 NaCl; B: PPS/10 PTFE/7 M-TiO_2-W/30 NaCl). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

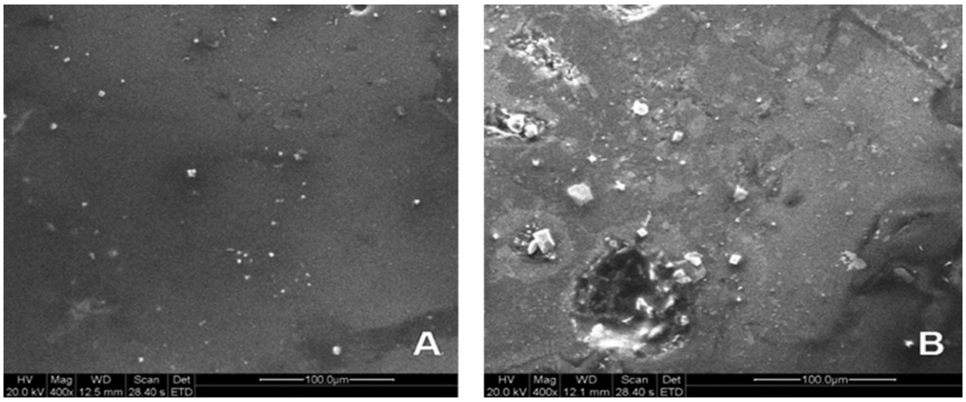

Figure 10. The worn surfaces of porous PPS/PTFE composite at 1.40 m/s and 200 N (×400) (A: PPS/10 PTFE/3 M-TiO_2-W/30 NaCl; B: PPS/10 PTFE/7 M-TiO_2-W/30 NaCl).

wt % M-TiO_2-W. It can be seen that the pores are uniformly distributed throughout the two composites. Under vacuum conditions, lithium-base grease can be stored and exists in solid state in these orderly pores. In addition, well distribution of M-TiO_2-W can be found in Figure 9(A,B). It reveals that M-TiO_2-W can reinforce the structure of porous PPS composites. The roles of these uniformly distributed pores in the composite are not only storing grease, providing self-lubricating, but also seizuring some debrises generated during sliding process.

To better understand the friction and wear behaviors, the worn surfaces of porous PPS/PTFE composites were studied with SEM, as shown in Figure 10. From Figure 10(A), it can be seen that the worn surface of porous PPS/PTFE composite filled with M-TiO_2-W is relatively smooth and covered with grease lubricating layer, which attributes to the lower friction coefficient and wear rate under 200 N condition. In Figure 10(B), pores with grease covered can be seen on the worn surface, which also approves that M-TiO_2-W can reduce the friction coefficient and wear rate of porous PPS composites.

The SEM micrographs of the counterpart surfaces of porous PPS/PTFE composites are shown in Figure 11. From Figure 11(A), it can be seen that the surface of porous PPS/PTFE composites filled with 3 wt % M-TiO_2-W is relatively smooth and there is no obvious nicks on the counterpart surface. The surface is covered with continuous grease lubricating layer which can reduce markedly the friction coefficient and wear rate. However, obvious nicks appear on the counterpart ring of porous PPS/PTFE composites with 7 wt % M-TiO_2-W in Figure 11(B), and continuous grease lubricating layer can not be found on the worn surface. From the above examinations, the SEM investigations of the counterpart surfaces and the worn surfaces are consistent with the triboligical results.

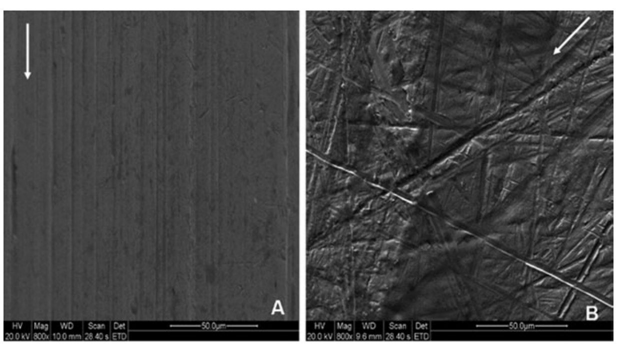

Figure 11. The counterpart surfaces of porous PPS/PTFE composite at 1.40 m/s and 200 N (×800) (A: PPS/10 PTFE/3 M-TiO_2-W/30 NaCl; B: PPS/10 PTFE/7 M-TiO_2-W/30 NaCl).

The increase in wear resistance and decrease in frictional coefficient of porous PPS composite modified with 3 wt % M-TiO_2-W under 200 N may be due to the smooth surface without obvious scratching traces and the formation of a continuous grease lubricating layer, which reduces the direct contact between polymer material and counterpart surface.

CONCLUSION

The nano-micro porous PPS/PTFE composites filled with TiO_2 whiskers were fabricated by mold-leaching and vacuum melting process under high temperature condition. The tribological properties and microstructures of porous PPS composites were studied. The following conclusions can be drawn on the basis of this study:

1. Self-lubricating porous PPS composite has been prepared by the aforementioned method. Under the load of 100 N, the lowest wear rate was obtained by filling 7 wt % M-TiO_2-W in porous PPS/PTFE composites, and the wear resistance was enhanced by a factor of 6.45×10^3 compared with pure PPS, showing outstanding wear resistance. It is also 65 times higher than that of PPS/10PTFE composite filled with 30% micro-porogen.
2. Under the load of 200 N, the lowest friction coefficient and wear rate were obtained by porous PPS/PTFE composites filled with 3 wt % M-TiO_2-W. The friction coefficient is only 0.019. The wear resistance enhanced enormously than that of pure PPS, and is five times higher than that of porous PPS/PTFE composites filled with 30% micro-porogen.
3. The pores of nano-micro porous PPS/PTFE composites filled with proper content M-TiO_2-W were uniformly distributed in the matrix, and grease can be stored in those pores. During sliding condition, grease could be squeezed

through the nano-micro hierarchical pores under the coupling effect of load and friction heat, and formed a stable lubricant layer on the friction surface, providing self-lubricating effect and high wear resistance.

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