Surface characterization of steel/steel contact lubricated by PAO6 with novel black phosphorus nanocomposites

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Abstract: In the present work, two types of novel nano additives, titanium sulfonate ligand/black phosphorus (TiL₄/BP) and titanium dioxide/black phosphorus (TiO₂/BP) nanocomposites, were prepared. The tribological behavior of the steel/steel friction pairs lubricated by polyalphaolefins type 6 (PAO6) containing the nanocomposites under boundary lubrication was studied. The worn surfaces were analyzed using modern surface techniques. The experimental results show that the rubbed surfaces became smooth and showed little wear with the addition of the nanocomposites. TiO₂/BP nanocomposites can significantly improve the lubricity of BP nanosheets under high contact stress. The synergistic roles of the load-bearing abilities and rolling effect of TiO₂ nanoparticles, the slip induced by the BP with its layered structure, and the establishment of a tribofilm on the sliding interface are the basis of the tribological mechanisms.

Keywords: surface characterization; black phosphorus (BP) nanosheets; nano titanium dioxide; boundary lubrication; steel/steel contact

1 Introduction

Steel/steel contact is one of the most common friction pairs in modern mechanical equipment. The use of lubricants can save energy and enhance the efficiency of mechanical equipment by reducing the friction and wear of the critical steel/steel friction pairs [1]. Therefore, it is vital to upgrade the lubrication performance of lubricants for friction pairs in mechanical instruments. Current research has found that many nanoparticle-based lubricant additives can significantly enhance the lubricities of lubricants because of the unique properties of these nanoparticles [2–4]. However, most of the current research has focused on traditional lubricants such as molybdenum disulfide [5] or newly-appeared graphene [6]. The development of new-additives and the surface characterization of steel/steel contact is urgently needed but is not well

studied.

Phosphorus is an active element during sliding and has excellent lubricating properties, especially incorporated in zinc dialkyldithiophosphate (ZDDP) [7–9], commonly incorporated in lubricating oils for mechanical equipment. Phosphorus, itself, is the eleventh most abundant element in the earth's crust. Moreover, phosphorus-containing additives can decrease the wear of contacts through the formation of a tribofilm on the sliding interfaces [10], thereby improving the service life of mechanical equipment.

Recently, black phosphorus (BP) has gained significant interest owing to its unique multi-layered structures [11–14]. Wang et al. [11] investigated the tribological behavior of BP nanosheets in liquid paraffin. The research results indicate that the primary mechanism for the antifriction and lubrication role of BP nanosheets was the interlaminar slip between the

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nanosheets and the formation of a tribofilm over the frictional surfaces. Lv et al. [12] studied the friction and wear properties of BP mixed with PTFE-based composites. Their experimental results show that BP might be able to decrease the wear rate of the composites significantly. The underlying lubricating mechanism for BP is the formation of transfer films at the frictional interface. Nevertheless, in a recent study of BP nanosheets [15], it was found that the lubricity of BP nanosheets under high contact stress conditions is insufficient, restricting its tribological application in the most commonly used steel/steel contact applications under harsh conditions, such as heavy equipment.

Combining BP with other lubricating components is a promising way to improve the lubricity of the nanosheets under high contact stress. Titanium dioxide is a common mineral with excellent lubricating and self-healing properties under certain contact stress conditions [16–18]. In this work, experiments measured and characterised the tribological properties of two types of novel BP nanocomposites, titanium sulfonate ligand/black phosphorus (TiL_4/BP) and titanium dioxide/black phosphorus (TiO_2/BP), under steel/steel contact surfaces and lubricated with polyalphaolefins type 6 (PAO6).

2 Experimental details

2.1 Materials

The lubricant was PAO6, purchased from Shandong Yousuo Chemical Reagent Co., Ltd., China. BP nanosheets were prepared from red phosphorus using ball milling techniques based on previous work [15]. Titanium tetraisopropoxide was the product of Shanghai Maclean Biochemical Technology Co., Ltd., China. Also, all the chemicals used in the experiments were of analytical reagent grade, and in their initial states without further treatment. Table 1 defines the underlying physical parameters of the steel/steel contact.

Table 1 Parameters of the steel/steel contact.

Specimen	Material	Diameter (mm)	Hardness (HV)	Roughness (μm)	Thickness (mm)
Upper ball	GCr15	6	660–880	0.05	—
Lower disk	GCr15	30	190–210	0.20	3

2.2 Synthesis of TiO_2/BP and TiL_4/BP nanocomposites

TiO_2/BP nanocomposites were synthesized with a sol-gel method [19]. A typical synthesis is as follows: Initially, 3 mg of BP nanosheets is dispersed in 50 mL of absolute ethanol. Then, 1 mL of acetic acid is placed into absolute ethanol, after which the mixture is evenly stirred. Next, 10.7 mg of titanium tetraisopropoxide is added to 10 mL of absolute ethanol, and is then poured into the former mixed solution, combined with intensive stirring. The re-mixed solution is then sonicated for 30 min, after which 1 mL of distilled water (DI) is introduced (drop by drop), followed by stirring for 1 h. Finally, the TiO_2/BP nanocomposites are separated by centrifugation and dried at 60 °C.

The preparation of TiL_4/BP nanocomposites referred to the previous work [20]. In a typical synthesis, 15.2176 g of p-toluenesulfonic acid is dissolved in absolute ethanol, and 5.6844 g of titanium tetraisopropoxide is introduced (drop-by-drop) into solution. The mixed solution is stirred at 50 °C, reacting for 3 h. Titanium benzenesulfonate is then obtained after removing the solvent by rotary evaporation. Subsequently, 3 mg of titanium benzenesulfonate is added into a 50 mL BP N-methyl-2-pyrrolidinone solution and stirred for 15 h in the dark. Finally, solid TiL_4/BP nanocomposites are obtained after centrifugation and drying.

2.3 Tribological tests

Before the tribological tests, the two types of as-prepared nanocomposites, TiO_2/BP and TiL_4/BP , were dispersed in the PAO6 lubricant with mass concentrations of 0%, 0.005%, 0.01%, 0.05%, and 0.2%, respectively, with oleic acid as the dispersant. The lubricants were then treated by ultrasound for 30 min before the tribological tests, conducted using a CFT-1 ball-on-disk tribometer (Jinan Yihua Tribological Test Technology Co., Ltd.). The dispersions were kept stable during the entire sliding process. Figure 1 shows

Fig. 1 Schematic of tribological tests.

the test rig schematic and the Table 2 lists the test parameters.

The film thickness ratio confirmed the lubrication regime. According to Hertz's theory, the contact stress of a ball-on-disk contact was [21]:

$$P = \frac{4W}{\pi a^2} \quad (1)$$

$$a = 2 \left(\frac{2}{3} \times \frac{WR}{E'} \right)^{\frac{1}{3}} \quad (2)$$

where P and a represent the Hertz contact stress and contact diameter; W is the normal pressure ($W = 8, 20$, and 30 N); R , the equivalent radius of curvature ($R = 3$ mm); E' , the finite elastic modulus ($E' = 233$ GPa). According to Eqs. (1) and (2), the contact stresses of the steel/steel contact were 1.67, 2.34, and 2.36 GPa, respectively for each pressure.

The Hamrock and Dowson formula estimates the film thickness ratio λ using the formula of the minimum thickness of oil film [2].

$$h_{\min} = 3.63R \frac{G^{*0.49} U^{*0.68}}{W^{*0.073}} (1 - e^{-0.068k}) \quad (3)$$

$$\lambda = \frac{h_{\min}}{(Ra_1^2 + Ra_2^2)^{\frac{1}{2}}} \quad (4)$$

where $G^* = \alpha E'$; $U^* = \eta_0 U / E' R$; $W^* = W / E' R^2$; U represents

the sliding velocity ($U = 83$ mm/s); α , the pressure-viscosity coefficient; η_0 , the dynamic viscosity ($\eta_0 \approx 30.5 \times 10^{-3}$ (N·s)/m²); k , the elliptical parameter; Ra , the surface roughness of the upper and lower samples ($Ra_1 = 50$ nm, $Ra_2 = 200$ nm). According to the calculated results, the maximum lambda ratio is 0.216 for all the tests, suggesting that all the sliding tests remain within the boundary lubrication regime.

2.4 Characterization

Microscopic confocal laser Raman spectroscopy (HR Evolution) determined the structure of the BP powder and BP nanosheets. A JEOL EM-2100F high-resolution transmission electron microscope (TEM) and a digital camera characterized the microscopic and macromorphologies of BP nanocomposites and their dispersions, respectively. The Keyence VK-X1003 Dimension laser scanning microscopy was selected to obtain the surface profile. The SU8020 high-resolution scanning electron microscopy (SEM) was employed to observe the microscopic morphologies of the worn surfaces after sliding. The chemical components of the rubbed surfaces were detected using the ESCALAB 250Xi X-ray photoelectron spectroscopy (XPS).

3 Results and discussion

3.1 Characterization of TiO₂/BP and TiL₄/BP nanocomposites

Figure 2 shows the Raman spectra of BP nanosheets (BP-ns) and BP nanocomposites. As shown in Fig. 2, all three characteristic peaks of BP occurred at ~ 360 cm⁻¹ (A_g^1), ~ 440 cm⁻¹ (B_{2g}), and ~ 466 cm⁻¹ (A_g^2), respectively. The BP nanosheets had higher peak intensity ratios of A_g^2 to B_{2g} than the bulk BP powder, indicating the successful reduction of the layers [15]. However, from Fig. 2(a) the characteristic peaks of TiL₄/BP had a redshift compared to those of the BP nanosheets, which may have resulted from restricted vibration of the phosphorus atoms, caused by the affiliated surface TiL₄ [20]. However, the TiO₂ had little influence on the reduction of the corresponding Raman scattering energy owing to its small particle size. From Fig. 2(b), the characteristic peaks of the BP nanosheets and TiO₂ [21, 22] are present in the TiO₂/BP nanocomposites, which agrees well with their constituent components.

Table 2 Tribological testing conditions.

Testing condition	Unit	Value
Sliding speed	m/s	0.083
Stroke length	mm	5
Loads	N	8, 20, 30
Sliding time	min	15
Temperature	°C	25

Fig. 2 Raman spectra of the nanocomposites: (a) TiL_4/BP and (b) TiO_2/BP .

Figure 3 shows the TEM images of BP nanocomposites and the digital photos PAO6 containing different mass concentrations of the nanocomposites, after standing for 48 h. Note the typical thin and lamellar heterostructures of the TiL_4/BP nanocomposites (Fig. 3(a)), the composite sheets had a dimension of approximately $250 \text{ nm} \times 300 \text{ nm}$. As shown in Fig. 3(c), many TiO_2 nanoballs were well dispersed over the surface of the BP nanosheets (of dimensions approximately $300 \text{ nm} \times 500 \text{ nm}$). All the nanocomposites with different concentrations, shown in Figs. 3(b) and 3(d), exhibit excellent dispersive effects after standing for 48 h, except for 0.2% concentration TiL_4/BP . Figures 2 and 3 confirm successful preparation of the BP nanocomposites stable dispersions.

3.2 Tribological properties

Figure 4 shows the average coefficients of friction (COFs) of steel/steel contact lubricated by PAO6

Fig. 3 TEM images of the nanocomposites and digital photos of PAO6 containing different mass concentrations of the nanocomposites after standing for 48 h: (a, b) TiL_4/BP , and (c, d) TiO_2/BP .

containing or without BP nanocomposites under different loads. As can be observed from Fig. 4, with the introduction of TiO_2/BP nanocomposites under different loads, all the average COF initially decreased before increasing. This trend is a result of the low concentrations of additives, forming a tribolayer to separate the friction pairs. Higher concentrations of additives may lead to aggregation [15], resulting in reduced lubricity. Compared with the BP nanosheets in previous work [15], the nanocomposites improved the tribological performance at high contact stress for steel/steel contact. TiL_4/BP nanocomposites reduce friction up to a moderate load of 20 N. This suggests either TiL_4/BP nanocomposites do not form tribofilms under low pressure, or they cannot enter the sliding interface under high load [23].

Figure 5 shows the average wear scar diameter (WSD) of the upper ball under different lubrication conditions. As shown in Fig. 5, the WSD increased with the increasing load, which may have resulted from the destructive probability of asperities of the rubbing surfaces under higher pressure [24]. Compared with the pure PAO6, the PAO6 with nanocomposites had a smaller WSD under a moderate load of 20 N, especially at the mass concentration of 0.01%. Additionally, the lubricating effects of TiO_2/BP nanocomposites increased compared to the TiL_4/BP nanocomposites, which also agreed well with the results shown in Fig. 4. The following surface analysis will disclose the reason.

Fig. 4 Average COF of steel/steel contact lubricated by PAO6 containing or without BP nanocomposites under different loads: (a) 8 N, (b) 20 N, and (c) 30 N.

Fig. 5 Average WSD of the upper ball under different loads: (a) 8 N, (b) 20 N, and (c) 30 N.

3.3 Analysis of the worn surfaces

Figure 6 depicts the wear profiles of the lower disk under PAO6 containing or without TiL₄/BP nanocomposites. As can be seen from Fig. 6, with the increase of the loads, the wear depth and width of the lower disk increased, suggesting more severe wear. The concentration of TiL₄/BP nanocomposites plays a critical role at the load of 20 N, but the additive concentration had little effect on the WSD of the lower disk at lower or higher pressures, which is consistent with the wear result of the upper sample shown in Fig. 5.

Figure 7 shows the wear surface outlines of the lower disk lubricated by PAO6 containing or without

Fig. 6 Wear profiles of the lower disk lubricated by PAO6 containing or without TiL₄/BP nanocomposites under different loads: (a) 8 N, (b) 20 N, and (c) 30 N.

Fig. 7 Wear profiles of the lower disk lubricated by PAO6 containing or without TiO₂/BP nanocomposites under different loads: (a) 8 N, (b) 20 N, and (c) 30 N.

TiO₂/BP nanocomposites. With the addition of TiO₂/BP nanocomposites, the wear depth and width of the lower disk decreases. Furthermore, with the increase of nanocomposite contents in the lubricants, the size of the furrows on the specimen initially reduce before increasing. Under the same condition, the wear depth and width were smaller than those lubricated by PAO6 with TiL₄/BP nanocomposites. This topology shows that the wear of the lower disk kept pace with those of the upper ball, which may be due to the friction pairs being of the same material.

Considering the dispersive effects and potential application, surface analysis of the specimens concentrated on those lubricated by PAO6 having mass concentrations less than 0.1%. Figure 8 shows the SEM micrographs of the rubbed surfaces of the lower disk lubricated with PAO6 with different mass concentrations of TiL₄/BP nanocomposites. Although using the same material in friction pairs could cause higher adhesive wear under high contact stress [25], no evident adhesive wear was observed in the SEM images owing to full lubrication. As can be seen, conspicuous dense furrows occurred at the worn surfaces at concentrations of 0.005% and 0.05%, respectively. However, a relatively polished surface was noticed at the nanocomposite content of 0.01%, suggesting that appropriate content of BP nanocomposites reduce friction and the wear of the sliding pairs. Some aggregation regions on the worn surface are evident at high concentrations, confirming former inferences.

Fig. 8 SEM micrographs of the rubbed surfaces of the lower disk lubricated by PAO6 containing different mass concentrations of TiL_4/BP nanocomposites under the load of 20 N: (a) 0.005%, (b) 0.01%, and (c) 0.05%.

Figure 9 shows the SEM micrographs of the rubbed surfaces of the lower disk lubricated by PAO6 containing different concentrations of TiO_2/BP nanocomposites. There are many pits, deep furrows, and cracks over the rubbed surfaces being lubricated by pure PAO6, as shown in Fig. 9(a), suggesting severe wear. With the addition of TiO_2/BP nanocomposites, the worn surfaces became smoother and the furrows lighter, as shown in Figs. 9(b)–9(d), improved by the lubricity of the nanocomposites. The surfaces became smoothest at the concentration of 0.01%. Higher levels

Fig. 9 SEM micrographs of the rubbed surfaces of the lower disk lubricated by PAO6 containing different mass concentrations of TiO_2/BP nanocomposites under the load of 20 N: (a) 0%, (b) 0.005%, (c) 0.01%, and (d) 0.05%.

of additive aggravated the surface roughness owing to the aggregation of the nanocomposites [26]. The worn surfaces displayed no aggregated regions, suggesting removal of the nanocomposites from the interface as a result of the ‘ball-bearing’ characteristics of nano- TiO_2 [27].

The Raman spectra of the rubbed surfaces after sliding (Fig. 10) show two specific Raman peaks at approximately 250 and 670 cm^{-1} , respectively, with the introduction of nanocomposites. These two peaks belong to FeOOH and Fe_3O_4 , respectively [28]. These suggest that the addition of nanocomposites helped to generate an oxidation film on the sliding surfaces, reducing friction and wear [29]. However, these two peaks are small at the concentration of 0.01%, where the average COF and WSD were lower. This can be demonstrated by the fact that the tribofilm dominates tribological behavior of the steel/steel contact and not the oxidation film.

To accurately discern the chemical components of the tribofilm, XPS spectra of the rubbed surfaces of the lower disk were detected. Figure 11 shows the XPS spectra of the rubbed surfaces lubricated with PAO6 containing or without TiL_4/BP nanocomposites. As can be seen from Fig. 11(a), full-spectrum scanning detected three specific peaks of C 1s, O 1s, and Fe 2p. However, the expected P 2p and Ti 2p characteristic peaks were not found, which may be due to low concentrations on the worn surfaces. Moreover, the nanocomposite content of 0.01% had the highest intensity of C 1s shown in Fig. 11(a), indicating the formation of the thickest adsorbed film from the base oil. This peak is ratified by the lowest Fe 2p intensity, shown in Fig. 11(b), suggesting that the thickest adsorbed film covered the substrate steel surface [30]. These trends may be one reason for the best antifriction

Fig. 10 Raman spectra of the rubbed surfaces lubricated by PAO6 containing different mass concentrations of nanocomposites under the load of 20 N: (a) TiO_2/BP and (b) TiL_4/BP .

Fig. 11 XPS spectra of the rubbed surfaces lubricated by PAO6 containing or without TiL_4/BP nanocomposites under the load of 20 N: (a) Survey and (b) Fe 2p.

and antiwear roles at this concentration for TiL_4/BP nanocomposites as additives.

The C 1s spectra of the rubbed surface lubricated with PAO6 containing different mass concentrations of TiL_4/BP nanocomposites (Fig. 12) split into three components at approximately 285 (peak 1), 285.5 (peak 2), and 289 eV (peak 3), corresponding to the C–C/H, C–O, and C=O chemical bonds, respectively [31]. The pure PAO6 lubricated surface had a higher content of C–C/H, indicating that the adsorbed molecules mainly covered the sliding surface from the PAO6. With the introduction of TiL_4/BP nanocomposites the area of peak 2 and 3 increased and peak 1 decreased, indicating that the content of the oxide film and tribofilm increased accordingly. The content of C–O was highest when the concentration was 0.01%, suggesting the thickest tribofilm over the rubbing

Fig. 12 XPS spectra of C 1s of the rubbed surfaces lubricate by PAO6 containing different mass concentrations of TiL_4/BP nanocomposites under the load of 20 N: (a) 0%, (b) 0.005%, (c) 0.01%, and (d) 0.05%.

surface, which was helpful for their antifriction and antiwear roles [31].

Figure 13 shows the O 1s XPS spectra of the rubbed surface lubricated by PAO6 containing different mass concentrations of TiL_4/BP nanocomposites. For the steel surfaces lubricated with pure PAO6, the peaks (1–3) at approximately 529.7, 530.3, and ~531.4 eV belonged to Fe_3O_4 , or FeOOH , C–O, and C=O [31–33], respectively. The same oxide components detected by the Raman spectra shown in Fig. 10, confirming the formation of an oxide layer on the sliding surfaces. With the addition of TiL_4/BP nanocomposites, two different peaks (4 and 5) located at approximately 532.9 and 535 eV occurred. These belonged to FePO_4 and FeSO_4 , respectively [34, 35]. That is, the nanocomposites participated in a tribo-reaction and formed the film, which contributed to the lubrication. Furthermore, there was a higher content of FePO_4 measured at the nanocomposite content of 0.01%, which accounted for the better antifriction and antiwear performance [32].

Figure 14 depicts the XPS spectra of the rubbed surfaces lubricated by PAO6 containing or without TiO_2/BP nanocomposites under the load of 20 N. As can be seen from Fig. 14(a), full-spectrum scanning detected three specific peaks of C 1s, O 1s, and Fe 2p. Meanwhile, the expected P 2p and Ti 2p characteristic peaks were missing, which was due to the low content of the components on the rubbed surfaces.

Fig. 13 XPS spectra of O 1s of the rubbed surfaces lubricate by PAO6 containing different mass concentrations of TiL_4/BP nanocomposites under the load of 20 N: (a) 0%, (b) 0.005%, (c) 0.01%, and (d) 0.05%.

Fig. 14 XPS spectra of the rubbed surfaces lubricated by PAO6 containing or without different mass concentrations of TiO_2/BP nanocomposites under the load of 20 N: (a) Survey, (b) Fe 2p, (c) Fe 2p at 0%, and (d) Fe 2p at 0.01%.

Additionally, the ‘ball-bearing’ effects of nano- TiO_2 [27] and the interlaminar slip between BP nanosheets [11] also contributed to the lubrication and decreased the concentration of P 2p and Ti 2p on the rubbed surfaces. Furthermore, with the concentration of the nanocomposites, reaching 0.01% and 0.05%, both the carbon and oxygen content on the rubbed surface was much larger than other levels. This spectra shows that the introduction of TiO_2/BP nanocomposites was good for the establishment of the adsorbing film, which has a different role than that of the TiL_4/BP nanocomposites. At the same time, higher concentrations of TiO_2/BP nanocomposites resulted in higher Fe 2p content, which can be seen from Fig. 14(b). Additionally, for pure PAO6 lubrication (Fig. 14(c)), the main components in Fe 2p were Fe, Fe_3O_4 , and FeOOH. However, high content of FePO_4 was detected (Fig. 14(d)) in the tribofilm with the introduction of TiO_2/BP nanocomposites at a concentration of 0.01%, which favored better lubrication performance of the steel/steel contact at this condition [32].

Figure 15 shows the XPS spectrum of C 1s of the rubbed surface lubricated by PAO6 containing different mass concentrations of TiO_2/BP nanocomposites under the load of 20 N. As can be seen, the total C 1s spectra split into three peaks: peak 1 located at approximately 285 eV, assigned to the C–C or C–H vibrational peak; peak 2 located at 285–286 eV, attributed to the C–O

Fig. 15 XPS spectra of C 1s of the rubbed surfaces lubricated by PAO6 containing different mass concentrations of TiO_2/BP nanocomposites under the load of 20 N: (a) 0%, (b) 0.005%, (c) 0.01%, and (d) 0.05%.

vibration peak; peak 3 situated at approximately 289 eV, assigned to the C=O vibration peak.

Pure PAO6 lubrication provided the lowest content of C–O and C=O peaks, indicating the thinnest oxide layer. With the introduction of TiO_2/BP nanocomposites, a higher concentration of the oxide layer on the worn steel surface was obtained, especially at a levels of 0.01%. These results confirm that the TiO_2/BP nanocomposites are good for the formation of the oxide layer.

Figure 16 shows the XPS spectra of O 1s of the rubbed surface lubricated by PAO6 containing different mass concentrations of TiO_2/BP nanocomposites under the load of 20 N. For rubbing surfaces lubricated by pure PAO6, shown in Fig. 16(a), peaks (1–3) positioned at 529.7, 530.3, and 531.4 eV belonged to Fe–O in Fe_3O_4 or FeOOH, C–O, and C=O, respectively, which agreed well with the Raman spectra results. These spectra again support the view that the oxide layer forms by adsorption and frictional oxidation. When the TiO_2/BP nanocomposites disperse in PAO6, a new peak (4) forms at 532.4 eV, attributed to FePO_4 . The relative peak area of FePO_4 was highest at the TiO_2/BP nanocomposites concentration of 0.01% indicating that the nanocomposites are adsorbed on the frictional surface and create a tribofilm, including FePO_4 , and playing a critical antifriction and antiwear role.

Fig. 16 XPS spectra of O 1s of the rubbed surfaces lubricated by PAO6 containing different mass concentrations of TiO_2/BP nanocomposites under the load of 20 N: (a) 0%, (b) 0.005%, (c) 0.01%, and (d) 0.05%.

The boundary lubrication process of the steel/steel friction pairs lubricated by the PAO6 containing BP nanocomposites additives is active, the mechanisms work as follows. The PAO6 and nanocomposites are adsorbed on the sliding interfaces and form an adsorption film, an oxide film, and a tribofilm during the frictional process. For the PAO6 lubricating process, the adsorption film containing organic molecules from PAO6 and the oxide film containing Fe_3O_4 or FeOOH play a friction-reducing and antiwear role, and the adsorption film mainly dominated the friction and wear behavior. During the PAO6 containing BP nanocomposites lubricating process, the tribofilm dominated the sliding process. However, excessive concentrations of nanocomposites do not make for optimum lubrication performance owing to aggregation. Under the same conditions, TiO_2/BP nanocomposites have better lubricating effects than TiL_4/BP nanocomposites, besides the formation of tribofilm, partially due to the synergistic effect of the bearing capacity, the rolling effects of nano- TiO_2 , and the interlaminar slip between BP nanosheets.

4 Conclusions

In summary, to reduce the friction and wear effects of steel/steel tribo-pairs, two types of BP nanocomposites

were synthesized and dispersed in PAO6 as additives. A ball-on-disk tribometer configured to produce boundary lubrication conditions measured the tribological behavior of steel/steel contacts. Several advanced surface analysis techniques characterized the sliding surfaces. The primary conclusions obtained from this investigation are as follows:

1) Titanium dioxide with the size of 10–30 nm can be evenly deposited over the surface of BP nanosheets by the sol-gel method; and titanium sulfonate ligand can be successfully adsorbed outside the BP nanosheets to form TiL_4/BP nanocomposites.

2) For steel/steel contact lubrication, the optimal mass concentration of these two BP nanocomposites in PAO6 is 0.01%. Excessive high levels lead to aggregation of the additives and deterioration of the lubrication effects.

3) The addition of TiL_4/BP nanocomposites improved the tribological performance of the steel/steel contact when compared with the BP nanosheets, especially under a load of 20 N. Lower loads inhibited the formation of a tribofilm. In contrast, higher pressures decreased the interval between friction pairs and adversely limited the entrance of nanocomposites.

4) With the introduction of TiO_2/BP nanocomposites, the worn steel surface changed from severe to slight wear. The tribological mechanism on the sliding surface was a combination of the bearing capacity and rolling effects of nano titanium dioxide, the formation of a tribofilm including FePO_4 , and the interlaminar slip of BP nanosheets.

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