

Effects of Lubricating-Oil Additives on the Friction and Wear Properties of Polymers and Their Composites Sliding against Steel under Oil-Lubricated Conditions

ZHAO-ZHU ZHANG, QUN-JI XUE, WEI-MIN LIU, WEI-CHANG SHEN

Laboratory of Solid Lubrication, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, People's Republic of China

Received 17 May 1999; accepted 22 June 1999

ABSTRACT: The effects of lubricating-oil additive zinc dialkyldithiophosphate (ZDDP) on the friction and wear properties of polymers and their composites sliding against GCr15 bearing steel were studied by using an MHK-500 ring-on-block wear tester (Timken wear tester). Then the frictional surfaces of the friction pairs were examined by using electron probe microanalysis (EPMA). Experimental results show that the ZDDP contained in liquid paraffin has little effect on the friction coefficients of the polyimide (PI) or polyamide 66 (PA66) against GCr15 bearing steel friction pairs compared with that under the lubrication of liquid paraffin, but it slightly reduces the friction coefficients of polytetrafluoroethylene (PTFE) or its composites against GCr15 bearing steel friction pairs. Under lubrication of liquid paraffin containing 2 wt % ZDDP, the ZDDP film absorbed on the frictional surfaces of the PTFE composites–GCr15 bearing steel friction pairs exhibits obvious antiwear properties; it greatly reduces the wear of pure PTFE and the PTFE composites filled with Pb, PbO, and MoS₂; and the wear of the PTFE composites can be reduced by one order of magnitude compared with that under lubrication of pure liquid paraffin. Meanwhile, the inorganic fillers Pb, PbO, and MoS₂ contained in PTFE have little effect on the absorption of ZDDP to the frictional surfaces, so they have little effect on the friction coefficients of the PTFE composites–GCr15 bearing steel friction pairs under the lubrication of liquid paraffin containing 2 wt % ZDDP. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 76: 1240–1247, 2000

Key words: polymer; composites; lubricating-oil additive; friction; wear; frictional surfaces

INTRODUCTION

Polymers such as polytetrafluoroethylene (PTFE), polyamide 66 (PA66), and polyimide (PI) are important engineering materials, and they have been widely used in practice as self-lubricating materials under dry friction conditions. However, with the enlargement of application fields of poly-

mers and their composites in oil-lubricated conditions in recent years, it is essential to study the friction and wear behaviors, as well as the mechanisms of polymers and their composites in oil-lubricated conditions. The friction and wear behaviors of polymers (such as PTFE, PI, and PA66) and their composites under lubrication of base-oil (liquid paraffin) have been studied by Zhang et al.,^{1–6} but the lubricating oils used in practice usually contain various kinds of additives, such as antiwear additives, extreme-pressure additives, antioxidation additives, and anticorrosion

Correspondence to: Z. Z. Zhang.

Journal of Applied Polymer Science, Vol. 76, 1240–1247 (2000)
© 2000 John Wiley & Sons, Inc.

Table I Typical Characteristics of Liquid Paraffin

Viscosity ($\times 10^{-6} \text{ m}^2 \text{ s}^{-1}$)		Viscosity Index	Flash Point ($^{\circ}\text{C}$)	Boiling Point ($^{\circ}\text{C}$)	Main Composition
40 $^{\circ}\text{C}$	100 $^{\circ}\text{C}$				
21.49	4.42	117	226	>300	paraffin

additives. At present, the effects of lubricating-oil additives on the friction and wear properties of metal-metal friction pairs under oil-lubricated conditions have been studied by many coworkers.⁷⁻¹⁰ However, up to now, much less information has been available about the effects of lubricating-oil additives on the friction and wear properties of polymers and their composites under oil-lubricated conditions.

It is well known that zinc dialkyldithiophosphate (ZDDP) is the most widely used multieffective lubricating-oil additive in practice, it has excellent antioxidation, anticorrosion and antiwear properties as well as good extreme pressure and thermal stability properties.¹¹⁻¹⁷ Therefore, the purpose of this work is to study the effects of lubricating-oil additive (ZDDP) on the friction and wear properties of PA66, PI, PTFE, and PTFE composites sliding against GCr15 bearing steel under oil-lubricated conditions. It is expected that this study may be helpful to the application of lubricating-oil additives in polymers or their composites against metal systems under oil-lubricated conditions in practice.

EXPERIMENTAL

In this experiment, the friction and wear tests were carried out on an MHK-500 ring-on-block wear tester (Timken wear tester) with a steel ring (49.2 mm in diameter and 13.0 mm in length) rotating on a polymer or its composite block (12.3 \times 12.3 \times 18.9 mm in size). The steel ring, made of GCr15 bearing steel (SAE 52100 steel), was polished with number-900-grade SiC abrasive paper to a surface roughness of $Ra = 0.15 \mu\text{m}$. Meanwhile, the surfaces of the polymers and their composite blocks were polished with number-800-grade SiC abrasive paper to a surface roughness of $Ra = 0.2 \sim 0.4 \mu\text{m}$.

The polymers and their composites used in this experiment were PA66, PI, PTFE, and PTFE composites. The preparation of PA66 and PI was described in Zhang et al.¹ and the preparation of the PTFE composites was described in Zhang et al.²⁻⁵ In this experiment, four kinds of PTFE-based composites, such as pure PTFE, PTFE+30 vol % Pb, PTFE+30 vol % PbO, and PTFE+30 vol %

Friction coefficient

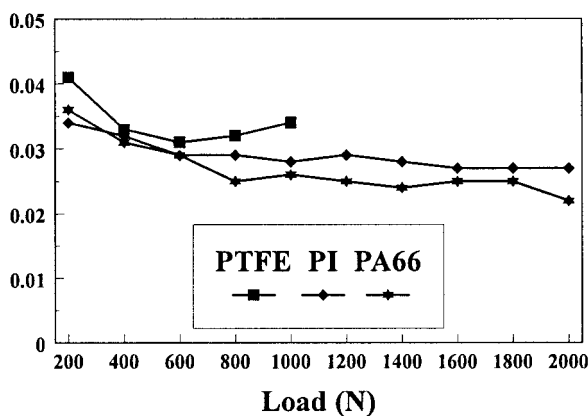


Figure 1 Variations of friction coefficients with load for the PTFE, PI, and PA66 sliding against GCr15 bearing steel under the lubrication of liquid paraffin (2.5 m/s sliding speed).

Friction coefficient

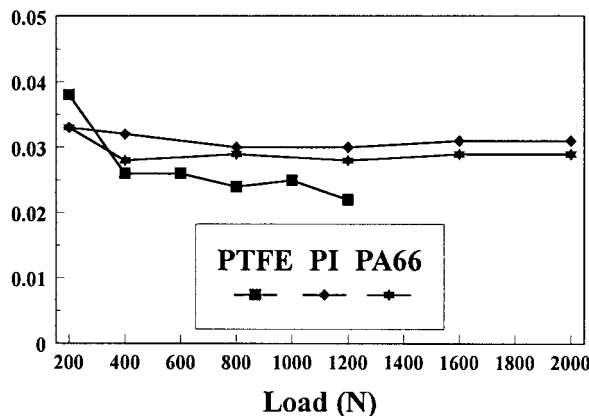


Figure 2 Variations of friction coefficients with load for the PTFE, PI, and PA66 sliding against GCr15 bearing steel under the lubrication of liquid paraffin containing 2 wt % ZDDP (2.5 m/s sliding speed).

MoS₂ composites, were prepared. The liquid paraffin (its typical characteristics are listed in Table I) was used as the base oil, and the ZDDP (T204) was used as the lubricating-oil additive. The addition content of ZDDP in liquid paraffin was 2 wt %, and the lubricating oils were added to the rubbing surfaces at a rate of 30 drops per minute during the tests.

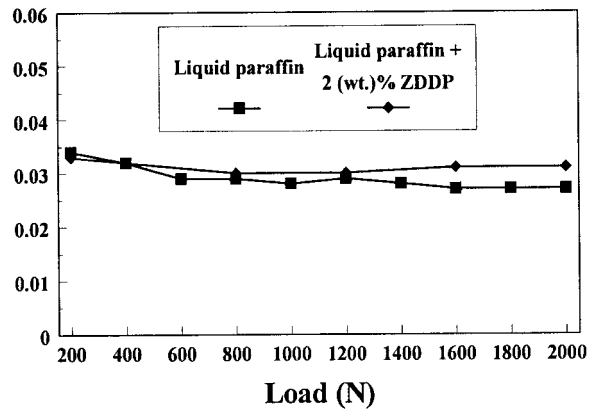
The friction and wear tests were performed at room temperature in an atmosphere with a sliding speed of 2.5 m/s and loads from 200 to 2000N for oil lubricated conditions. Before each test started, the surfaces of the polymers and their composite blocks, as well as the GCr15 bearing steel ring, were cleaned by rubbing with a soft cloth dipped in acetone and then dried in air. Each friction and wear test was performed for 30 min. The wear was detected by the weight loss of the polymer and its composite blocks after each test to an accuracy of 0.1 mg. The friction coefficient was determined by measuring the friction torque, while the friction torque was detected by a torque measuring system. The friction coefficient was the average value of those in the steady stage of the friction (the last 10 min) for each test. In this work, three to five samples were tested at each condition, and the friction coefficients and the wear were the average values of these tests for each condition. Finally, the frictional surfaces of the friction pairs were investigated by using an EPM-810Q electron probe microanalysis (EPMA).

RESULTS AND DISCUSSION

Effect of ZDDP on the Friction Properties of Polymers

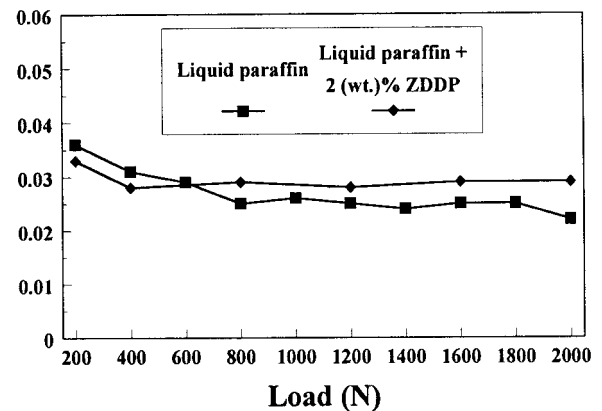
The variations of friction coefficients with load for the polymers PTFE, PI, and PA66 sliding against GCr15 bearing steel under lubrication of liquid paraffin and the liquid paraffin containing 2 wt % ZDDP are shown in Figures 1 and 2, respectively. The results in Figure 1 show that, under the lubrication of liquid paraffin, the friction properties of PA66 and PI are better than that of PTFE, and the friction coefficients of PTFE, PI, and PA66 decrease with the increase of load under lower loads. However, under higher loads (>600N) in liquid paraffin lubrication, the friction coefficient of PTFE increases slightly with the increase of load, but the variations of friction coefficients with load are little for PI and PA66.

Friction coefficient



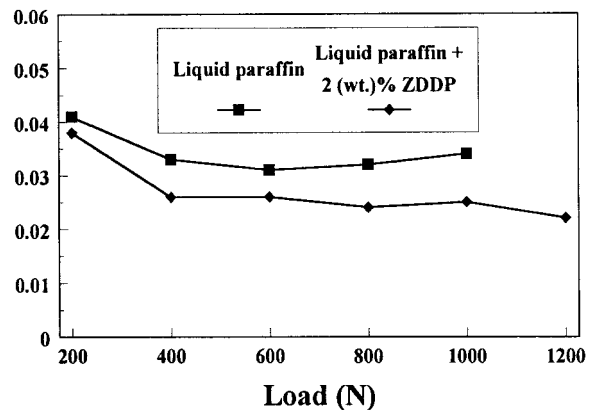
3(a) PI

Friction coefficient



3(b) PA66

Friction coefficient



3(c) PTFE

Figure 3 Comparison of the friction coefficients of the polymer-GCr15 bearing steel sliding systems under lubrication of liquid paraffin and the liquid paraffin containing 2 wt % ZDDP (2.5 m/s sliding speed).

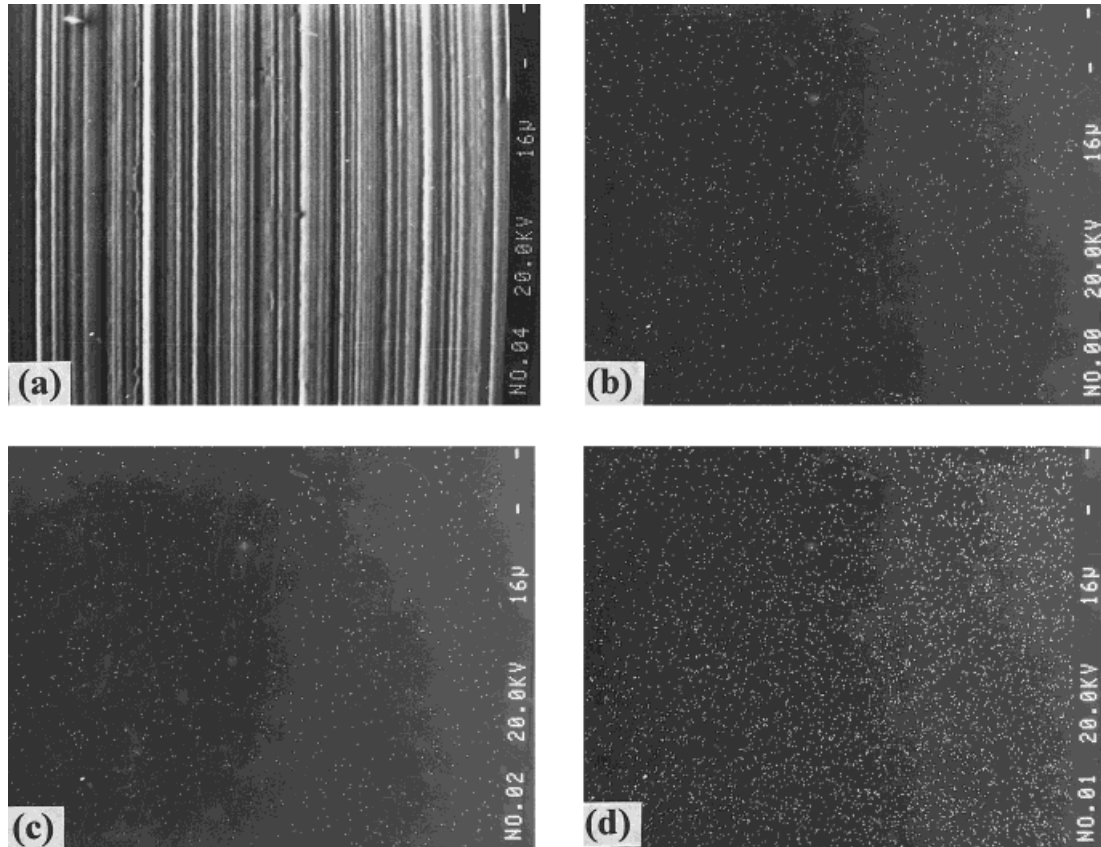


Figure 4 Electron micrograph and the X-ray images of the elements absorbed on the surface of GCr15 bearing steel sliding against the PA66 under lubrication of liquid paraffin containing 2 wt % ZDDP (600 \times ; 2.5 m/s sliding speed; 2000N load): (a) electron micrograph, (b) X-ray image of S, (c) X-ray image of P, and (d) X-ray image of Zn.

The results in Figure 2 show that under the lubrication of liquid paraffin containing 2 wt % ZDDP, the friction coefficients of PI and PA66 almost don't vary with the load; but the friction coefficient of PTFE decreases with the increase of load. However, under higher loads ($> 400N$) in lubrication of liquid paraffin containing 2 wt % ZDDP, the variation of friction coefficient with load is little for PTFE. This indicates that with the increase of load under the lubrication of liquid paraffin containing 2 wt % ZDDP, a steady ZDDP absorption film is gradually formed on the frictional surfaces; so the friction coefficients of PTFE, PI, and PA66 almost don't vary with the load under higher loads ($> 400N$). The results in Figure 2 also show that under the loads from 400 to 1200N in lubrication of liquid paraffin containing 2 wt % ZDDP, the friction property of PTFE is better than those of PI and PA66; this is contrary to the results of the friction tests under the lubrication of liquid paraffin. This indicates that the

formation of ZDDP absorption film on the frictional surfaces improves the friction property of the PTFE against GCr15 bearing steel system.

The comparison of the friction coefficients of the polymers PTFE, PI, and PA66 sliding against GCr15 bearing steel under lubrication of liquid paraffin and the liquid paraffin containing 2 wt % ZDDP is shown in Figure 3. The results in Figure 3 show that under the given conditions in this experiment, the effects of ZDDP contained in liquid paraffin on the friction properties of different polymer against steel systems are different. The effects of ZDDP contained in liquid paraffin on the friction coefficients of the PI or PA66 against steel systems are very little, but it slightly reduces the friction coefficient of the PTFE against steel system.

It has been found that with the increase of load under oil-lubricated conditions, the lubrication states of polymer against steel systems gradually transform from fluid lubrication to mixed lubrica-

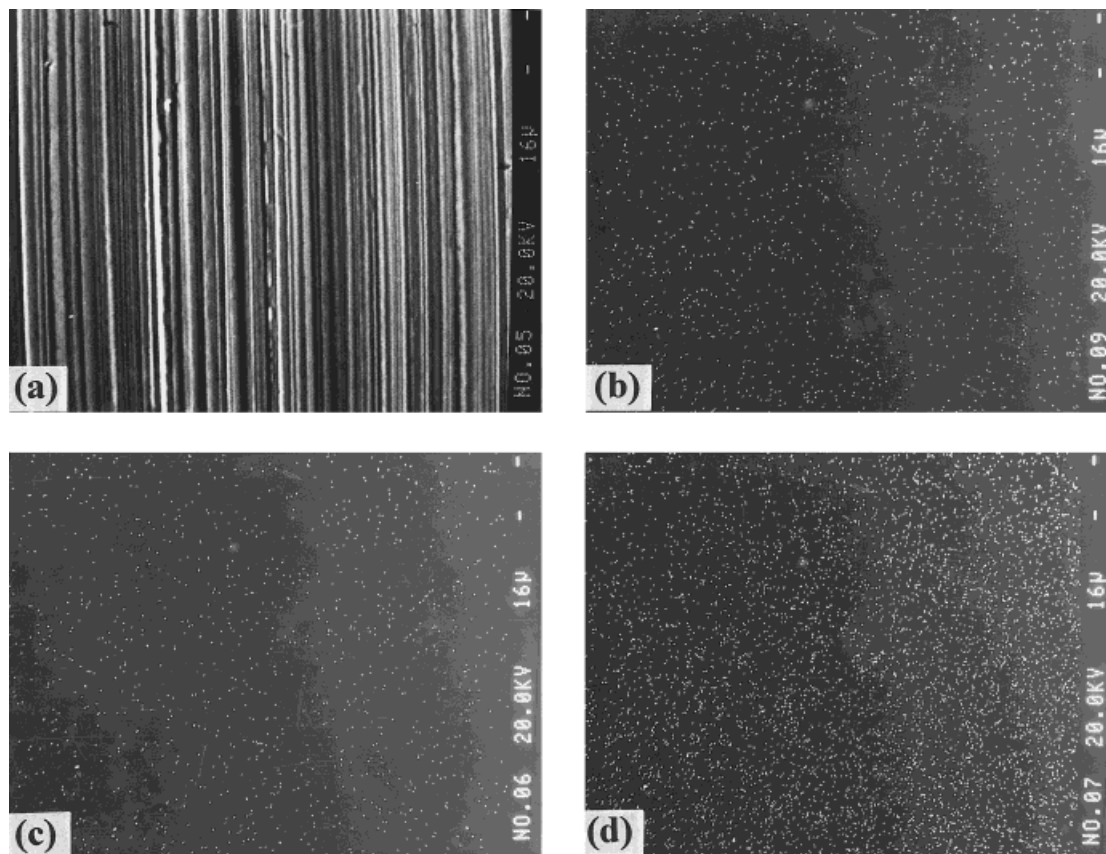


Figure 5 Electron micrograph and the X-ray images of the elements absorbed on the surface of GCr15 bearing steel sliding against the PTFE under lubrication of liquid paraffin containing 2 wt % ZDDP (600 \times ; 2.5 m/s sliding speed; 1000N load): (a) electron micrograph, (b) X-ray image of S, (c) X-ray image of P, and (d) X-ray image of Zn.

tion because of the effects of the mechanical and viscoelastic properties of polymers; and the differences of the mechanical and viscoelastic properties of the polymers result in the difference of the process, in which they transform from fluid lubrication to mixed lubrication.¹ Under the given conditions in this experiment, the lubrication states of the PA66 or PI against steel systems are basically in the fluid lubrication regime because of the high mechanical strength and load-supporting capacities of PA66 and PI, the concentration of the ZDDP absorbed on the frictional surfaces is low (as shown in Fig. 4), so the effects of ZDDP on the friction coefficients of the PA66 or PI against steel systems are very little. However, the low mechanical strength and load-supporting capacity as well as the high viscoelastic deformation under load of PTFE make the system of PTFE against steel easily transform from fluid lubrication to mixed lubrication, this would lead to the increase of the temperature and the surface activities of the fric-

tional surfaces and so, in turn, lead to the increase of the absorption of ZDDP to the frictional surfaces. Therefore, the concentration of the ZDDP absorbed on the frictional surfaces of the PTFE against steel system (as shown in Fig. 5) is higher than that of the PA66 or PI against steel systems (as shown in Fig. 4), and the effect of ZDDP contained in liquid paraffin on the friction coefficient of the PTFE against steel system is greater than that of the PA66 or PI against steel systems under the given conditions in this experiment.

Effect of ZDDP on the Friction and Wear Properties of Polymer Composites

The comparison of the friction coefficients of the PTFE composites filled with Pb, PbO, or MoS₂ sliding against GCr15 bearing steel under lubrication of liquid paraffin and the liquid paraffin containing 2 wt % ZDDP is shown in Figure 6. It

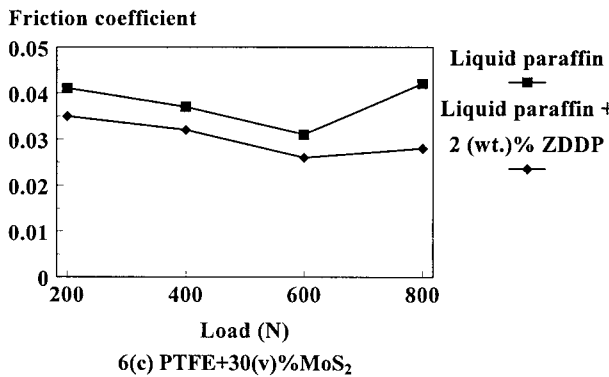
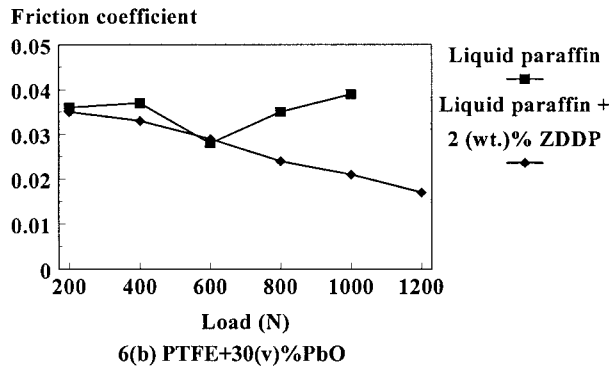
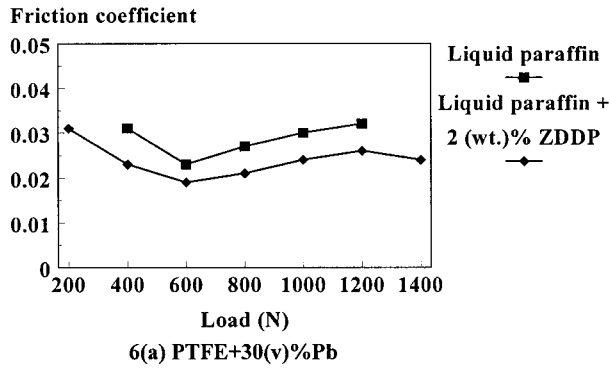


Figure 6 Comparison of friction coefficients of the PTFE composite–GCr15 bearing steel sliding systems under lubrication of liquid paraffin and the liquid paraffin containing 2 wt % ZDDP (2.5 m/s sliding speed): PTFE + 30 vol % (a) Pb, (b) PbO, and (c) MoS₂.

can be seen from Figure 6 that under the lubrication of liquid paraffin, the friction coefficients of the PTFE composites first decrease with the increase of load; but when the load is higher than 600N, the friction coefficients of the PTFE composites increase with the increase of load. However, under the lubrication of liquid paraffin containing 2 wt % ZDDP, the friction coefficients of the PTFE composites decrease with the increase of load, and the friction properties of the PTFE composites are better than those under liquid paraffin lubricated conditions. This indicates that the ZDDP absorption film formed on the frictional surfaces reduces the friction coefficients of the PTFE composites against steel systems.

The effects of ZDDP contained in liquid paraffin on the wear of the PTFE composites sliding against GCr15 bearing steel under oil lubricated conditions are shown in Figure 7. It can be seen from Figure 7 that the antiwear properties of the Pb-, PbO-, or MoS₂-filled PTFE composites can be greatly improved by adding 2 wt % ZDDP to liquid paraffin, and the wear of the PTFE composites can be decreased by about one order of magnitude compared with that under the lubrication of pure liquid paraffin. This indicates that the ZDDP absorption films formed on the surfaces of the friction pairs have obvious antiwear properties, so they greatly reduce the wear of the PTFE composites. Therefore, it can be concluded from the results of Figures 6 and 7 that the friction and

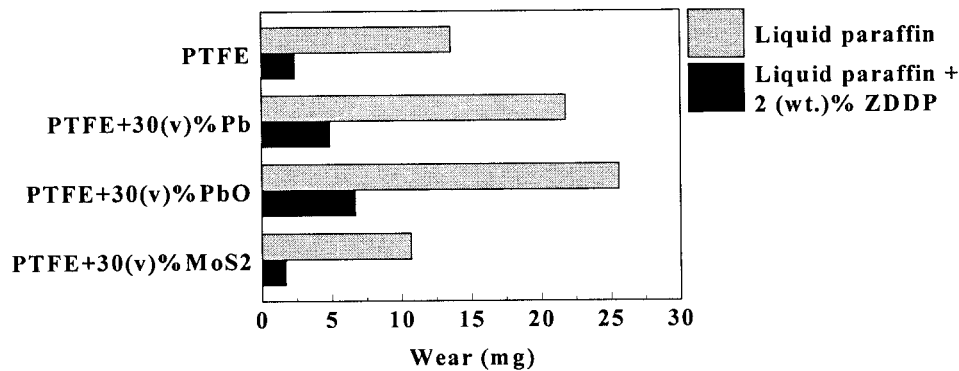


Figure 7 Effect of the ZDDP contained in liquid paraffin on the wear of the Pb-, PbO-, and MoS₂-filled PTFE composites sliding against GCr15 bearing steel under oil-lubricated conditions (2.5 m/s sliding speed; load are as follows: PTFE, 1000N; PTFE+30 vol % Pb, 1200N; PTFE+30 vol % PbO, 1000N; and PTFE+30 vol % MoS₂, 800N).

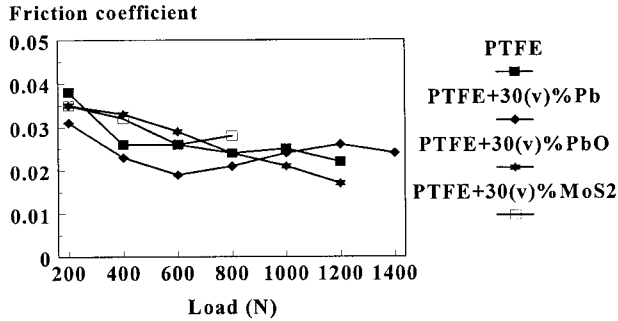


Figure 8 Variations of friction coefficients with load for the PTFE composites filled with Pb, PbO, and MoS₂ sliding against GCr15 bearing steel under the lubrication of liquid paraffin containing 2 wt % ZDDP (2.5 m/s sliding speed).

wear of the PTFE composites filled with Pb, PbO, or MoS₂ can be reduced at different content by adding 2 wt % ZDDP to liquid paraffin, but the

effects of ZDDP contained in liquid paraffin on the friction coefficients of the PTFE composites against steel systems are not very great.

The variations of friction coefficients with load for the PTFE composites sliding against GCr15 bearing steel under lubrication of liquid paraffin containing 2 wt % ZDDP are shown in Figure 8. It can be seen from Figure 8 that under lubrication of liquid paraffin containing 2 wt % ZDDP, the effects of the inorganic fillers (Pb, PbO, and MoS₂) in PTFE on the friction coefficients of the PTFE composites are very little. This indicates that the effects of the fillers Pb, PbO, and MoS₂ in PTFE on the absorption of ZDDP to the frictional surfaces are very little (this can be confirmed by the comparison of the results in Fig. 9 with those in Fig. 5). Therefore, the effects of the inorganic fillers Pb, PbO, and MoS₂ in PTFE on the friction coefficients of the PTFE composites are little under the lubrication of liquid paraffin containing 2 wt % ZDDP.

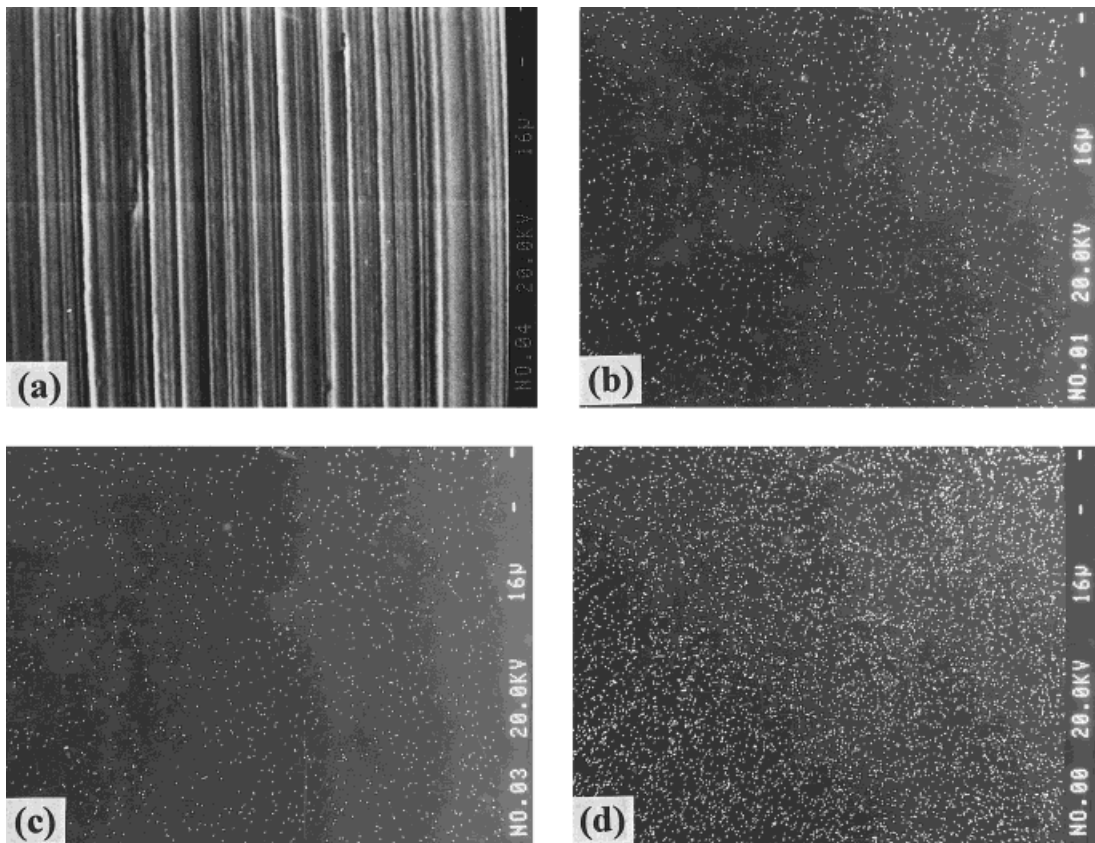


Figure 9 Electron micrograph and the X-ray images of the elements absorbed on the surface of GCr15 bearing steel sliding against the PTFE+30 vol % Pb composite under the lubrication of liquid paraffin containing 2 wt % ZDDP (600 \times ; 2.5 m/s sliding speed; 1200N load): (a) electron micrograph, (b) X-ray image of S, (c) X-ray image of P, and (d) X-ray image of Zn.

CONCLUSIONS

1. The effects of ZDDP contained in liquid paraffin on the friction properties of different polymer against steel systems are different. The ZDDP contained in liquid paraffin has little effect on the friction coefficients of PI or PA66 against steel systems, but it slightly reduces the friction coefficient of PTFE against the steel system.
2. The ZDDP contained in liquid paraffin slightly reduces the friction coefficients of the PTFE composites against steel systems. However, since the ZDDP absorption films formed on the frictional surfaces of the PTFE composites against steel systems have obvious antiwear properties, they greatly improve the antiwear properties of the PTFE composites; and the wear of the PTFE composites can be decreased by about one order of magnitude compared with that under the lubrication of pure liquid paraffin.
3. The inorganic fillers (such as Pb, PbO, and MoS₂) contained in PTFE have little effect on the absorption of ZDDP to the frictional surfaces of the PTFE composites, so they have little effect on the friction coefficients of the PTFE composites against steel systems under the lubrication of liquid paraffin containing 2 wt % ZDDP.

REFERENCES

1. Zhang, Z. Z.; Xue, Q. J.; Liu, W. M.; Shen, W. C. *J Appl Polym Sci* 1998, 68, 2175.
2. Zhang, Z. Z.; Xue, Q. J.; Liu, W. M.; Shen, W. C. *Wear* 1997, 210, 151.
3. Zhang, Z. Z.; Liu, W. M.; Xue, Q. J.; Shen, W. C. *J Appl Polym Sci* 1997, 66, 85.
4. Zhang, Z. Z.; Xue, Q. J.; Liu, W. M.; Shen, W. C. *J Appl Polym Sci* 1998, 70, 1455.
5. Zhang, Z. Z.; Xue, Q. J.; Liu, W. M.; Shen, W. C. *Tribology Int* 1998, 31, 361.
6. Xue, Q. J.; Zhang, Z. Z.; Liu, W. M.; Shen, W. C. *J Appl Polym Sci* 1998, 69, 1393.
7. Ranney, M. W. *Lubricant Additives*; Noyes Data Corporation: Park Ridge, NJ, 1973.
8. Satriana, M. J. *Synthetic Oils and Lubricant Additives*; Noyes Data Corporation: Park Ridge, NJ, 1982.
9. Loomis, W. R. *New Directions in Lubrication, Materials, Wear, and Surface Interactions*; Noyes Publications: Park Ridge, NJ, 1985; p. 354.
10. Lansdown, A. R. in *Chemistry and Technology of Lubricants*; Mortier, R. M.; Orszulik, S. T., Eds.; VCH Publishers: New York, NY, 1992; p. 269.
11. Brazier, A. D.; Elliott, J. S. *J Inst Pet* 1967, 53, 518.
12. Ming, F. I. *Wear* 1960, 3, 309.
13. Rounds, F. G. *ASLE Trans* 1975, 18, 79.
14. Spedding, H.; Watkins, R. C. *Tribology Int* 1982, 15, 9.
15. Watkins, R. C. *Tribology Int* 1982, 15, 13.
16. Dacre, B.; Borington, C. H. *ASLE Preprints 81-LC-6A-5*; American Society of Lubrication Engineers: Park Ridge, IL, 1981.
17. Dacre, B.; Borington, C. H. *ASLE Trans* 1982, 25, 546.