Study on Temperature-Resistant Properties of Polymer–Matrix Solid Film Lubricants

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Abstract: The temperature-resistant properties of some polymer–matrix solid film lubricants were studied. Different chemically modified methods were used in this study to enhance, their temperature-resistant properties. The friction and wear mechanism of polymer–matrix solid film lubricants rubbing at different temperatures in air were explored with differential scanning calorimetry (DSC), scanning electron microscope (SEM), and X-ray photoelectron spectroscopy (XPS). The test results showed that the blending modification of polymer and the application of certain of filler were beneficial to enhance heat resistance of polymer–matrix solid film lubricants, and therefore, improved their lubricating properties at different temperatures in air. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 93: 2180–2184, 2004

Key words: temperature-resistant properties; polymer–matrix solid film lubricant; modification; blending; resin; tribological property

INTRODUCTION

The polymer–matrix solid film lubricants were extensively applied to mechanical parts in various engineering applications because of their antifrictional properties, strong adhesion with metal base, convenient practice, etc.[1] In recent years, better tribological properties at high temperature are demanded on them from development of advanced technology.[2,3] A lot of engineering practices[4] have proved that the transformation of gathering morphology of polymer and the oxidation of other components of solid film lubricant could occur with temperature raising in air. Those led their tribological properties, especially lubricating life, to be decreased. Therefore, their application was greatly limited under such condition.

Two types of polymer–matrix solid film lubricants were selected in this study. To enhance their temperature resistances and tribological properties, different modifications were used: blending a polymer with others for increasing the glassy temperature of polymer, or adding LaF_3 into solid film lubricant to reduce the oxidation of solid lubricant, such as MoS_2. The friction and wear mechanisms of them also were explored with scanning electron microscopy (SEM) (JEOL Ltd., Tokyo, Japan), differential scanning calorimetry (DSC) (Perkin Elmer Life and Analytical Sciences, Inc., Boston, MA), and X-ray photoelectron spectroscopy (XPS) (Physical Electronics, Inc., Eden Prairie, MN).

EXPERIMENTAL

Materials

The materials used in this study are listed in Table I.

Apparatus

The friction and wear tests of solid film lubricants were carried out with a Timken tester and a pin-disk tester, as in Figure 1.

The thermal properties of polymers used as binders were studied by DSC.

The worn surfaces of solid film lubricants and its opposite transfer films were analyzed by means of SEM and XPS.

RESULTS AND DISCUSSION

The friction and wear results of solid film lubricants 1-1, 1–2 (disk) rubbing with $1Cr_{18}Ni_9Ti$ stainless steel (pin) at different temperatures in air are shown in Table II and Figure 2. Those of solid film lubricant 2 (block) rubbing with GCr_{15} steel (ring) are shown in Figure 3.

DSC determination results of thermal properties of polymers as binders of solid film lubricants 1-1 and 1–2 are shown in Figure 4.

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TABLE I
Materials Used in the Study

	Polymer–matrix solid film lubricants			
Film no.	1-1	1–2	2	Metal base
Binder	Bismaleimide (BMI)[5] blended with phenolepoxy resin	Bismaleimide resin (BMI)	Phenolepoxy resin	$1Cr_{18}Ni_9Ti$ stainless steel with surface finish: Ra = 0.16–0.63 μ m
Solid lubricant	Graphite	Graphite	MoS_2	
Others	Sb_2O_3, etc	Sb_2O_3, etc	LaF_3, Sb_2O_3, etc	

SEM analysis results of worn surfaces of solid film lubricant 1-1 and its transfer film after rubbing with $1Cr_{18}Ni_9Ti$ stainless steel at room temperature, 200°C, and 300°C, respectively, are shown in Figures 5 and 6.

XPS analysis results of worn surfaces of solid film lubricant 2 and its transfer film after rubbing with GCr_{15} steel at room temperature are listed in Table III.

As mentioned earlier, bismaleimide (BMI)[5] modified with phenol epoxy resin and pure BMI were used as binders of solid film lubricants 1-1 and 1–2, respectively. The data in Table II indicate that frictional coefficients of solid film lubricant 1-1 were slightly lower than those of solid film lubricant 1–2, when rubbing with stainless steel at different temperatures. However, the differences of wear lives between them grew to be larger with the temperature raising. The wear lives of the former were slightly larger than those of the latter at 18 and 150°C, whereas they were 1.5–1.7 times as large as those of the latter at 200 and 250°C, but were the same as those of the latter at 300°C (refer to Fig. 2). It proved that the blending modification to BMI with phenolepoxy resin could enhance wear life of BMI–matrix solid film lubricant efficiently.

The data in Figure 3 show that the frictional coefficient of solid film lubricant 2 lowered with time, in its rubbing with GCr_{15} steel at room temperature. The initiative frictional coefficient of the solid film lubricant without LaF_3 was the highest. The wear lives of the solid film lubricant containing 2.0–2.5% LaF_3 were the largest, being 1.5 times as large as that without LaF_3.

Thermal behaviors of pure BMI and BMI modified with phenol epoxy resin could be seen from the DSC curves in Figure 4. The glassy temperature (T_g) of modified BMI was 309.69°C, which was 35.67°C higher than that of pure BMI. Viscous flow temperature (T_f; 478.23°C) of modified BMI was near to that (480.49°C) of pure BMI.

SEM analyses to worn surfaces of solid film lubricant 1-1 and its transfer films on opposite surfaces were carried out, respectively, after rubbing for 60 min at room temperature, 200°C, and 300°C in air. The analysis results are shown in Figures 5 and 6. Only the convex parts on solid film lubricant 1-1 were worn out, and very thin transfer film formed on steel pin surface after rubbing at room temperature [refer to Fig. 5(a) and Fig. 6(a)]. It shows in Fig. 5(b) and Fig. 6(b) that the element distributions were more homogeneous on both frictional surfaces after rubbing at 200°C. A complete transfer film formed on both frictional surfaces after rubbing at 200°C. A complete transfer film formed on the opposite surface. Then, the frictional coefficient was the lowest: 0.02–0:052 [refer to Table II]. However, by rubbing at 300°C, the polymers in solid film lubricant and transfer film turned into viscous flow state on frictional surfaces [refer to Fig. 5(c) and Fig. 6(c)]. The solid film lubricant could be easily worn off from frictional surfaces and instantaneous contact of metal/metal occurred. Therefore, the frictional coefficient rose and the wear life was severely reduced [refer to Table II and Fig. 2].

XPS analysis results to both frictional surfaces of solid film lubricant 2 and its transfer film after rubbing for 60 min are listed in Table III. It might be seen from the data[6] that the atom concentration ratios of S/Mo on worn surface of solid film lubricant 2 containing

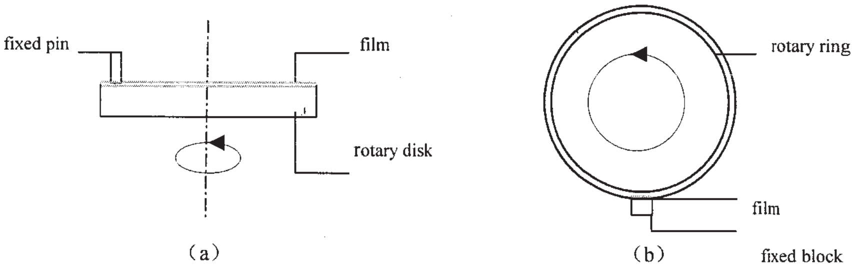


Figure 1 Schematic diagram of frictional tests. (a) Pin-disk friction tester at high temperature; (b) Timken (ring/block) friction tester at ambient temperature.

TABLE II
Effect of Environmental Temperature on Frictional Coefficient of Solid Film Lubricant 1-1 and 1–2[a]

Environmental temperature (°C)	Solid film lubricant 1-1	Solid film lubricant 1–2
80	0.18–0.21	0.20–0.22
100	0.05–0.09	0.09–0.14
150	0.03–0.06	0.04–0.07
200	0.02–0.05	0.03–0.06
250	0.06–0.07	0.04–0.08
300	0.09–0.11	0.10–0.12

[a] Test condition: pin/disk tester, line speed, 1.05 m/s; nominal pressure, 7.76 MPa; in air.

2.5% LaF_3 and its transfer film wholly were larger than those without LaF_3. In other words, a larger amount of element S still kept on the frictional surfaces after rubbing of solid film lubricant 2 containing 2.5% LaF_3. The peak intensity ratios of $Mo^{6+}3d/Mo^{4+}3d$ on worn surfaces of solid film lubricant containing LaF_3 and its transfer film were lower than those without LaF_3. It proved that adding LaF_3 into solid film lubricant 2 was beneficial to maintain the stability of Mo^{4+} compound, such as MoS_2, when rubbing at room temperature in air.

Once the load, speed, and frictional way are determined, the temperature becomes one of most important factors influencing tribological properties of solid film lubricant. Klagelski[7] suggested three types of temperatures related to substantial friction: (1) bulk temperature; (2) surface temperature; and (3) flash temperature of individual point on frictional surfaces in contact. In this study, the surface temperature in rubbing was higher than not only environmental temperature, but bulk temperature of metal bases as well.

When temperature raising, thermal kinetic energy of molecular chain of polymer increased, then molecular chain looseness took place. The free volume in bulk polymer expanded. It provided enough space for transformation of molecular structural image.

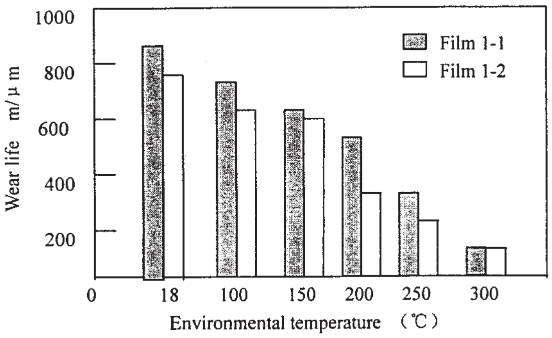


Figure 2 Effect of environmental temperature on wear life of solid film lubricant 1-1 and 1–2. Test condition was as same as Table II.

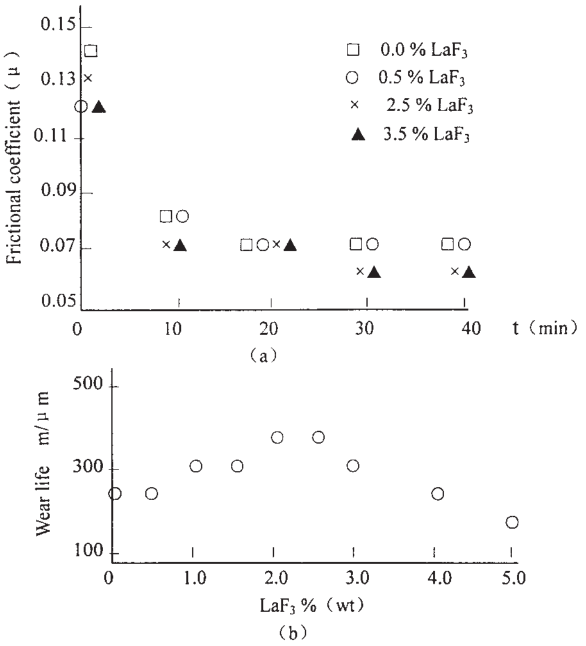


Figure 3 Frictional test results of solid film lubricant 2 (block) versus GCr_{15} steel (ring). Test condition: Timken tester, line speed, 2.57 m/s; load, 311.6*N*, at ambient temperature, in air. (a) Effect of LaF_3 content on friction coefficient (μ) of solid film lubricant 2; (b) effect of LaF_3 content on wear life of solid film lubricant 2.

The polymer in solid film lubricant 1-1 was in a glassy state under rubbing at 18 and 150°C. The thermal kinetic energy of the molecular chain was lower, and only the revolution of individual binding and the slipping between chain sections occurred in polymer. Outer appearance of the solid film lubricant was basically maintained, even if it was subjected to friction action. While rubbing at 200°C, the friction surface temperature of solid film lubricant 1-1 actually exceeded the glassy temperature (309.69°C) of the blending polymer. The polymer was in a high elastic state. Its molecular chains might suffer compressing and drawing, but would then return to initial state in periodical friction. It was beneficial to the mean distribution of solid lubricant (graphite) on frictional surfaces and the formation of complete transfer film on opposite surfaces. Therefore, the frictional efficient of solid film lubricant 1-1 decreased. Under rubbing at 300°C, friction surface temperature exceeded the viscous flow temperature (478.23°C) of blending polymer, leading to viscous flowing of polymer molecules on surfaces. No-returnable flowing deformation of solid film lubricant 1-1 took place, and the wear lives severely decreased.

Chemical composition and structure of molecular basic unit, steric structural image of individual molecule, as well as gathering morphology of bulk polymer are all internal factors influencing friction and wear

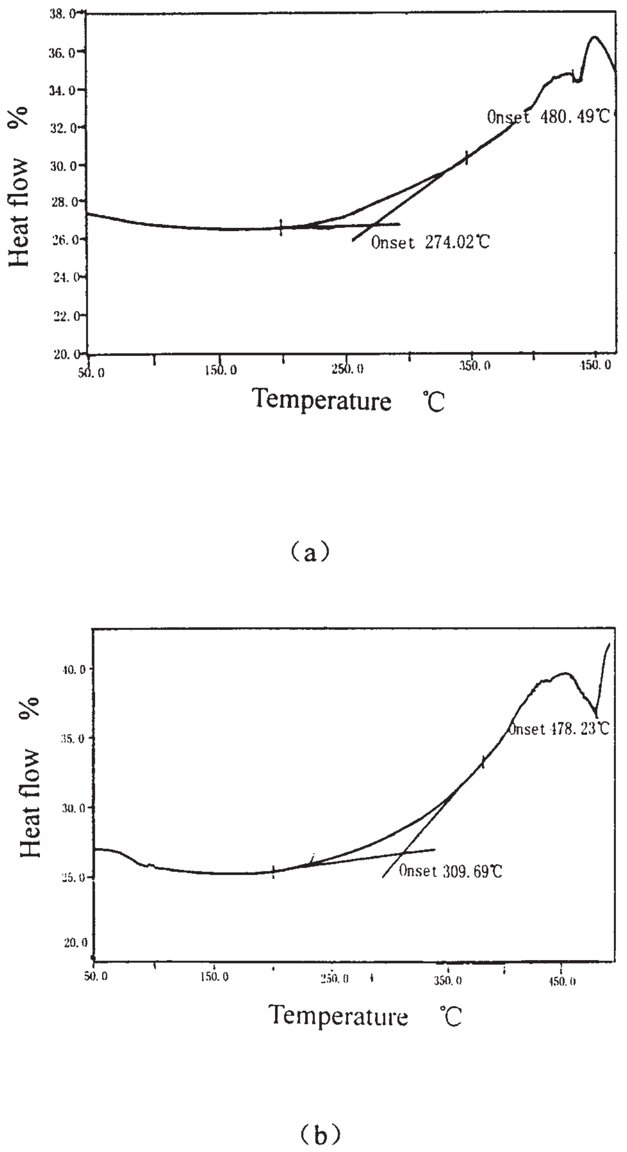


Figure 4 DSC curves of pure BMI and BMI blended with phenolepoxy resin. (a) Pure BMI; (b) BMI blended with phenolepoxy resin.

properties of polymer.[8,9] The gathering morphology of polymer is the most important factor influencing polymer property. It could be transformed by a blended processing of two or more types of polymers, leading the polymer to have some advanced properties. In general, it can improve physicochemical properties of polymer in the rubbing process, as a result of the mechanical twist or (and) the bridge-joint between molecule chains of different polymers.[10] In this study, BMI blended with phenol epoxy resin was possessed of higher T_g. In addition, the epoxy group in the blending polymer also played an important role in enhancing adhesive strength between film lubricant and metal base. Therefore, the friction and wear were all reduced.

Even when rubbing at room temperature, oxidation of MoS_2 in air begins to become significant with temperature raising of frictional surfaces as follows:

$$2MoS_2 + 7O_2 \rightarrow 2MoO_3 + 4SO_2 \uparrow \tag{1}$$

Decreasing of MoS_2 content and MoO_3 emerging in solid film lubricant led the frictional coefficient to increase. It was not beneficial to the formation of transfer film on the opposite surface. Adding an amount of LaF_3 into solid film lubricant can decrease oxidation of MoS_2 to a certain extent. It might be suggested that a binding between MoS_2/LaF_3, just like hydrogen binding, was produced on the crystal face of MoS_2 by outer shearing stress and mechanic–chemical action in rubbing. A new solid compound LaF_3-$nMoS_2$ formed on frictional surface, covering the active points on crystal face of MoS_2. Then, the adherence and the oxidation of oxygen to MoS_2 were decreased.

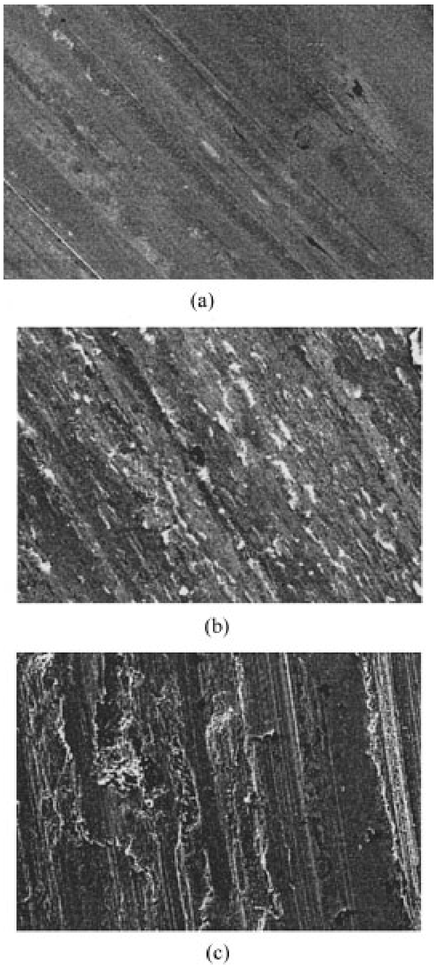


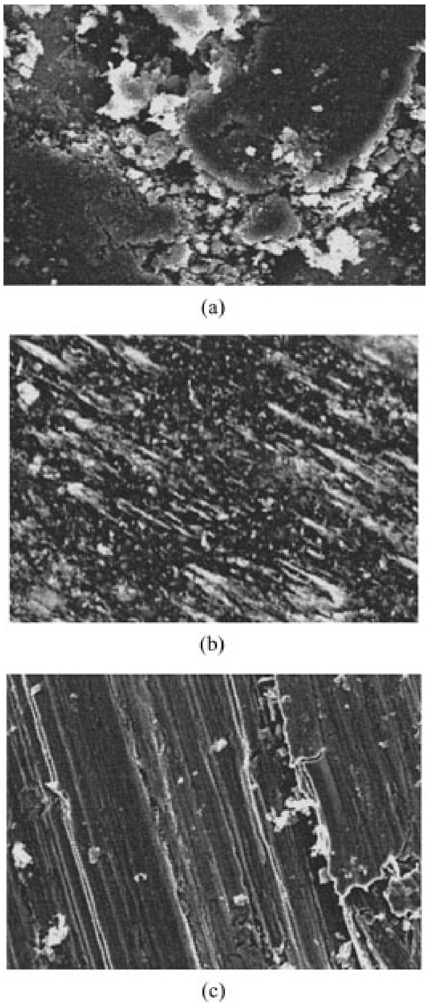
Figure 5 SEM photographs of stainless steel pin surfaces rubbing with solid film lubricant 1-1 for 60 min at different temperatures (×200). Friction test condition as same as Table II. (a) Room temperature; (b) 200°C; (c) 300°C.

CONCLUSION

Frictional coefficients of the solid film lubricant were lowered at 18–300°C, in which BMI modified by blending of phenol epoxy resin was used as a binder, while its wear lives were enhanced. In rubbing at 200 and 250°C especially, the wear lives, were 1.5–1.7 times as large as that with the binder of pure BMI.

The oxidation of MoS_2 on the frictional surface can be effectively decreased by adding an amount of LaF_3 into solid film lubricant, increasing its wear life. The wear lives of solid film lubricant containing 2.0 and 2.5% LaF_3 were 1.5 times as large as that without LaF_3.

In summary, the heat resistance of polymer–matrix solid film lubricant could be increased by the polymer blending or the LaF_3 application. At same time, their tribological property was also improved at different temperatures in air.


(a)

(b)

(c)

Figure 6 SEM photographs of worn surfaces of solid film lubricant 1-1 (disk) rubbing with stainless steel for 60 min at different temperatures (×1000). Friction test condition same as Table II. (a) Room temperature; (b) 200°C; (c) 300°C.

TABLE III
XPS Analysis Results of Worn Surfaces of Film Lubricant 2 (disk) and Transfer Film (ring)[a]

	Worn surface of film lubricant 2		Transfer film	
Analysis item	Without LaF_3	Containing 2.5% LaF_3	Without LaF_3	Containing 2.5% LaF_3
Atom concentration ratios of S/Mo	1.51	1.76	0.96	1.38
Peak intensity ratio of $Mo^{6+}3d/Mo^{4+}3d$	0.69	0.32	1.01	0.72

[a] Frictional conditions were the same as that in Figure 3, except for frictional time of 60 min.

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