Correlation between Nano-Mechanical and Macro-Tribological Properties of Tribofilms Derived from Organic Phosphoric Additives

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Correlation between nano-mechanical and macro-tribological properties of the tribofilm derived from phosphoric additives was investigated. Macro friction test was performed at steel/steel contact under lubrication with poly-alpha olefin (PAO) containing these types of phosphoric additives; tricresyl phosphate (TCP), diphenyl phosphate (DPP), triphenyl phosphate (TPP). The nano-mechanical properties (viscoelasticity, adhesion, hardness, friction coefficient, and effective elastic modulus) of the tribofilms were evaluated by using atomic force microscopy (AFM) and nanoindentation tester. From the results of friction tests and surface analysis, the macro-tribological properties depended on the nano-mechanical properties of tribofilms derived from phosphoric additives under the boundary lubrication. In particular, the thick viscous tribofilm derived from the phosphoric additive exhibited the low friction phenomena. It was suggested that the nano-mechanical properties of tribofilms were the important factors governing the macro-tribological properties under the boundary lubrication.

Keywords: friction, tribofilm, mechanical property, phosphate, atomic force microscopy, nanoindentation

1. Introduction

Lubricant additives are crucial components of lubricants used in a wide range of tribological application in industrial fields [1]. Friction modifiers and anti-wear additives play important roles to extend the lifetimes of industrial applications and result in considerable energy and material savings.

Extreme pressure (EP) additives can reduce friction and protect against wear by forming tribofilms on sliding surfaces under boundary lubrication [2]. Zinc dialkyldithiophosphate (ZDDP) is one of the crucial EP additives with several advantages such as anti-wear, anti-oxidant and corrosion inhibitor. The tribofilm derived from ZDDPs have been investigated to clarify the structure, growing mechanism and tribological properties [3-12]. ZDDPs, however, have a demerit to lead degradation of the efficiency of the catalytic converter in automobile engines. Therefore, there is a strong need in developing an environmental friendly EP additive. Attention of developing EP additives has recently been shifting toward ashless organic compound [13,14]. It is well known that tribological properties of EP

additives are affected by the chemical composition, mechanical properties of tribofilms derived from EP additives on sliding surfaces [2-8,13-20]. The relationship between the mechanical properties and the structures of anti-wear films was reported by Bec et al.[9]. Aktary. et al. also reported that the morphology and the nano-mechanical properties of ZDDP anti-wear films as a function of tribological contact time by using scanning force microscopy (SFM) [6]. It is important to realize the relationship between the mechanical properties of EP additives-derived tribofilms and the macro-tribological properties since the mechanical properties of tribofilms may strongly affect the tribological properties. Kano et al. reported that the mechanical properties of the tribofilms related to the frictional properties of ferrous-based materials [21]. Miklozic and Spikes reported that a viscous layer on ZDDP-derived films influenced the friction properties under lubrication with ZDDP solution [12]. Okubo et al. also reported that the viscous layer on ZDDP-derived tribofilms led to low friction properties at DLC/DLC contacts under boundary lubrication [22]. However, there are few reports about the relationship between various mechanical properties of ashless

organic EP additives-derived tribofilms (viscoelasticity, adhesion, and hardness) and macro-tribological properties.

In this study, we focused on to the correlation between the nano-mechanical properties of organic phosphoric additives-derived tribofilms and the macro-tribological properties. Macro friction tests were performed at steel/steel contacts under lubrication with poly-alpha olefin (PAO) and PAO containing these types of organic phosphoric additives; tricresyl phosphate (TCP), triphenyl phosphate (TPP), diphenyl phosphate (DPP). The various nano-mechanical properties (viscoelasticity, adhesion, hardness, and effective elastic modulus) of the tribofilms were evaluated by using atomic force microscopy (AFM) and TriboIndenter.

2. Experimental details

2.1. Materials

Cylinders (diameter = 15 mm; length = 22 mm, AISI52100, bearing steel, hardness = 850 HV, surface roughness $\leq 0.1 \mu\text{m}$) and disks (diameter = 24 mm; thickness = 7.9 mm, AISI52100, bearing steel, hardness = 850 HV, surface roughness $\leq 0.1 \mu\text{m}$) were used as specimens in the sliding test. PAO (VG16) was used as the base fluid. TCP, TPP, and DPP were used as additives. The test lubricants were prepared by adding 0.1 mass% solutions of each phosphate in PAO. Table 1 shows the molecular structure of each additive.

2.2. Sliding test in the macro-scale

The sliding tests were conducted by using the cylinder-on-disk reciprocating tribo-tester (SRV2, Optimol, DE). The sliding test conditions are listed in Table 2. The Hertz contact area was 0.484 mm^2 . Before the sliding test, the cylinders and disks were cleaned in the ultrasonic bath with the mixture of acetone and petroleum benzene. After the sliding test, the disk was rinsed by using n-hexane to measure surface profile of the worn surface.

Table 1 Chemical structure of additives

Tricresyl Phosphate (TCP)
Triphenyl Phosphate (TPP)
Diphenyl Phosphate (DPP)

Table 2 Sliding test condition

Load	20 N
Stroke	1 mm
Frequency	50 Hz
Temperature	80°C
Test time	1 h
Lubricant	100 μL

2.3. Measurement of mechanical properties

2.3.1 Measurement of nano-mechanical properties

The frictional and force curves were measured by using AFM (Nanonavi Real, SII, JP) with a cantilever made of Si (Si-DF20, SII, JP). The tip radius of the cantilever was adopted using the 10 nm of the manufacturer specifications.

The frictional curve was measured to obtain the friction force of the tribofilms. The friction force was calculated from the displacement in the torsion direction of the cantilever. We set the measurement range and speed to 20 nm and 12 nm s^{-1} , respectively, and the load of the cantilever was fixed to 0 nN considering the adhesion force. The adhesion force was measured by using the AFM force curve.

The force curve was measured to obtain the adhesion energy of the tribofilms. For the force curve, the tip moves up and down over a single location as it moves in and out of contact with the sample. The contact speed was set to 22 nm s^{-1} . The adhesion energy was calculated from the force curve in conformity with the Johnson-Kendall-Roberts (JKR) theory [23,24].

2.3.2 Nanoindenter measurement

The nano-indentation test, dynamic viscoelasticity measurement, and nano-wear test were performed by using Triboindenter (Ti-950, Hysitron, US). Berkovich diamond tip was used for the nano-indentation method and dynamic viscoelasticity measurement, and a spherical diamond tip was used for the nano-wear test.

The nano-indentation test was performed to obtain the effective elastic modulus and hardness of the tribofilms. In the nano-indentation test, the indentation depth was set to 30-60 nm. The nano-indentation tests were carried out measurement of 36 points for each tribofilm. The effective elastic modulus and hardness were calculated from the load-displacement curves in conformity with the Oliver-Pharr theory. The dynamic viscoelasticity was measured to obtain the tan delta, which was defined as the ratio of the loss modulus to the storage modulus. This experiment was performed at frequency of 300 Hz.

In the nano-wear test, the thickness of the tribofilm was estimated. First, we scanned the surface under a low load and measured the surface topology. Then, in the actual wear test we scanned a smaller area under a higher load to scrape off the tribofilm. Finally, we reduced the load and scanned the surface again. The wear depth was

Fig. 1 Appearance of scraping tribofilms in nano-wear test to measure the film thickness

Table 3 FT-IR analysis conditions

Detection circuit	MCT_M
Spectral range	14000 ~ 700 cm^{-1}
Number of integration	256
Resolution	84 cm^{-1}
Atmosphere	Vacuum

estimated from the section profile of the background-corrected image taken after the wear test. This process was performed as the load was increased in various places. As shown in Figure 1, the probe scraped only the tribofilm under the low load. The probe continued to scrape only the tribofilm when the load was increased until the probe was in contact with the substrate. The wear depth continued to remain constant under this load. Further increasing the load caused the probe to scrape not only the tribofilm but also the substrate. When the progress of the wear depth was saturated, it was judged that the tip reached the substrate by scraping out the tribofilm. The saturated wear depth was measured as the thickness of the tribofilm. In the case of TCP and TPP, the nano-wear tests were conducted at a load of 50, 100, 150, 200, 250, 300 and 350 μN , and the saturation of wear depth was observed at a load of 300 μN . Also, the load was 1 μN in the scanning process. As for DPP, the load was 15, 20, 30, 40, 50 μN , and the saturation occurred at 40 μN .

2.4. Surface chemical analysis

Surface analysis was performed by using Fourier transform infrared (FT-IR) spectroscopy (FT/IR-6100, Jasco, JP) with the reflection absorption spectrometry (RAS) method in a sample chamber under a vacuum. The analysis involved only the additives and the surfaces after the sliding test. Table 3 lists the analysis conditions.

3. Results and discussion

3.1. Sliding test

Figure 2 shows the frictional behavior of each lubricant measured by using the SRV tribo-tester. For PAO, the friction coefficient rose to about 0.3 and was unstable. For TCP and TPP, the friction coefficients showed the same behavior and were stable at 0.18. In contrast, using DPP resulted in a large friction reduction

Fig. 2 Comparison of Friction coefficient

Fig. 3 Worn surface profiles after sliding test

to 0.04.

Figure 3 shows the wear depth of the sliding surface of the disk. For PAO, the wear depth was not very much but was uneven. For TCP and TPP, the wear depth was almost too small to measure. DPP showed a wear depth of a few microns. A similar tendency was observed among other subjects as well.

3.2. Mechanical properties

3.2.1 AFM measurement

Figure 4 shows the frictional force of each tribofilm measured by using AFM. The tribofilm derived from DPP showed a lower friction (almost 10 nN) than those of TCP and TPP (almost 50-60 nN). At both the macro-scale and nanoscale, the tribofilm derived from DPP showed a lower friction coefficient and friction force than both TCP and TPP. This suggests that the nano-mechanical properties of tribofilms dominate the

Fig. 4 Comparison of Frictional curve on the tribofilms

Fig. 5 Adhesion energy on surfaces of the tribofilms obtained from the force curve

macro-tribological properties.

Figure 5 shows the adhesion energy of each tribofilm calculated from the force curve. The adhesion force of the tribofilm derived from DPP was almost 3.5 J/m^2 , and those of TCP and TPP were 1.5 J/m^2 . DPP had higher adhesion than TCP and TPP. This result implies the tribofilm derived from DPP has a high surface free energy [25].

Fig. 6 Effective reduced modulus of the tribofilms obtained from the nano-indentation test

Fig. 7 Hardness of the tribofilms obtained from the nano-indentation test

3.2.2 TriboIndenter measurement

Figures (6,7) show the effective elastic modulus and hardness of each tribofilm calculated from the nano-indentation test [26-30] by using TriboIndenter. The average modulus and hardness of the tribofilm derived from DPP were 100 and 2 GPa, respectively. Those of TCP and TPP were almost 180 and 5 GPa, respectively. DPP was clearly weaker than TCP and TPP.

Figure 8 shows the tangent delta of each tribofilm obtained from the dynamic viscoelasticity measurement [31]. For DPP, the tangent delta was 0.35. For TCP and TPP, it was almost 0.25. The tribofilm derived from DPP had a higher tangent delta [32] than those of TCP and TPP. The tribofilm derived from DPP was more liquid than the other two.

Figure 9 shows the section profile of the constant wear depth in the nano-wear test. The average wear depth was considered to be the thickness of the tribofilm, as shown in Figure 10. The thickness of the tribofilm derived from DPP was 70 nm. For TCP and TPP, they were almost 25nm. The tribofilm derived from DPP was much thicker than those of TCP and TPP.

3.3. Surface chemical analysis

Figure 11 shows the IR spectra of each lubricant after the sliding test. In terms of quantifying the tribofilms, DPP showed a much higher peak intensity than TCP and

Fig. 8 Tangent delta of the tribofilms obtained from the dynamic viscoelasticity measurement

Fig. 9 Section profile of the wear after the nano-wear test

Fig. 10 Film thickness obtained from the nano-wear test

Fig. 11 Comparison of IR spectra after the sliding test

TPP. This suggests that the thickness of the tribofilm derived from DPP was much thicker than those of TCP and TPP, which agrees with the nanoindentation measurement results. We compared three spectra and normalized the size of the maximum peak to focus on the compositions of the tribofilms. Figure 12 shows the spectra normalized the size of the maximum peak. A broad band of the phosphate stretch was confirmed at $1300\text{--}900\text{ cm}^{-1}$ in TCP after sliding. In the case of DPP, several sharp peaks were confirmed at $1500\text{--}700\text{ cm}^{-1}$. The spectrum of TPP was not as wide as that of TCP and not as sharp as that of DPP. TCP has been reported to generate a phosphorus compound when it reacts with iron due to sliding, and the compound provides friction and wear protection [33,34]. This compound exhibits a broad peak at $1300\text{--}900\text{ cm}^{-1}$. Figure 13 shows the analysis results of the additive alone without PAO. As shown in Figs. (12,13), the sharp peaks changed to a broad band for TCP by the reaction due to friction. Although the tribofilms derived from TCP and TPP were the same, TPP did not show the broad band of TCP. This result suggests that TCP generated inorganic phosphorus. The inorganic phosphorus combined with iron to become inorganic iron phosphate, and it covered the surface. TPP

Fig. 12 Comparison of IR spectra normalized the size of the maximum peak (after sliding test)

Fig. 13 Comparison of IR spectra (only additives)

generated a tribofilm that mixed organic substances with the inorganic substance because a change in the spectrum was confirmed after sliding. The tribofilms derived from TCP and TPP were hard and elastic because the film were mainly inorganic. For DPP, many sharp peaks were confirmed in the results for only the additive as well as the sliding surface. A reaction was not caused like in TCP and TPP, and the original structure was mostly maintained. The organic phosphorus combined with iron and became organic iron phosphate, and it covered the surface. The tribofilm derived from DPP was soft and viscous because the film was organic.

3.4. Relationship between nano-mechanical and tribological properties

The tribofilms derived from TCP and TPP showed the same tribological properties at the macro-scale. These showed the same mechanical properties at the nanoscale, while only DPP showed a different tendency. In the chemical analysis using FT-IR, the three kinds of

tribofilms showed different properties. The tribofilms derived from TCP and TPP, which showed the same tribological properties at the macro-scale, should have different properties according to the chemical analysis. However, these tribofilms had nearly the same mechanical properties at the nanoscale. If the nano-mechanical properties of tribofilms are the same, the difference in the components do not greatly influence the friction properties at the macro-scale.

With regard to the wear-resistance mechanism of TCP and TPP, phosphate is known to generate inorganic iron phosphate by reaction due to friction after adsorbing onto iron and becoming organic iron phosphate [35]. TCP and TPP generated films made of inorganic iron phosphate. The hard solid-like film protected the surface from wear. The additives were poorly adsorbed because they did not contact with the new surface, so chemical wear was not promoted. This is why, the films derived from TCP and TPP were thin.

For DPP, no reaction occurred like in TCP and TPP. DPP maintained the original structure even when sliding friction occurred. A film made of organic iron phosphate was generated. The soft film wore on the surface by flowing like a liquid and revealing a new surface. Chemical wear was accelerated because the adsorption of the additive was repeated. This is why the films derived from DPP were thick. With regard to the low friction mechanism of DPP, the tribofilm made of organic iron phosphate derived from DPP had a high surface free energy because of the high adhesion energy. This suggests that the lubricant containing DPP provides good wettability. The tribofilm derived from DPP had low hardness, a high tangent delta, and thick film. These results suggest that the shear of the thick viscous film provides low friction by preventing direct contact between solids flowing like a liquid.

4. Conclusions

The correlation between the tribological properties and nano-mechanical properties of three kinds of phosphates was investigated by using a sliding tester and surface analysis instruments. The main conclusions are as follows:

1. The nano-mechanical properties of the tribofilms were confirmed to affect the tribological properties at the macro-scale.
2. The thick tribofilm derived from DPP had a high adhesion energy, high tangent delta, and was soft. The tribofilm reduced friction significantly while showing a large amount of wear.
3. The thin tribofilms derived from TCP and TPP had lower adhesion energy and tangent delta than DPP and were hard. The tribofilms showed excellent wear resistance but did not reduce the friction like DPP.
4. The nano-mechanical properties of the tribofilms provide more valid information than chemical

analysis when considering the tribological properties at the macro-scale.

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