Article

In Situ Observation of EHL Films of Greases by Micro Infrared Spectroscopy

Yasushi Hoshi^{1)*}, Koji Takiwatari²⁾, Hidetaka Nanao³⁾, Hitoshi Yashiro³⁾ and Shigeyuki Mori¹⁾

¹⁾ Faculty of Engineering, Iwate University, 4-3-5 Ueda, Morioka, Iwate 020-8551, Japan

²⁾ Ichinoseki National College of Technology, Takanashi, Hagisho, Ichinoseki, Iwate 021-8511, Japan

³⁾ Department of Chemistry and Bioengineering, Faculty of Engineering, Iwate University, 4-3-5 Ueda, Morioka, Iwate 020-8551, Japan

*Corresponding author: Yasushi Hoshi (yhoshi@iwate-u.ac.jp)

Manuscript received 31 March 2019; accepted 21 April 2019; published 15 June 2019

Translation from the Japanese original: Journal of Japanese Society of Tribologists, 60, 2, 2015, 153-159, the Best Paper Award Winner in 2016

Abstract

In situ observation of lubricant films formed with greases was performed with a micro Fourier transform infrared spectrometer (FT-IR) under elastohydrodynamic lubrication (EHL) conditions between a steel ball and a single-crystal silicon disk. Twelve mass percent of lithium stearate or aromatic-type urea compound were added as thickener to polyalphaolefin base oil. Peaks relating to CH, C=O and NH were monitored in the FT-IR analysis. The film thickness and the concentration of thickener were estimated from the absorbance of CH and the ratio of absorbance of C=O and CH. Two-dimensional distribution of the thickness and the concentration around EHL contact was obtained at a resolution of 50 μm . It was found that the concentration of thickener at EHL contact area was dependent on the type of thickener. Although the concentration of Li grease decreased at the EHL contact area, that of urea increased even at low entrainment speed. The thickener of urea grease was concentrated on the ball and the disk surfaces. The film thickness at EHL contact of each grease can be explained by the concentration of thickener at the contact. Lubricating characteristics of urea grease are discussed based on the concentration of thickener at the EHL contact.

Keywords

grease, thickener, film thickness, concentration, EHL, *in situ*, FTIR

1 Introduction

To understand a dynamic phenomenon such as elastohydrodynamic lubrication (EHL), *in situ* observation of lubricant film is essential. Since the establishment of EHL theory, film thickness can be predicted with precision. However, phenomena such as starvation, shear heating, and change in concentration of lubricant film component, are still unexplained by the conventional EHL theory that treats fluid as a homogeneous system, thus requiring observation of EHL films.

One method to measure film thickness in lubrication is optical interferometry, which measures the shape of the film by determining the film thickness from the contrasting fringes created by optical interference. Thickness of an extremely thin film in a few nm range can be measured by overlaying a silica layer on the Cr vapor deposited film [1], and this is the main basic EHL research technique. However, only the film thickness is measured, and not the chemical composition of lubricating oil in the contact area.

The emission spectrum method obtains chemical information by diffracting infrared light generated from the heated sample oil. The solidification behavior of sample oil and

the oriented state of the molecules have been analyzed using this method [2,3], but the resolution was poor and made the analysis difficult.

Recent advancements in micro Fourier transform infrared spectroscopy (FT-IR) facilitate measurement of lubricating film thickness, and observation of the orientation of synthetic oil, grease thickener molecules, and polymer additive at the inlet of the Hertzian contact region [4-6]. The characteristics of this method are that the structure of the lubricating film in EHL can be directly observed, and the film thickness can be measured by the absorbance of the sample oil. A high wavenumber shift at the absorbing position under high pressure enables obtaining pressure distribution in the Hertzian contact region, and also reveals the orientation of lubricating oil molecules using polarized light.

We previously used the micro FT-IR method to observe and report the concentration change and interaction of the additives with the base oils in the EHL film [7, 8] and oil-water concentration in aqueous lubricant such as emulsion [9-11]. We also discovered the effect of shearing orientation of liquid crystal molecules on the traction coefficient [12], high-pressure reactions in the Hertzian contact region [13, 14], and

that hydrogen-bonding of lubricating oil molecules is stabilized under high pressure [15].

In addition to determining the film thickness, *in situ* observation of lubricating film using a micro FT-IR is very useful for obtaining physical and chemical information, such as the pressure of the contact point, the concentration of mixture such as additives, the orientation of lubricating oil molecules, and the reaction and structural change of the lubricating oil.

Regarding rolling contact of grease lubrication, thickening of the EHL film due to thickener deposit to the contact area at low entrainment speed has been reported [16], and we previously conducted *in situ* observation of EHL films of greases using a micro FT-IR and reported how the thickener concentrated to form boundary films in rolling contact [17]. We also observed the film shapes and concentration distribution of thickeners for three types of diurea grease and showed the transient response of film thickness and thickener concentration changes when the slip ratio changed [18].

The present study enabled observation in low wavenumber ranges, which was not possible with conventional window materials, by using single crystal silicon (Si) as the disk material for a ball-on-disk type EHL tester (tribo-tester). Further, we observed *in situ* the Li and urea grease film shapes and concentration distribution of thickeners by combining an auto-mapping-equipped micro FT-IR and lubrication tester, with the objective to examine the effect of the thickeners on the lubrication film structure.

2 Experimental methods

The lubrication test was performed using a ball-on-disk type EHL tester (tribo-tester) as shown in Fig. 1, comprising a single crystal Si disk (105-mm diameter, 5-mm thickness) as the IR transmitting material and a 19-mm-diameter SUJ2 steel ball. The disk and the ball can be independently driven, and the speed and slip rate can be freely set. The load is applied by pushing the ball upward.

The lubricating oil subject for observation is restricted by the disk material, as being the window material for the infrared light. Sapphire has been used as the disk material in previous reports [14, 15], but has a narrow infrared transmission wavenumber range, where only high wavenumber at 2000 cm^{-1} and above, such as for stretching vibrations of C-H, N-H, and

O-H bonds. A CaF_2 disk will allow observation of absorbing vibration at lower wavenumbers including C=O stretching [7, 8], but it is calcium salt and thus may dissolve in polar base oils or additives. A spectrum can be obtained from all wavenumbers through a diamond window [12-14], but it is fixed and its size is limited, and therefore measurement can be carried out only under the pure sliding condition. Si allows observation of absorption of C=O stretching vibration. This Si has similar Young's modulus, Poisson's ratio, and Hertzian pressure distribution to the SUJ2 steel, the bearing material. This makes Si a suitable window material for observation of lubrication conditions for contact conditions close to that of an actual bearing. The Hertzian radius was $88\text{ }\mu\text{m}$ and the maximum Hertzian pressure was 0.61 GPa under the test load of 10 N .

Observation of the contact area was performed using a micro FT-IR. The infrared light, irradiated by a Cassegrain mirror, transmits through the Si disk and the lubricating film, is reflected by the steel ball surface, then absorbed via the mirror again into the spectrometer. Mapping measurement was performed over an area of $500 \times 500\text{ }\mu\text{m}$, with one measuring point being $50 \times 50\text{ }\mu\text{m}$ and the center of the Hertzian contact region as the origin, at 11×11 points in $50\text{-}\mu\text{m}$ intervals, totaling 121 points (Fig. 2). Although mapping measurement typically requires a motorized stage, the micro FT-IR contained an internal optical system scanning mechanism, which facilitates mapping without moving the stage. FT-IR measurement of each point was acquired 16 times, and the measuring time was 15 s. It is also possible to increase the time resolution of measurements by reducing the number of measuring points, and the change in the film thickness and thickener concentration with time were observed, by measuring them at only 1 point at the center of the contact area, immediately after the start of the experiment and at 45 s intervals.

This study carried out experiments under the pure rolling condition and a load of 10 N , an entrainment speed at 0.07 m/s for mapping measurement, and change with time measurement immediately after the start of the experiment. For the measurement of velocity dependence, a running-in was performed for about 20 min every time the speed was increased between the 0.07 to 0.35 m/s range before the FT-IR measurement.

Lithium stearate and aromatic diurea greases with polyalphaolefin (PAO) as base oil were used as sample greases.

Fig. 1 Tribo-tester for *in situ* IR measurement

Table 1 Chemical composition of sample greases

Grease	Worked penetration	Thickener
Li grease	323	Li stearate (12%)
Urea grease	417	Aromatic diurea (12%)

Fig. 2 Position of IR measurement around EHL contact area

Thickener concentration was 12% for both greases. The molecular structures of the thickeners along with the worked penetration are shown in Table 1.

Film thickness and thickener concentration were calculated from the infrared absorption spectrum of the lubricating film created by these greases. The film thickness was calculated from the integrated intensity of CH stretching vibration generated by the base oil, thickener concentration from the ratio of integrated intensity of C=O stretching vibration and CH stretching vibration generated by the thickener for the Li grease and ratio of integrated intensity of NH stretching vibration and CH stretching vibration generated by the thickener for the urea grease. Calibration curves were plotted for film thickness and thickener concentration, and the coefficients to calculate the film thickness and thickener concentration were determined from the integrated intensity and ratio of integrated intensity, respectively.

To prevent starvation, the greases were force-fed to the contact area with a syringe pump.

3 Results and discussion

Representative IR absorption spectra of EHL films generated by the Li and urea greases are shown in Fig. 3. "Position" in the figure indicates the measuring position from the center of Hertzian contact to the inlet. At around 1700–1600 cm^{-1} , carboxylate was observed in the Li grease, and C=O stretching vibration generated by the amide group thickener were observed in the urea grease. In addition, absorption of NH stretching vibration (amide group) was observed at 3300 cm^{-1} in the urea grease. In the Li grease, absorption of C=O stretching

Fig. 3 Typical IR spectra of EHL film of (a) Li grease and (b) urea grease

vibration has disappeared at the Hertzian contact inlet (-100 μm), while absorptions of NH and C=O stretching vibrations were observed at the center of the Hertzian contact in the urea grease.

Figure 4 shows the film shape and the thickener concentration of the contact area, obtained simultaneously from the spectra of the lubricating films through observation and mapping measurement of EHL films of Li and urea greases. The outlet side of concentration distribution is noisy as the signal-to-noise ratio of the spectra is low owing to the effect of cavitation. It was found that the thickener concentration of the Li grease is decreased compared to the bulk concentration of the preparation at the inlet and lateral periphery of the contact area. On the other hand, the thickener concentration of the urea grease increased starting at the inlet of the contact area, reached the maximum in the contact area, and retained the concentration as it existed from the contact outlet. In the study using a sapphire disk [17, 18], the thickener was also concentrated at the contact area. The concentration of the thickener at the sides of the contact area remained the same as the prepared concentration. These different behaviors of thickeners in the Li and urea greases clarified that the concentration is dependent on the thickener.

Figure 5 shows the film thickness and the thickener

Fig. 4 3D images of film thickness and thickener concentration

Fig. 5 Time dependence of film thickness and thickener concentration at the center of contact area

concentration at the center of the contact area immediately after the start of the experiment and the subsequent change with time in the Li and urea greases. The film thickness of the base oil and the Li grease was constant, while that of the urea grease increased with time until it reached a steady thickness. The figure also shows that the concentration of the thickener only doubled approximately in the Li grease, while that of urea grease increased to almost 100%, indicating that boundary films of concentrated thickener were formed on the surface of the ball and disk. This result suggests that the “running-in” phenomenon of lubricants could occur at the EHL area. When Kaneta et al. observed urea grease EHL films by optical interferometry, they observed a phenomenon that the groove provided on the ball was filled, and assumed the cause to be deposition of the thickener [19].

The ball and the disk used were rinsed with hexane after the test with the urea grease to remove the adhered oil content and were observed under a laser microscope (Fig. 6). A boundary film 0.1 to 0.3 μm thick was observed on the rolling contact surface of both the ball and the disk. This demonstrates that most of the thickness of the steady oil film observed in Fig. 5 was that of the boundary films. The width of the very thin boundary film indicated by “x” in the figure, observed on the disk side, is consistent with the Hertzian diameter, but the width of the boundary films indicated by “y” on both ball and disk images in the figure was 104 μm , narrower than the Hertzian diameter by 176 μm . This is assumed to reflect the thinnest part of the film existing inside the wings of a horseshoe

Fig. 6 Optical microscope images of surface after the lubrication test with urea grease

Fig. 7 IR spectra of adherent film and deoiled urea grease thickener

shape observed in an EHL point contact. Figure 7 shows the results of the IR measurement of the boundary film on the ball side. It is almost a match with the spectrum of the urea grease, obtained by deoiling the base oil by hexane, and the fact supports that boundary film is formed by the concentrated thickener.

The effect of entrainment speed on the EHL film structure in the Li and urea greases were examined. After observing the EHL film in oil-in-water emulsion under a micro FT-IR, concentration of oil and the film thickness at the inlet of the contact area (at $-150\ \mu\text{m}$) were previously reported to be highly interrelated [11], indicating that the film thickened due to the wedge effect brought on by the increased concentration of oil at the inlet. Based on this finding, the thickener concentrations at the inlets of the contact area (at $-150\ \mu\text{m}$) of the two greases in the present study are also shown in Fig. 8 along with the central film thicknesses. The film thickness of PAO, the base oil, is dependent on speed to the power 0.67, consistent with the EHL theory. The thickener concentration of Li grease decreases at low speed, and the film thickness was equivalent to that of the base oil. In other words, the lubrication was provided by the oil content separated from Li grease at low speed. At higher speed, the thickener concentrated, and the film became thicker than that of the base oil. Since the velocity dependency of the film thickness is parallel to that of the base oil, the thickener content caused the viscosity to increase and contributed to formation of the film. On the other hand, the phenomenon of forming a thick

Fig. 8 Effects of entrainment speed on the film thickness and the thickener concentration at the center of EHL contact

film even at low speed [20] was observed in the urea grease, but its velocity dependency was small. This reason for the small dependency is attributed to the boundary films formed by the thickener adhered to the ball and disk surfaces, as explained above. It is further thought that the decrease in thickener concentration at the inlet below 30%, as the speed increased, indicates the boundary film abrasion process with the speed increase.

Thus, it is clear that the EHL lubricating film structure of the greases is highly dependent on the thickener. The oil content of the Li grease is thought to separate easily at the inlet of the contact area, while the grease lubricates in a manner similar to the base oil at low speed. When the entrainment speed was increased, the thickener drawn to the inlet of the Hertzian contact region contributed to the formation of the film, causing the film thickness to be about double the thickness of the base oil. The urea grease, on the other hand, displayed a characteristic that its thickener concentrates, and therefore the boundary films at the contact area are thought to be formed almost entirely by the thickener. Owing to this characteristic, the grease formed a lubricating film a few times thicker than that of the base oil, with little velocity dependence. The cause of the thickener concentration in the urea grease is thought to be the adhesion by interaction of the thickener molecules and the surfaces and coagulation by interaction of the thickener molecules, and its mechanism is a topic for future examination.

This study revealed that the EHL film structure in grease lubrication is highly dependent on the thickener. Specially, the thickener in the urea grease formed boundary films, and this is thought to affect the lubricant properties. For example, use of urea grease is known to provide fretting wear resistance and anti-wear property under severe conditions and thus extend material life [21-23]. This can be attributed to the thick and soft boundary films formed by the thickener that protect the material surface. Urea grease is also known to be noisy and have poor acoustic properties [24], but this is partly attributed to the boundary films made of the thickener contacting with each other. Such dynamic structural change of the boundary films is thought to affect the tribological properties, and therefore is under further examination.

4 Conclusion

In situ observation of lubrication behavior was performed using a micro FT-IR to understand the structure of grease lubrication film in elastohydrodynamic lubrication (EHL) conditions. The effect of the thickeners on the lubricating film structure was examined using Li and urea greases. Comparison of the concentration at the EHL contact area showed that the concentration differed substantially according to the types of thickener. The thickener in the Li grease thinned at the Hertzian contact region while that in the urea grease thickened. Film thickness was dependent on the thickener concentration. The thickener concentration of the Li grease decreases at low speed, and the film thickness was equivalent to that of the base oil, but it formed a film approximately twice the thickness of that of the base oil at high speed, affected by the increased viscosity owing to the thickener concentration. The thickener in the urea grease, on the other hand, concentrated, and formed a well-adhered lubricating film at the Hertzian contact region. The effect of the entrainment speed on film thickness was small, and the lubricating film was formed by the boundary films made primarily of the thickener. The boundary films formed in the

urea grease grew out of the thickener adhered to the material surfaces, revealing the importance of the role of thickener boundary films in the lubrication performance of the grease.

Acknowledgement

The authors would like to thank the "Green Tribology Innovation Network," Green Network of Excellence (GRENE) program sponsored by the Ministry of Education, Culture, Sports, Science and Technology for support of this study.

References

- [1] Johnston, G. J., Wayte, R. and Spikes, H. A., "The Measurement and Study of Very Thin Lubricant Films in Concentrated Contacts," *Tribology Transactions*, 34, 2, 1991, 187-194.
- [2] Lauer, J. L., "Study of Polyphenyl Ether Fluid (5P4E) in Operating Elastohydrodynamic Contacts by Infrared Emission Spectroscopy," *Journal of Lubrication Technology*, 101, 1, 1979, 67-73.
- [3] Lauer, J. L., Keller, L. E., Choi, F. H. and King, V. W., "Alignment of Fluid Molecules in an EHD Contact," *ASLE Transactions*, 25, 3, 1982, 329-336.
- [4] Cann, P. M. and Spikes, H. A., "In Lubro Studies of Lubricants in EHD Contacts Using FTIR Absorption Spectroscopy," *Tribology Transactions*, 34, 2, 1991, 248-256.
- [5] Cann, P. M., Aderin, M., Johnston, G. J. and Spikes, H. A., "An Investigation into the Orientation of Lubricant Molecules in EHD Contacts," *Tribology Series*, 21, 1992, 209-218.
- [6] Cann, P. M., "The Influence of Temperature on the Lubricating Behavior of a Lithium Hydroxystearate Grease," *Eurogrease*, 8, 1995, 25-32.
- [7] Hoshi, Y., Shimotomai, N., Sato, M. and Mori, S., "Change of Concentration of Additives under EHL Condition -Observation by micro-FTIR-," *Journal of Japanese Society of Tribologists*, 44, 9, 1999, 736-743 (in Japanese).
- [8] Takiwatari, K., Nanao, H., Minami, I. and Mori, S., "The Interaction between Oleic Acid and Base Oils at Elastohydrodynamic Lubrication," *Journal of Japanese Society of Tribologists*, 54, 1, 2009, 48-53 (in Japanese).
- [9] Hoshi, Y., Minami, I. and Mori, S., "Change in Concentration of Water-Glycol Hydraulic Fluid near the EHL Contact Region -Observation by Micro FT-IR-," *Journal of Japanese Society of Tribologists*, 49, 11, 2004, 878-885 (in Japanese).
- [10] Shitara, Y., Yasutomi, S. and Mori, S., "Direct Observation of W/O Emulsion in Concentrated Contact by FT-IR Microspectroscopy," *Journal of Japanese Society of Tribologists*, 55, 10, 2010, 736-744 (in Japanese).
- [11] Shimotomai, N. and Mori, S., "In-Situ Observation of the Lubrication Film in O/W Emulsion by Micro FT-IR," *Journal of Japanese Society of Tribologists*, 56, 1, 2011, 47-54 (in Japanese).
- [12] Mori, S. and Iwata, H., "Relationship between Tribological Performance of Liquid Crystals and Their Molecular Structure," *Tribology International*, 29, 1, 1996, 35-39.
- [13] Mori, S., Shimotomai, N., Shimoguchi, A. and Imai, J., "Observation of a High Pressure Reaction Using a Lubrication Field," *Proc. JAST Tribology Conference, Tokyo, 1998*, 302-303 (in Japanese).
- [14] Ishikawa, J., Nanao, H., Minami, I. and Mori, S., "High-Pressure Polymerization Reaction of Vinyl Monomer in EHL Contact," *Proc. JAST Tribology Conference, Tottori, 2004*, 243-244 (in Japanese).
- [15] Takiwatari, K., Nanao, H. and Mori, S., "Effect of High Pressure on Molecular Interaction between Oleic Acid and Base Oils at Elastohydrodynamic Lubrication Contact," *Lubrication Science*, 22, 3, 2010, 89-101.

- [16] Cann, P. M. and Spikes, H. A., "Film Thickness Measurements of Lubricating Greases Under Normally Starved Conditions," *NLGI Spokesman*, 56, 2, 1992, 61-67.
- [17] Hoshi, Y., Sato, M., Takiwatari, K., Nanao, H., Yashiro, H. and Mori, S., "3D Imaging of EHL Film by a Micro Infrared Spectroscopy," *Proc. JAST Tribology Conference*, Tokyo, 2013, B5 (in Japanese).
- [18] Hoshi, Y., Takiwatari, K., Sasaki, R., Nanao, H., Yashiro, H. and Mori, S., "Observation of Transient Responses in Grease Lubrication by a Micro Infrared Spectroscopy," *Proceedings of JAST Tribology Conference*, Tokyo, 2014, E18 (in Japanese).
- [19] Kaneta, M., Nishikawa, H. and Naka, M., "Effects of Transversely Oriented Defects and Thickener Lumps on Grease Elastohydrodynamic Lubrication Films," *Proceedings of the Institution of Mechanical Engineers, Part J: Journal of Engineering Tribology*, 215, 3, 2001, 279-288.
- [20] Dong, D. and Endo, T., "EHL with Various Lubricants –Grease–," *Journal of Japanese Society of Tribologists*, 56, 1, 2011, 24-29 (in Japanese).
- [21] Takeuchi, K., "Grease," *Journal of Japanese Society of Tribologists*, 38, 2, 1993, 181-184 (in Japanese).
- [22] Maruyama, T. and Saitoh, T., "Difference in Preventive Mechanism for Fretting Wear between Oil and Grease Lubrication," *Journal of Japanese Society of Tribologists*, 56, 12, 2011, 788-796 (in Japanese).
- [23] Nakajima, S., Izaki, K., Takemura, K., Kimura, Y. and Cann, P. M., "Development of New Urea Grease for Steel Continuous Casting Machine Under Boundary Lubrication," *NLGL Spokesman*, 68, 8, 2004, 8-16.
- [24] Watanabe, E., Sonoda, K., Toda, Y., Hachiya, K., Yamamoto, A., Yamamoto, M., Matsubara, K. and Imai, J., "Rolling Device," *WIPO Patent WO/2014/088006A1*, 2014.