



Article

In Situ Observation of Transient Responses in Grease Lubrication by Micro Infrared Spectroscopy

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Abstract

In situ observation of lubricant films formed with greases was carried out at EHL conditions with a micro-FTIR. Three urea compounds were used as a thickener and 12 mass percent of the thickener was added in PAO, respectively. From the IR spectra, CH and NH stretching vibration peaks were observed from urea greases. The film thickness and the concentration of thickener were estimated from the absorbance of CH and the ratio of absorbance of NH and CH. Two-dimensional distribution of the thickness and the concentration around Hertzian contact was obtained at the resolution of 50 μm . The thickener of urea grease was concentrated on ball and disk surfaces. It was found that the concentrate on thickener at Hertzian contact region was dependent on thickener itself. Time dependence of the thickness and the concentration at Hertzian contact were obtained at the resolution of 45 s under shearing conditions. The film thickness of urea greases at Hertzian contact was greatly decreased by shearing and the film thickness and the concentration were recovered when the condition was changed to rolling. This behavior was supposed with detachment and growth of the adhered film of the thickener. Lubricating characteristics of urea greases were discussed based on the concentration of thickener at Hertzian contact.

Keywords

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

1 Introduction

In recent years, urea grease, the use of which has been expanding, has attracted significant attention owing to its superior properties such as thermal and mechanical stabilities and a longer lifespan compared to metal soap grease. There have been various reports on the rheological properties of the mesh structure of the thickener and its structural changes [1, 2], as well as on thick elastohydrodynamic lubrication (EHL) films at low speed [3, 4]. An observation of the rolling surface after testing using micro-Fourier transform infrared spectroscopy (micro-FTIR) suggests that the thickness of the film is due to the adhesion/deposition of the thickener [5]. Furthermore, a thick film was not found with a polar base oil under an *in situ* micro-FTIR observation [6], suggesting the inhibition of growth of the adhered film by the polar base oil. In addition, urea grease is known to prolong the material life under severe conditions such as fretting resistance and abrasion resistance [7, 8]. That is thought to be due to the protection of the material surface by an adhered film from the adhesion/deposition of the thickener.

We observed previously a grease EHL film *in situ* using micro-FTIR, and confirmed that the thickener was condensed at the rolling contact area of the urea grease, and revealed that a thick film was caused by the formation of an adhered film from the condensed thickener [9].

The behaviors of a thickener in a grease lubrication are complex. In actual grease lubrication, the performance must be capable of responding to changes to the various contact conditions such as a sliding contact and starvation. To understand the grease lubrication occurring under EHL conditions, there have been reports on the *in situ* observation of the increase in oil film thickness within the low-speed region of the rolling contact using optical interferometry [10], as well as an *in situ* observation of the orientation of the grease thickener molecules using micro-FTIR [11]. In both studies, measurements were conducted under a steady state of EHL. However, in reality, the lubrication conditions fluctuate, and it is therefore necessary to observe the "living" lubrication site *in situ*.

Regarding the formation of an adhered film under EHL conditions, an optical interference method was used to observe

the time course of the growth of a metal-detergent adhered film [12], although this method requires the observation to be conducted in a stationary state. Another study reported an *in situ* observation of the formation of an adhered film by urea grease using an optical interference method under fretting conditions [13]. In both cases, however, only the oil film thickness was obtained and no chemical information of the adhered film was obtained. In addition, urea grease is known to have higher noise and poorer acoustic characteristics than lithium soap grease [14, 15], which may possibly result from the behavior of the adhered film of the thickener in response to changes in the lubrication conditions, such as the rotational speed, slide-to-roll ratio, and load. To observe an adhered film sensitive to the formation conditions, such as urea grease, an *in situ* observation is necessary to study the responses to dynamic changes to the lubrication conditions such as a variance of the slide-to-roll ratio, particularly under EHL conditions.

In this study, the purpose is first to observe a grease lubrication film using micro-FTIR, and then observe the transient responses of the oil film thickness and thickener concentration to changes in the slide-to-roll ratio, and clarify the dynamic structural change of the adhered film of the thickener.

2 Experimental methods

A ball-on-disk type lubrication tester shown in Fig. 1 was used. The disk (105 mm in diameter, 11.5 mm in thickness) was made of sapphire, which is an IR transmitting material, and a 19-mm diameter SUJ2 steel ball was applied. The disk and ball can be driven independently, and any speed and slide-to-roll ratio can be set. The load is applied by pushing the ball up. A torque meter is connected to the rotating shaft of the ball to measure the traction force when a slip is applied. In this study, tests were carried out at an entrainment speeds of 0.05–0.07 m/s, slide-to-roll ratios of 0–70%, and a load of 20 N. The Hertzian radius was 98 μm and the maximum Hertzian pressure was 0.99 GPa under a test load of 20 N.

The contact area was observed using micro-FTIR. The infrared light, focused using a Cassegrain mirror, was reflected onto the ball surface, and the IR spectrum of the lubricant film was obtained. The measurement range was 50 μm × 50 μm, and mapping measurements were conducted at 11 × 11 points in 50-μm intervals with the origin at the center of the Hertzian contact region, as shown in Fig. 2. By contrast, the IR spectra of the lubricant films were also obtained as a 45-s line scan at only

three measurement points at 0, 150, and 300 μm from the inlet to the center of the contact area. A single line scan took 45 s, and the time-dependent changes in the spectrum at the three points were monitored. In particular, we observed changes over time in the oil film thickness and the thickener concentration when the slide-to-roll ratio was changed.

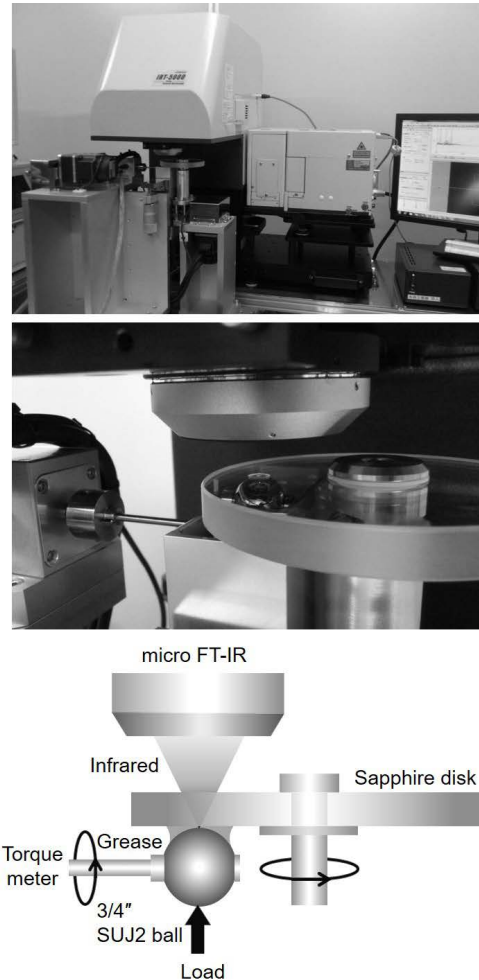


Fig. 1 Tribo-tester for *in situ* IR measurement; reproduced with permission from [18] Copyright (2016) Japanese Society of Tribologists

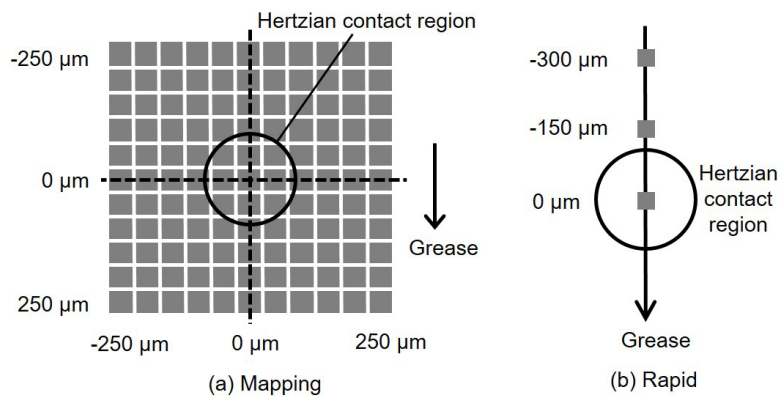
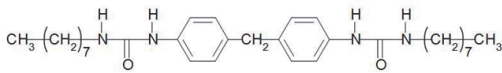
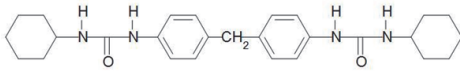
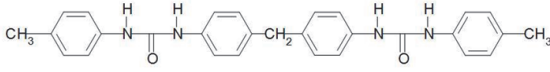


Fig. 2 Position of IR measurement around EHL contact area; reproduced with permission from [18] Copyright (2016) Japanese Society of Tribologists

Table 1 Chemical composition of sample greases; reproduced with permission from [18] Copyright (2016) Japanese Society of Tribologists

Base oil	Thickener Concentration: 12%	Worked penetration
Poly- α -olefin (PAO) 48 mm ² /s (40°C)	 Aliphatic diurea	242
	 Alicyclic diurea	287
	 Aromatic diurea	356

As shown in Table 1, three types of diurea grease, aliphatic, alicyclic, and aromatic, with polyalphaolefin as the base oil, were used as the samples. The thickener concentration was 12% in each case. The oil film thickness was calculated from the area intensity of the CH stretching vibration generated by the base oil, and the thickener concentration was calculated from the area intensity ratio between the NH and CH stretching vibrations by the thickener and the base oil, respectively. Grease was force-fed to the contact area using a syringe pump.

3 Results and discussion

Figure 3 shows a typical IR spectra of the aromatic diurea grease lubricant film. Because the urea grease thickener has NH bonds, absorption by NH stretching vibration can be seen. The base oil, polyalphaolefin, can be confirmed by the absorption through the CH stretching vibration. Each mark in the figure indicates the measurement position from the center of the Hertzian contact region to the inlet. As the measurement moves closer to the center of the Hertzian contact region, the absorption from the CH stretching vibration by the base oil decreases as the oil film thickness decreases, whereas the absorption intensity of the NH stretching vibration of the urea grease does not change substantially. This indicates an increase in the thickener concentration with a decrease in the oil film thickness. Here, the film thickness was calculated from the absorption intensity of the CH stretching vibration, and the thickener concentration was calculated from the absorption intensity ratio between the NH and CH stretching vibrations. Calibration curves were created for the oil film thickness and thickener concentration, and the coefficients for calculating the oil film thickness and thickener concentration were determined based on the area intensity and its ratio.

Three-dimensional images of the oil film shape and thickener concentration obtained from the mapping measurements are presented in Fig. 4. The lubricant oil enters from the rear-left side and exits the front-right side. The thickener concentration increases from the contact area inlet side, reaches the maximum at the contact area, and exits at the same concentration. By contrast, the thickener concentration on the side of the contact area was found to remain at the initial concentration. Whereas a similar condensation of

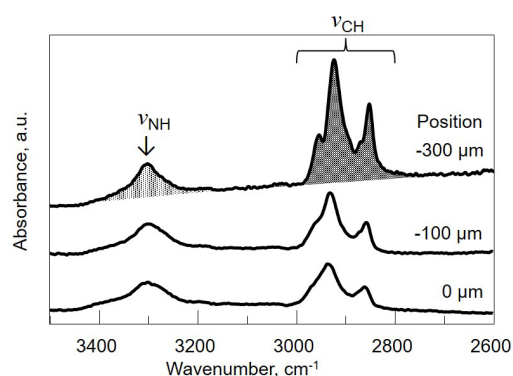


Fig. 3 Typical IR spectra of EHL film of aromatic diurea grease; reproduced with permission from [18] Copyright (2016) Japanese Society of Tribologists

the thickener was observed for all types of urea grease, a thickener concentration of over 90% was found for the aliphatic and aromatic diurea grease types and a concentration of approximately 80% was found for the alicyclic diurea grease.

This condensation of the thickener may occur for two different reasons: Bulk condensation with a loss of the base oil from the grease; and the apparent condensation by the adhesion of the thickener on the surfaces of the disk and ball. Here, the film thickness and concentration of the aromatic diurea grease in a stationary state after the lubrication test are shown in Fig. 5. Despite the remaining stationary state, a thick film of 1 μm was detected, and we confirmed the presence of a film with a thickener concentration of close to 100%. Similar film formations were observed for aliphatic and alicyclic types of diurea grease. This result indicates that an adhered thickener film was formed on the ball and disk surfaces. The formation of the adhered thickener film with urea grease was also found in a previous study using Si disks [9], which supports the observation of the present study.

Furthermore, using urea grease, we previously observed that the oil film thickness gradually increased approximately 2 min after the start of the test and then reached a steady state [9]. Based on this result, in this study, we thus observed a time-dependent response to changes in the lubrication conditions.

Grease exhibits thixotropy, in which the viscosity changes over time under continuous shear stress. In addition, it also exhibits shear thinning, in which the viscosity decreases with an increase in the shear rate owing to the shear orientation of the thickener molecules. In a study on the rheological properties of grease [2], it was claimed that urea grease mostly has a mesh

structure with a high shear strength. Regarding the thick film that occurs during low-speed grease lubrication, there have also been reports indicating that the phenomenon occurs as an EHL when applying the Carreau-Yasuda model equation to the grease rheological properties [3, 4]. In our study, we focused on shearing, and investigated the change in the lubricant film

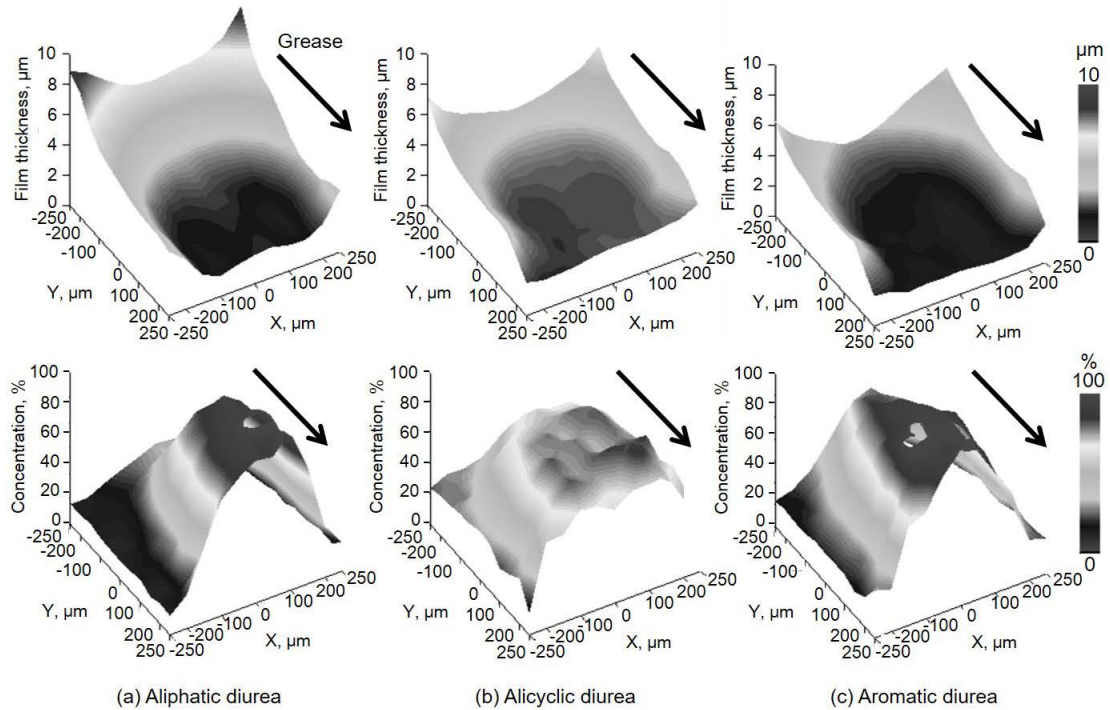


Fig. 4 3D images of film thickness and thickener concentration; reproduced with permission from [18] Copyright (2016) Japanese Society of Tribologists

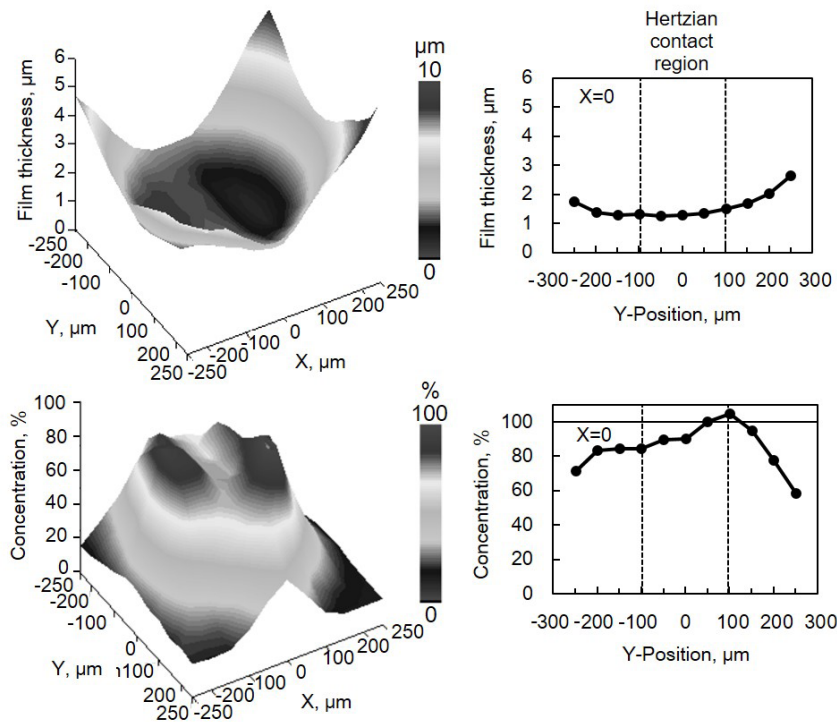


Fig. 5 Film thickness and thickener concentration of aromatic diurea grease after testing; reproduced with permission from [18] Copyright (2016) Japanese Society of Tribologists

structure in response to changes from rolling to sliding, and vice versa. Herein, we presented the time dependence of each diurea grease lubricant film at three measurement points. First, the time dependence of the aliphatic diurea grease is shown in Fig. 6. Initially, under rolling conditions, the oil film thickness increased with the condensation of the thickener, and the film thickness and thickener concentration reached a steady state after a few minutes. That showed that an adhered film of condensed thickener was formed on the surfaces of the ball and disk within a few minutes. After a steady state, the slide-to-roll ratio was changed from 0 to 70%. Sudden drops in the film thickness and thickener concentration were then observed. That was thought to be the process through which

the adhered film is removed by shearing force. The thickener concentration at the Hertzian contact inlet decreased to almost the bulk concentration by sliding. When the slide-to-roll ratio was repeatedly changed from 0%→70%→0%→70%, the formation and detachment of the adhered film of the thickener were repeated with good reproducibility. Interestingly, the rate of detachment was higher than the growth rate of the thickener-adhered film for all thickeners tested.

As shown in Fig. 7, the alicyclic diurea grease showed fewer changes in film thickness and thickener concentration than the aliphatic diurea grease. In the case of the aromatic diurea grease shown in Fig. 8, changes in film thickness and thickener concentration were also observed, but not as much as for the

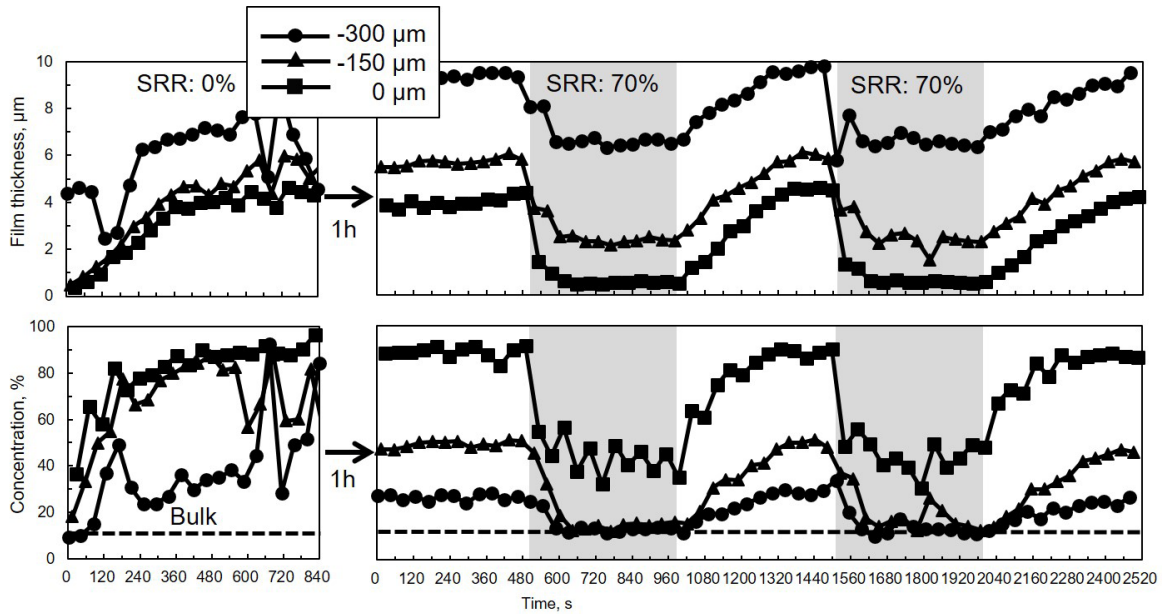


Fig. 6 Time dependence of film thickness and thickener concentration of aliphatic diurea; reproduced with permission from [18] Copyright (2016) Japanese Society of Tribologists

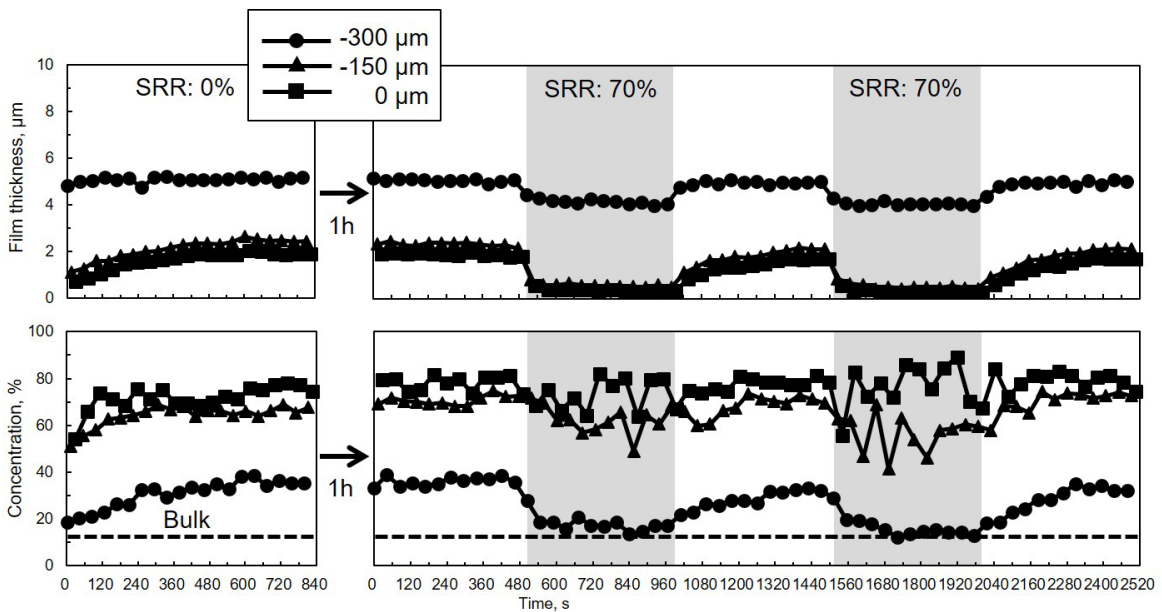


Fig. 7 Time dependence of film thickness and thickener concentration of alicyclic diurea; reproduced with permission from [18] Copyright (2016) Japanese Society of Tribologists

aliphatic diurea grease. A faster response of the film thickness and thickener concentration to changes in the slide-to-roll ratio than that of the aliphatic and alicyclic diurea grease types was also demonstrated. We thereby zoomed in on the region where the slide-to-roll ratio was changed and compared the results, as shown in Fig. 9. The detachment of the adhered film occurred under the sliding conditions, adhered film was reformed under the rolling conditions. Interestingly, the response of the grease to the slide-to-roll ratio was found to depend on the type of thickener applied. Regarding the change in film thickness, the growth rate was lower than the detachment rate, and the growth rate for the aromatic diurea type grease tended to be higher. The detachment of the adhered film was presumably dependent on the shear owing to the contact between the adhered films on the ball and disk surfaces. However, the formation of the adhered film is likely to depend on the readiness of the separation of

the base oil and thickener. The consistency of the urea grease is correlated with the oil separation [16]. Oil separation increases as the high consistency and softness increases. Because the aromatic diurea greases achieves the highest consistency among the three types of grease used in this study, and thereby separates easily from the oil, we speculated that it leads to a high growth rate of the thickener squeezed out from the base oil.

Variations in the film thickness and the thickener concentration with the change in slide-to-roll ratio is shown in Fig. 10. Based on the results of the transient responses in Figs. 6–8, we plotted the thickener concentration and oil film thickness at each measurement point when the slide-to-roll ratio was changed to 70% (closed dots) and 0% (open dots). The results show the correlation between the film thickness and thickener concentration. For example, the aliphatic diurea grease exhibited a significant change of 3 μm in thickness,

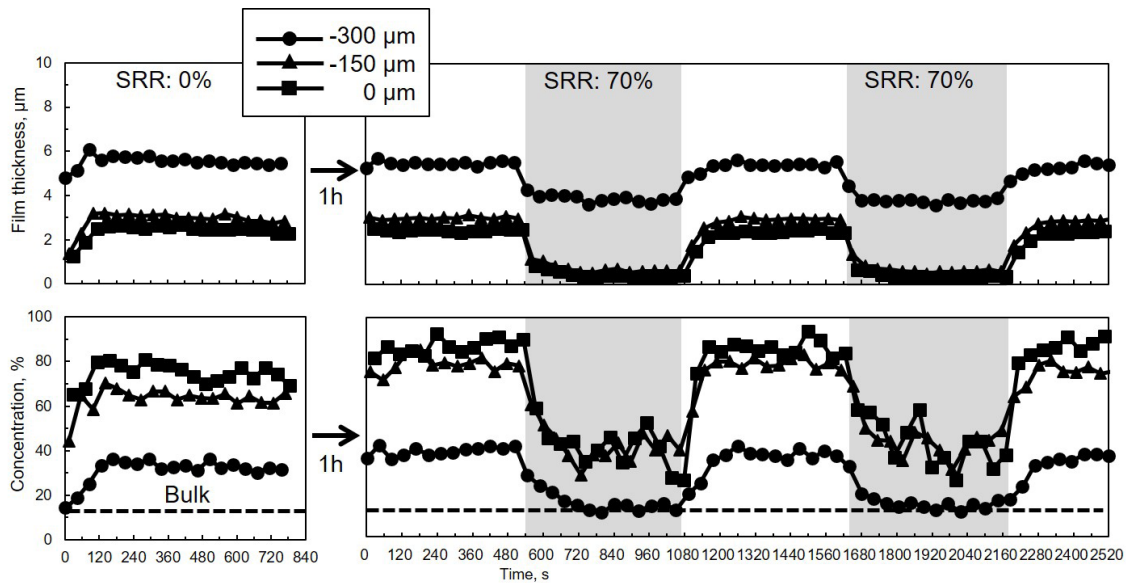


Fig. 8 Time dependence of film thickness and thickener concentration of aromatic diurea; reproduced with permission from [18] Copyright (2016) Japanese Society of Tribologists

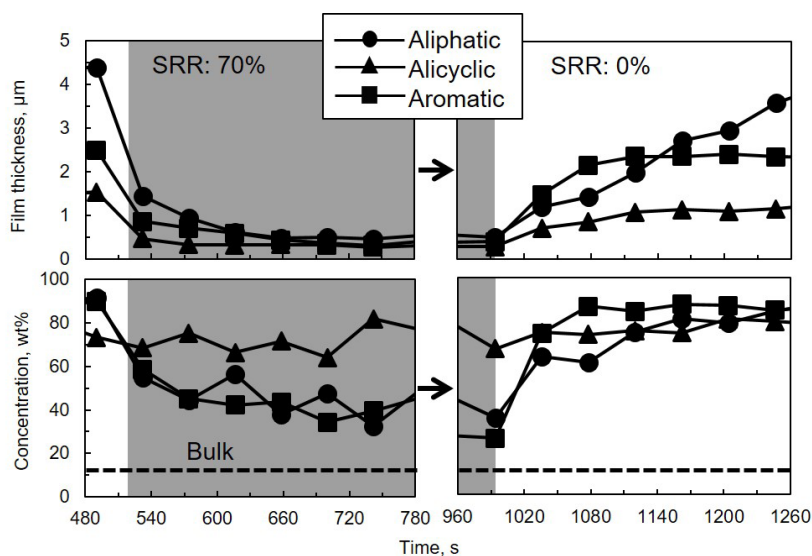


Fig. 9 Time dependence of film thickness and thickener concentration of each diurea; reproduced with permission from [18] Copyright (2016) Japanese Society of Tribologists

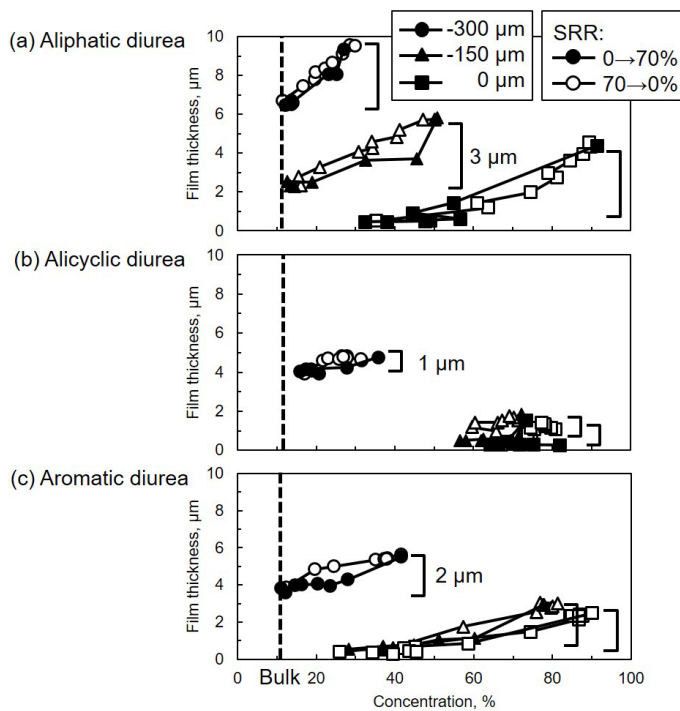


Fig. 10 Relationship of film thickness and thickener concentration; reproduced with permission from [18] Copyright (2016) Japanese Society of Tribologists

demonstrating the readiness of the formation and detachment of the adhered film. In contrast, for the case of the alicyclic diurea grease, the change was only 1 μm, showing a limited ability to grow the adhered film. In addition, the alicyclic diurea grease exhibited the least condensation of thickener in the Hertzian contact region under rolling conditions compared to the aliphatic and aromatic diurea grease types, but the highest condensation under sliding conditions. That indicates that the adhered film formed was resistant to a detachment under sliding conditions. The fluctuations in the film thickness by shearing were dependent on the type of thickener. Furthermore, the range of fluctuation of the film thickness for each thickener was constant for the three measurement points, which suggests that this fluctuation corresponds to the range of variations in the formation and detachment of the adhered film. Such a significant variations in oil film thickness under rolling-sliding conditions is thought to adversely affect the acoustic characteristics when used in bearings that require low noise, such as in motors. In fact, urea grease is inferior in terms of its acoustic characteristics [14, 15], one of the reasons for which is presumed to be the fluctuation in the thickness of the adhered film described in this study.

Compared to the adhered film thickness of the aromatic diurea grease previously observed [9], the adhered film thickness in this study was one order of magnitude greater. This is presumably due to the differences in the applied load and contact pressure resulting from the differences in materials of the Si and sapphire disks (where the maximum Hertzian pressure of the Si disk is 0.61 GPa, and that of the sapphire disk is 0.99 GPa). This implies a strong dependence of the adhered film formation on the contact pressure. In a previous study, in which the peak shift of the NH stretching vibration by the thickener was observed *in situ* using a similar method [17], a red shift of the NH stretching vibration was observed in the high-pressure contact region, indicating that the intermolecular

hydrogen bonds of the thickener were stabilized, thereby suggesting the agglomeration of thickener fibers through the contact pressure.

The response of the traction coefficient was measured simultaneously through *in situ* observations. Despite the changes in the film thickness and the thickener concentration, the traction coefficient remained almost constant. That indicates that, during the formation and detachment of the adhered film, there are two possible states: A three-layer structure comprised of an adhered film layer, an oil film layer, and an adhered film layer, where the traction coefficient mainly depends on the oil layer; or a mixed lubrication in which adhered films are partially in contact with each other without an oil layer and thus bringing about wear. The traction coefficient was 0.09 for the aromatic diurea grease, and higher than 0.06 for the base oil. If this system is in a state with a three-layer structure, the coefficient for the grease should be closer to the base oil. We thus presume the latter, and the mixed lubrication model (Fig. 11) is more appropriate. Under the mixed lubrication conditions, the solid adhered films are in contact with each other without having an oil film in between, which can explain the high traction coefficient of the grease.

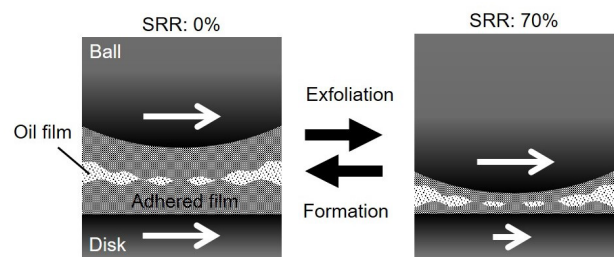


Fig. 11 Mixed lubrication model; reproduced with permission from [18] Copyright (2016) Japanese Society of Tribologists

4 Conclusion

An *in situ* observation of lubricant films formed using three types of diurea greases under lubrication conditions was conducted by applying micro-FTIR spectroscopy. The shape of the lubricant film and concentration distribution of the thickener around a Hertzian contact were studied under dynamic conditions. The results show that all three types of greases form lubricant film of 2–3 μm in thickness, and the thickener was condensed around the Hertzian contact at a concentration of more than 80%. In addition, a high concentration of thickener was detected even in a stationary state after the lubrication tests, which indicated that the condensation of the thickener was mainly due to its adhesion to the ball and disk surfaces. We also observed the transient response of the lubricant film structure when the lubrication conditions were changed from rolling to sliding (slide-to-roll ratio of 70%). Shear caused a reduction of the thickener concentration and the lubricant film thickness. It was found that the thickener concentration and thickness of the lubricant film was recovered to the initial steady-state values by switching back from sliding to rolling. The film thickness and thickener concentration were linearly correlated for all thickeners. The response of the film thickness and concentration of the thickener to the slide-to-roll ratio was dependent on the type of thickener applied. When this variance was considered in the formation of the adhered film and its detachment, the growth rate became slower than the detachment for all types of diurea grease, and the growth rate for aromatic diurea grease had a tendency to be high. The change in film thickness with roll-slide switching was dependent upon the thickener in order of alicyclic < aromatic < aliphatic grease.

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