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# Highly Swollen Adsorption Layer Formed by Polymeric Friction Modifier Providing Low Friction at Higher Temperature

Naoki Yamashita*, Tomoko Hirayama*, Norifumi L. Yamada**, Honami Watanabe***, Ko Onodera***, and Takehisa Sato***

*Department of Mechanical Engineering and Science, Graduate School of Engineering, Kyoto University, Katsura, Nishikyo-ku, Kyoto 615-8540, Japan
**Neutron Science Division, High Energy Accelerator Research Organization (KEK), 203-1 Shirakata, Tokai, Naka, 319-1106, Ibaraki, Japan
***EMG Lubricants Godo Kaisha, 6-1 Ukishima-cho, Kawasaki-ku, Kawasaki, Kanagawa 210-9526, Japan

## Abstract

To reduce friction, especially under high-temperature conditions, an oil-soluble polymeric friction modifier (polymeric FM) with a methacrylate backbone and hydroxyl groups has been developed. It was designed to have high adsorption performance and to increase in size when dissolved in base oil as the temperature is increased. To investigate the temperature dependence of the structural and tribological characteristics of the adsorbed layer formed on a metal surface by the polymeric FM, neutron reflectometry measurements and nano-to-macro tribological tests were conducted. The measurements revealed that the polymeric FM adsorbed efficiently on a Cu surface and formed a 6.0-nm-thick adsorbed layer at 23ºC. This adsorbed layer was highly swollen, and its thickness became about three times larger at 100°C. Nanoscale friction tests using an atomic force microscope showed that the swollen-state adsorbed polymeric FM layer exhibited low-friction and surface-protection performance at 100°C. Macroscale friction tests revealed the tribological behaviour of an adsorbed polymeric FM layer in elastohydrodynamic lubrication and mixed lubrication regimes. At higher temperatures, the increase in shear resistance due to the effect of thin-film lubrication was suppressed by the weaker segment-segment interaction, causing the boundary contact of the adsorbed polymeric FM layer to have low frictional properties on both ball and disk surfaces. The low-friction mechanism of the adsorbed polymeric FM layer at higher temperatures was justified by associating the temperature with the layer thickness.

Keywords: Polymeric friction modifier, Lubrication, neutron reflectometry, nanotribology

## 1. Introduction

To reduce friction loss in automotive engines, various methods for achieving good lubrication by the use of oil have been developed over the years. Using low-viscosity oil, which reduces viscous resistance, is one approach to further reducing friction loss and saving energy. However, using low-viscosity oil can cause high friction and thus increase wear, especially under high-temperature conditions, due to reduced oil film thickness on the sliding surface. In addition, the temperature of automotive engine oil usually rises to around 100°C, so additives that work effectively at higher temperatures are required.

Organometallic friction modifiers (FMs) and anti-wear agents, such as molybdenum dialkyldithiocarbamate (MoDTC) and zinc dialkylphosphate (ZDDP), have traditionally been used to reduce friction and wear on sliding surfaces [1–3]. However, sulphur and phosphorus oxides and metallic ash derived from these additives can reduce the effectiveness of automotive aftertreatment devices such as three-way catalysts and diesel particulate filters. Additionally, these additives need repeated friction under high-temperature and high-contact-pressure conditions to efficiently form reaction film on metal surfaces [1, 4, 5]. In contrast, adsorption-type organic FMs, such as palmitic acid and glycerol monooleate (GMO), reduce friction and wear without such reactions since they adsorb on metal surfaces and form functional film [6]. There are many types of organic FMs with various kinds of polar groups such as fatty acid [7], alcohol [8], and amine [9]. In general, they reduce friction and wear only under moderate temperature and load conditions because they have a weaker interaction with the surface compared with organometallic additives [10].

Recently proposed and developed polymer-type organic FMs (polymeric FMs) have multiple functional groups in their structure and thus strongly adsorb on metal surfaces, forming an adsorption layer. Their strong adsorption onto metal surfaces via functional groups enables them to work even under high-temperature and high-load conditions. The tribological properties of the adsorbed layer of polymeric FMs have been investigated by using a friction tester with an optical interferometer to measure the friction and oil film thickness between a rotating glass disk and metal ball [11–16]. Fan and Müller reported that amino groups and hydroxyl groups on polymethacrylate enhance oil film formation under low-speed conditions and exhibit low-friction characteristics even under high-temperature conditions (over 100°C) [12, 13]. Muraki evaluated the effect of the alkyl chain length of polyalkylmethacrylate and found that the film-forming capability was better with shorter alkyl chains and that friction was lower under low-speed conditions with longer alkyl chains [14].

These studies have shown that polymeric FMs effectively provide low friction in elastohydrodynamic lubrication (EHL) and mixed lubrication regimes by forming a thick adsorption layer on metal surfaces. However, one of the challenges of utilizing polymeric FMs is that it increases the viscosity of the lubricant oil due to their high molecular weight, which is typically over 10,000. To suppress this viscosity increase, it is necessary to design polymeric FMs with two particular features. First, the FM should efficiently form an adsorbed layer on metal surfaces to provide low-friction properties even at a low concentration in base oil. Second, it should shrink at lower temperatures in order not to affect the fluidity of the base oil [17–19].

In consideration of these two features, an oil-soluble polymeric FM with a methacrylate backbone and hydroxyl groups, which provide high-adsorption performance and swelling at high temperature, was developed. To investigate the temperature dependence of the structural and tribological characteristics of the adsorbed polymeric FM layer, we conducted a series of experiments. We first investigated its macroscale tribological characteristics in EHL and mixed lubrication regimes by using a mini traction machine (MTM) tribometer and evaluated the change in its characteristics due to temperature rise. Next, we examined the interfacial structural and nanoscale tribological characteristics of an adsorbed layer formed on a Cu surface by neutron reflectometry and friction tests using an atomic force microscope (AFM) with a colloidal probe cantilever. Finally, we clarified the mechanism of low friction at higher temperatures provided by the adsorbed polymeric FM layer by associating the temperature with the layer thickness.

## 2. Characteristics of developed polymeric FM

The developed oil-soluble polymeric FM has a molecular weight of ~20,000 g/mol and is composed of a polymethacrylate backbone and hydroxyl groups. A schematic illustration of its molecular structure is shown in Fig. 1. Since this polymeric FM is methacrylate-type, its conformation should more likely change with a temperature rise than a olefin copolymer-type FM [20]. Since it is expected to shrink at low temperature and less affect the fluidity of the base oil, it should negligibly affect oil viscosity. In addition, the polymeric FM was designed to swell at high temperature, which increases the thickness of its adsorbed layer and thereby improves the tribological properties. It is expected to exhibit good lubricity, like that of a polymer brush. Since it has many hydroxyl groups in its structure and can thus efficiently adsorb to a metal surface at multiple points, its functionality should be maintained even under high-temperature and high-load conditions compared with an ordinary organic FM with single-point adsorption [15].

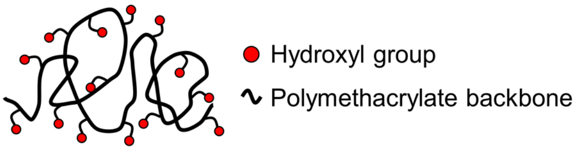


Fig. 1 Schematic illustration of oil-soluble polymer-type friction modifier.

## 3. Macroscale friction test using MTM tribometer

### 3.1 Experimental procedure

To determine whether the developed polymeric FM reduces friction at high temperature as expected, we evaluated the macro tribological properties of its adsorbed layer using an MTM tribometer (MTM2; PCS Instruments). A Stribeck-like curve for speed dependence from the EHL regime to the mixed lubrication regime was measured under several temperature conditions.

Table 1 Viscosities of lubricants used in friction tests.

| Lubricant | Kinematic viscosity [mm$^2$/s] | |
|---|---|---|
| | at 40°C | at 100°C |
| Gr. III base oil | 18.4 | 4.1 |
| Gr. III oil + polymeric FM (0.4 mass%) | 18.6 | 4.1 |
| Gr. III oil + GMO (1.0 mass%) | 18.6 | 4.2 |

We evaluated the macroscale frictional properties of the developed polymeric FM dissolved at a concentration of 0.4 mass% in Gr. III oil by using the MTM tribometer. To verify its effect, a lubricant with 1.0 mass% GMO in Gr. III oil, which is a sufficient concentration to reduce friction [21], was used for comparison as an ordinary organic FM. The viscosities of the lubricants used in the friction test are shown in Table 1. The concentrations of polymeric FM and GMO were low enough for the viscosities to be close to that of the Gr. III base oil alone. The experimental conditions are summarized in Table 2. A steel disk was soaked in a sufficient amount of 0.4 mass% polymeric FM or 1.0% GMO solution in Gr. III oil prior to friction force measurement. The rotational speeds of the ball and disk were independently controlled. The sliding-rolling ratio (*SRR*) was set to 50%, to investigate the

Table 2 Conditions for macroscale friction test using MTM tribometer.

| | | |
|---|---|---|
| Material | Ball | AISI 52100 steel<br>(Young's modulus: 210 GPa)<br>(Poisson's ratio: 0.3) |
| | Disk | |
| Roughness [μm] | Ball | < 0.01 |
| | Disk | |
| Hardness [HV] | Ball | 800-920 |
| | Disk | 720-780 |
| Ball diameter [mm] | | 19.05 |
| Sliding rolling ratio [%] | | 50 |
| Load [N] | | 36.6 |
| Hertzian contact pressure [GPa] | | 1.0 |
| Entrainment speed [mm/s] | | 5–3000 |
| Temperature [°C] | | 40, 60, 80, 100 |

tribological behaviour of polymeric FM in EHL and mixed lubrication regimes.

$$SRR = \frac{U_{ball} - U_{disk}}{U},$$

where $U_{ball} - U_{disk}$ is the sliding speed between the rotating steel disk and ball and $U$ is the entrainment speed:

$$U = \frac{U_{ball} + U_{disk}}{2}.$$

The entrainment speed of the ball and disk was initially 3000 mm/s and then gradually reduced every 6 s until it reached 5 mm/s. The test temperature was set at 40, 60, 80, and 100°C to evaluate the temperature dependence of the tribological properties.

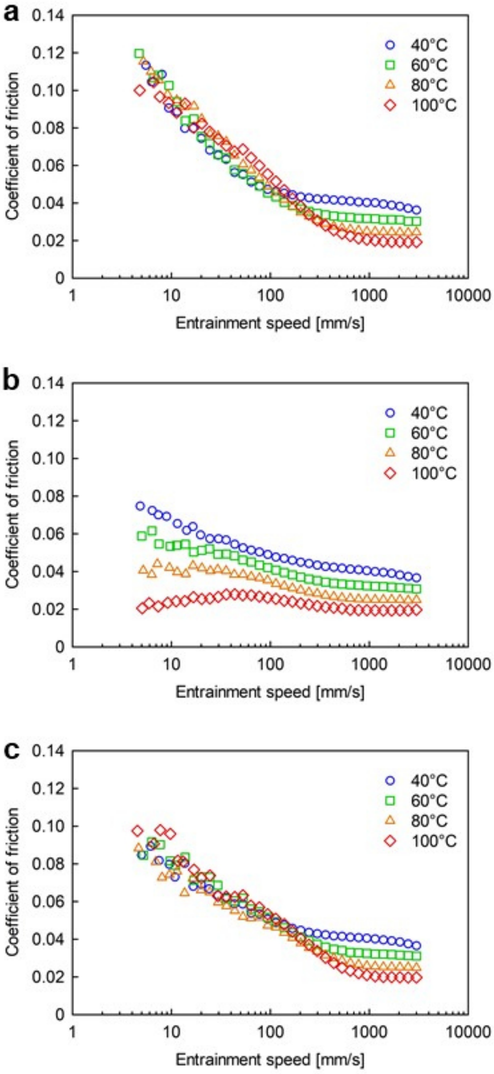


Fig. 2 Temperature and entrainment speed dependence of coefficient of friction measured in macroscale friction test (a) without FM, (b) with polymeric FM, and (c) with GMO dissolved in Gr. III oil.

### 3.2 Results of macroscale friction test

The entrainment speed dependences of the coefficient of friction (CoF) at each temperature in Gr. III base oil with and without polymeric FM, measured using the MTM tribometer, are shown in Figures 2a and b, respectively. For comparison, the dependence with GMO dissolved in Gr. III oil is shown in Fig. 2c.

At over 500 mm/s, no significant difference in the CoF was observed among the three oils. The lubrication state in this higher entrainment speed range corresponded to that for the EHL regime. In the EHL regime, since there was a thick enough oil film between the steel disk and ball, the CoF depended on the fluid resistance. Therefore, the adsorbed layer that formed on the steel surfaces with polymeric FM or GMO negligibly affected the frictional properties. Additionally, the CoF showed similar values regardless of the oil because the viscosities of the oils were almost the same, as shown in Table 1.

The entrainment speed dependence of the CoF at speeds below 500 mm/s indicates that the lubrication state corresponded to the mixed lubrication regime. In this regime, the temperature dependence of the CoF was smaller than that in the EHL regime since direct contact of the asperities on the steel disk and ball mainly affected the CoF rather than fluid resistance. In the measurement using Gr. III base oil alone, the CoF at the lowest entrainment speed was estimated to be ~0.12. When GMO was dissolved into the Gr. III base oil, a similar CoF tendency was observed, but the maximum CoF value, measured at an entrainment speed of ~5 mm/s, was smaller (~0.10). The GMO reduced the boundary friction by maintaining the adsorbed layer on the steel surfaces similarly from 40 to 100°C. In contrast, the polymeric FM dissolved into the Gr. III oil showed a clear decrease in the CoF, depending on the temperature; it exhibited lower friction at higher temperatures. Its frictional properties were better than those of GMO, especially at high temperatures. These results suggest that the polymeric FM strongly adsorbed onto the steel surfaces and then retained its functionality even at high temperature (100°C) under high contact pressure (1.0 GPa). As a result, direct contact of the asperities on the steel disk and ball was suppressed even under severe tribological conditions, and the CoF was dramatically reduced by the boundary contact of the adsorbed polymeric FM layers on the steel surfaces. The larger CoF reduction at higher temperatures suggests that the adsorption layer formed by the polymeric FM improves the macroscale tribological properties as the temperature is increased, as expected.

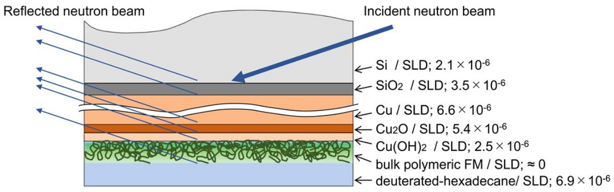


Fig. 3 Schematic illustration of neutron reflectometry and SLD values used in fitting analysis.

## 4. Neutron reflectometry

### 4.1 Experimental procedure

We used neutron reflectometry to investigate whether the friction reduction effect at high temperature described in Section 3 was due to the swelling of the adsorbed polymeric FM layer. Neutron reflectivity measurement is a powerful method for estimating the thickness and density of adsorbed FM layers under various temperature conditions.

A 50-nm-thick Cu film was first formed on a mirror-polished silicon block (50 × 50 × 10 mm) by using a sputtering system (KUR-IBS [22]). We used Cu as the substrate because it is one of the industrial metals widely used for sliding surfaces and has adsorption properties similar to those of additives to iron and steel. Copper forms a native oxide layer as well as other metals, and additives form an adsorption layer on the oxide surface sufficient for analysis. In addition, Cu is non-magnetic, which facilitates structural analysis of the adsorbed polymeric FM layer using neutron reflectometry [23, 24].

To clearly evaluate the interfacial structure of an adsorbed polymeric FM layer on a Cu surface, a large difference is necessary in the scattering length density (SLD) of the polymeric FM and base oil. SLD is a material-specific parameter calculated from the chemical composition and coherent scattering length of each element. The neutron reflection characteristics of protium and deuterium differ substantially while their chemical/physical properties are basically similar. Therefore, deuterated hexadecane was used as the base oil to achieve a clear contrast between the adsorbed polymeric FM layer and base oil. Hexadecane, a non-polar solvent composed of hydrocarbons, is widely used as a model base oil, and has characteristics similar to those of Gr. III oil. The polymeric FM was dissolved in deuterated hexadecane at a concentration of 0.4 mass%. This lubricant also contained 0.6 mass% Gr. III oil for sample preparation convenience, a negligible concentration compared with that of deuterated hexadecane and that has no effect on the formation of an adsorbed polymeric FM layer and the accuracy of the analysis.

All measurements were performed using the SOFIA horizontal-type neutron reflectometer in Beamline 16 at the Materials and Life Science Experimental Facility in the J-PARC facility [25]. Fitting analysis of the experimental results was performed using the Motofit software package [26]. A schematic illustration of the neutron reflectometry and SLD values used in the analysis are shown in Fig. 3 [23, 27]. First, to determine the thickness of the Cu and its native oxide thin film layer, deuterated hexadecane was placed on a silicon block mounted in a sample holder, and neutron reflectivity was measured. Then, the base oil on the silicon block was replaced with polymeric FM solution dissolved in deuterated hexadecane, and neutron reflectivity was again measured. To evaluate how the thickness and density of the adsorbed polymeric FM layer at room temperature depended on the length of time after lubricant placement, the measurements were carried out 10 and 120 minutes after injection. In experiments for evaluating the temperature dependence of the interfacial structure of the polymeric FM adsorbed layer, reflectivity profiles were measured at 40, 60, 80, and 100°C after heating for 1 hour at each temperature.

### 4.2 Time dependence of adsorbed polymeric FM layer

The neutron reflectivities for deuterated hexadecane base oil without polymeric FM and for polymeric FM solution dissolved in deuterated hexadecane measured at 23°C at 10 and 120 minutes after placing the lubricant are shown in Fig. 4. The vertical axis shows the reflectivity in log scale, and the horizontal axis shows scattering vector $Q_z$, which is proportional to the incident angle and inversely proportional to the wavelength of the neutrons. The plot at the bottom is for deuterated hexadecane base oil alone. For easy comparison, the profiles for the polymeric FM solutions are shifted toward the vertical axis while the reflectivities in the total reflection region ($Q_{z,}$<0.015) are the original ones. The circles represent the experimentally measured values, and the solid lines represent the optimized fitting results obtained from the analysis.

In this analysis, the density profile of polymeric FM layers was modelled to be distributed from 100 to 0% from the lubricant/metal interface along the z-axis in 10% steps under the assumption that polymeric FM has a higher density near the Cu surface. The thickness of each density layer was then optimized by the fitting.

The SLD profiles of the Cu and polymeric FM on the silicon block obtained from the optimal fitting results for each reflectivity profile are shown in Fig. 5. The vertical axis shows the SLD value, and the horizontal axis shows the vertical distance from the Cu surface. Although the surface roughness of each layer was excluded from the analysis by setting it to zero, the accuracy of the analyses was sufficiently high, and the fitting error parameter $\chi^2$ for all analyses was below 0.005.

The Cu layer, including CuO, $Cu_2O$, and $Cu(OH)_2$, was 52.8 nm thick, and the total thickness of the polymeric FM layers 10 and 120 minutes after placing the lubricant was 6.0 and 6.1 nm, respectively. The polymeric FM dissolved in the deuterated hexadecane and moved toward the Cu surface, where it quickly formed an adsorbed layer with a thickness of ~6 nm (within 10 minutes), at which point it reached an equilibrium state.

This polymeric FM is methacrylate-type and has a methyl group in its main chain, while other FMs such as acrylate-type ones have hydrogen atom instead of a methyl group. Therefore, the polymeric FM is difficult to form a stable structure in which the hydroxyl groups with low oil solubility face inward by rotating its polymer chain [28]. As a result, some of the hydroxyl groups faced outside the polymer structure, and an adsorbed layer of polymeric FM formed on the Cu surface due to physical adsorption in a relatively short time within 10 minutes.

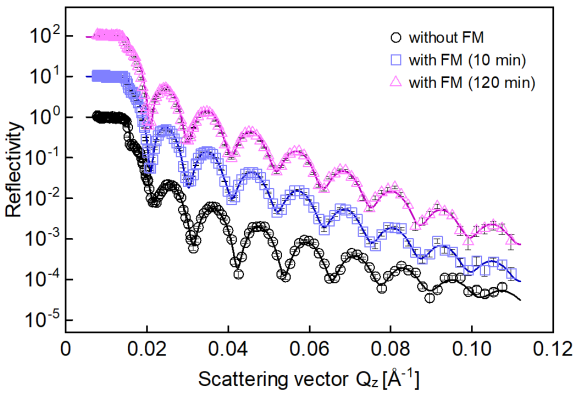


Fig. 4 Neutron reflectivities measured at 23°C for evaluating time dependence of polymeric FM adsorbed layer formation and optimum fitting line for each result. Solid lines are optimized fitting results.

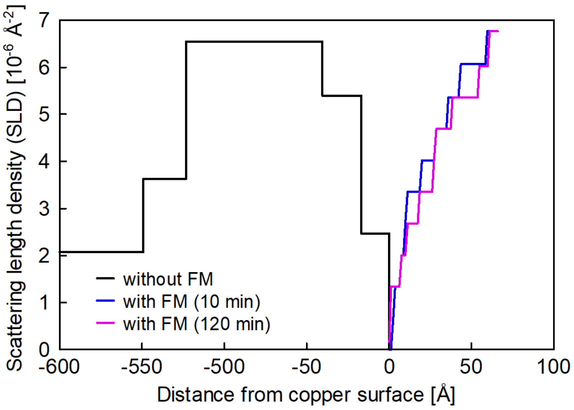


Fig. 5 SLD profiles obtained from optimum fitting analysis of results shown in Figure 4.

## 4.3 Temperature dependence of adsorbed polymeric FM layer

Figure 6 shows the reflectivity profiles obtained for the polymeric FM solution at various temperatures, and Fig. 7 shows the corresponding SLD profiles. The fitting error parameters $\chi^2$ for all measurements described in this section were also small enough (< 0.005). Analysis showed that the total thickness of the polymeric FM layer at 40, 60, 80, and 100°C was 6.5, 8.9, 11.2, and 17.7 nm, respectively. The thickness of the adsorbed polymeric FM layer thus depended on the temperature, as expected.

Interestingly, analysis showed that the total thickness at 23°C after cooling from 100°C was 16.4 nm, which is close to the value at 100°C. Since the polymeric FM has a methacrylate backbone, it tends to swell depending on the temperature compared with olefin copolymers [20]. At lower temperatures, the polymeric FM chains tended to coil because the segment-segment interactions were stronger than the solvent-segment ones. In contrast, at higher temperatures, the polymeric FM segments tended to be surrounded by deuterated hexadecane molecules since the solvent-segment interactions became stronger. Therefore, the

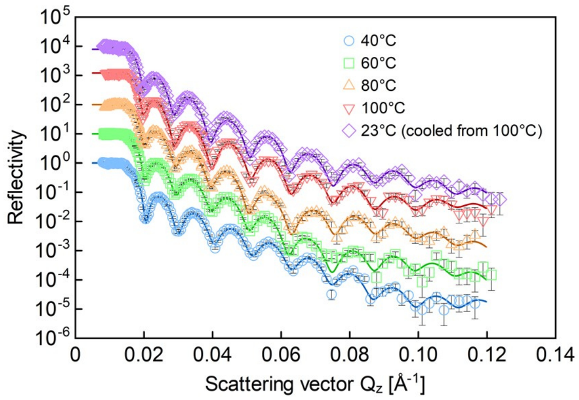


Fig. 6 Neutron reflectivities measured for evaluating temperature dependence of thickness of adsorbed polymeric FM layer and optimum fitting line for each result. Solid lines are optimized fitting results.

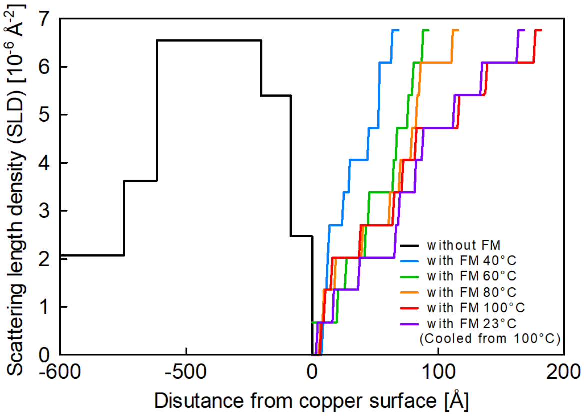


Fig. 7 SLD profiles obtained from optimum fitting analysis of results shown in Figure 6.

polymeric FM was more swelled, and the adsorbed layer was thicker. In addition, the adsorbed layer remained swollen even after cooling from 100°C. This indicates that the deuterated hexadecane molecules in an adsorbed polymeric FM layer are not easily exuded, at least in a static environment.

Figure 8 shows the 'compressed thickness ($d_c$)' of the adsorbed polymeric FM layer calculated under the assumption that the swollen-state adsorbed polymeric FM layer is compressed to 100% density:

$$d_c = \int_0^\infty \frac{SLD_{dHD} - SLD(z)}{SLD_{dHD}} dz,$$

where $SLD_{dHD}$ is the constant SLD value of deuterated hexadecane, and $SLD(z)$ is the distributed SLD profile from the Cu surface, as shown in Fig. 7. If the initial adsorbed polymeric FM swelled due only to heating, the compressed thickness should remain constant at the value calculated at 23°C before heating because the compressed thickness corresponds to the total volume of the polymeric FM on the Cu surface. However, the total volume clearly increased due to heating while it remained at almost the same value for up to 120 minutes when it was simply left at room temperature.

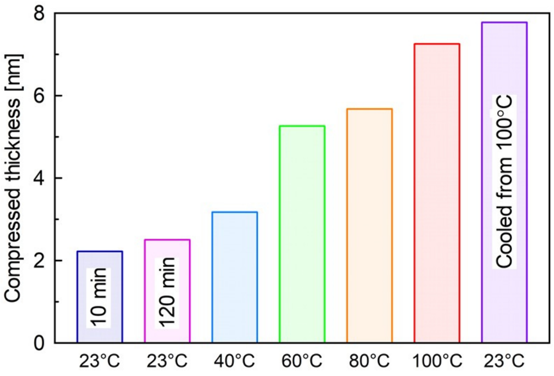


Fig. 8 Compressed thickness of adsorbed polymeric FM layer on copper surface.

These results indicate that the increase in total film thickness at high temperature (shown in Fig. 7) was caused not only by swelling of the adsorbed polymeric FM layer due to penetration of deuterated hexadecane into the originally formed layer at room temperature in the initial stage but also by new adsorption of polymeric FM into the space generated on the Cu surface due to the vigorous molecular motion of the adsorbed polymeric FM [29].

## 5. Nanoscale friction test using AFM

### 5.1 Experimental procedure

The effects of the increase in thickness of the adsorbed polymeric FM layer at high temperature during neutron reflectometry measurement on the friction and wear characteristics were investigated by nanotribological testing using an AFM at 23 and 100°C. Since scanning is very slow in AFM measurement, the minimum oil film thickness calculated using the Hamrock-Dowson equation [30] is usually extremely small (< 10 pm), so it is possible to measure the CoF values in boundary contact with little oil film. It is also possible to measure the wear or deformation of the surface as well as the CoF values after repeated friction testing. We used a silicon chip covered with a thin Cu layer as a substrate to investigate the nanoscale tribological properties of the adsorbed polymeric FM layer.

A silicon wafer (0.5 mm thick, (100) orientation) was cut into a 10-mm square chip and cleaned by sequential sonication in acetone, isopropanol, and ultrapure water (> 5 minutes per step). Finally, the chip was cleaned by oxygen plasma ashing for 5 minutes at 50 W in a reactive ion etching system (FA-1, Samco), and then a 50-nm-thick Cu layer was deposited on it by sputtering (EB1100, Canon Anelva). The substrate was fixed on a chip holder made from polyetheretherketone engineering plastic by using a heat-resistant adhesive. To evaluate the nanotribological properties of the adsorbed polymeric FM layer, friction tests were conducted using an AFM (SPM-9700, Shimadzu) with a colloidal probe cantilever (CP-FM-SIO, sQube). The cantilever, which had a 6.62-μm-diameter silica colloid, was used for surface imaging and friction measurement. Since a silica colloidal probe is not susceptible to abrasion, unlike a general point probe, which typically has a tip radius of ~10 nm, high reproducibility can be obtained during continuous friction measurement. The test procedure comprised three steps:

(i) Drop 0.4 mass% polymeric FM solution in Gr. III oil on Cu surface and leave for >12 hours, resulting in formation of polymeric FM adsorbed layer.

(ii) Perform friction test on 2 × 2 μm area 75 times with 256 lines per image at a scanning speed of 20 μm/s with a maximum Hertzian contact pressure of 350 MPa to measure CoF.

(iii) Scan entire 10 × 10 μm area including 2 × 2 μm area at 20 μm/s with contact pressure of 200 MPa to measure deformation in 2 × 2 μm area.

To evaluate the tribological properties of the polymeric FM at 100°C, the procedure was started after 30 min heating at 100°C by using the temperature control unit on the AFM. A friction test following the same procedure was carried out at 23°C, 2 hours after cooling from 100°C. For reference, friction tests using Gr. III base oil without polymeric FM were also performed at 23°C and 100°C.

### 5.2 Temperature dependence of adsorbed polymeric FM layer

Typical friction test results are shown in Fig. 9. The graph shows the shift in the CoF at the first scan and at every 5th scan from 5 to 75 with and without polymeric FM at 23°C and 100°C. Typical AFM images of the 10 × 10 μm chip surface, including the 2 × 2 μm area, after the 75-times-repeated friction test are shown in Figs. 10a–d.

The initial CoF without polymeric FM at 23°C was about 0.12; it then dropped sharply and remained low. A Cu surface was conformed within 10 scans, and the CoF remained ~0.05 thereafter. The CoF with polymeric FM at 23°C was from 0.12 to 0.14, a range of numbers that are not so small. The amount of wear or deformation at 23°C was similar (to a depth of 0.8 nm) regardless of whether polymeric FM was used. Neutron reflectometry showed that the compressed thickness of the adsorbed polymeric FM layer was about 2.5 nm at 23°C. Therefore, with polymeric FM, the adsorbed polymeric FM layer protected the Cu surface and the silica colloidal probe did not reach the Cu surface even after 75 scans because the 0.8-nm-deep deformation was much smaller than the compressed thickness.

The initial CoF without polymeric FM at 100°C was 0.08 (Fig. 9). Similar to the measurement at 23°C, a Cu surface was conformed, and the CoF became much smaller (~0.04). The wear depth was about 2.6 nm in the friction test at 100°C without polymeric FM, which probably accounts for the unstable CoF behaviour at around the 35th scan. In contrast, the CoF with polymeric FM at 100°C was lower (0.02–0.04), and the sliding was much stabler. The amount of deformation was small with polymeric FM at 100°C, but the surface of the adsorbed polymer FM layer became slightly roughened due to the repeated friction testing and rose to ~0.3 nm. These results demonstrate that a swollen-state adsorbed polymeric FM layer at high temperature is sufficiently rigid to protect a Cu surface.

Friction tests using an AFM performed at 23°C and 100°C revealed several tribological properties of the adsorbed layer on the developed polymeric FM. An adsorbed layer formed on the Cu surface at 23°C, preventing abrasion of the Cu surface at 23°C; but it made only a small contribution to achieving low friction. On the other hand, when the layer greatly swelled at 100°C, its tribological properties were substantially improved, and it exhibited much higher performance in terms of low friction and surface protection. These results demonstrate that the tribological properties of the adsorbed polymeric FM layer have temperature dependence and show excellent performance in the high-temperature condition, as also shown in the macroscale friction test.

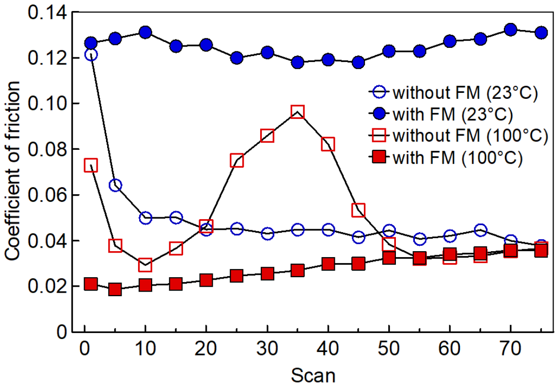
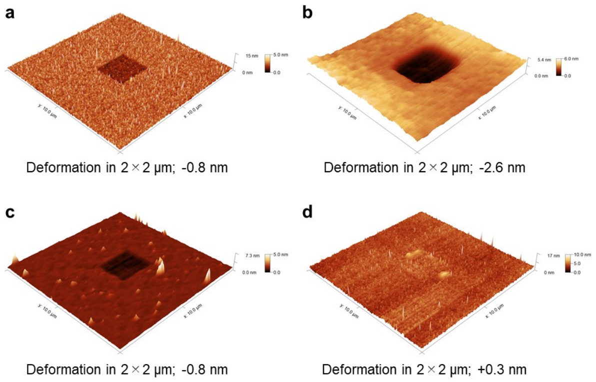


Fig. 9 75-times repeated friction measurement by AFM with or without polymeric FM at 23°C and 100°C.



Deformation in 2 × 2 μm; -0.8 nm

Deformation in 2 × 2 μm; -2.6 nm

Deformation in 2 × 2 μm; -0.8 nm

Deformation in 2 × 2 μm; +0.3 nm

Fig. 10 Typical surface profiles observed after 75-times-repeated friction test without polymeric FM (a) at 23°C, (b) 100°C, and with polymer FM (c) at 23°C, (d) 100°C.

### 5.3 Tribological behaviour of adsorbed polymeric FM layer after cooling from 100°C

We evaluated the tribological properties of an adsorbed polymeric FM layer that maintained its swollen state at room temperature, which was revealed by the neutron reflectivity measurement. Figure 11 shows the friction test results for polymeric FM at 23°C, 2 hours after cooling from 100°C. The CoF remained ~0.05 over the 75 scans, which is substantially smaller than that measured at 23°C before heating.

Figure 12a show a surface image after 75 scans, 2 hours after cooling from 100ºC. The depth of the 2 × 2 μm area was about 1.6 nm, twice that before heating. This relatively larger deformation indicates that a swollen-state adsorbed polymeric FM layer at 23°C is much softer than that before swelling at high temperature.

Neutron reflectometry revealed that the compressed thickness of the adsorbed polymeric FM layer was 7.8 nm, at least in a static state, which is larger than the deformation after 75 scans. Thus, the Cu surface was protected by the polymeric FM layer and was not worn down by the silica colloidal probe. These results demonstrate the importance of increasing the thickness and density of the adsorbed polymeric FM layer to reduce friction so that it exhibits good lubricity like that of a polymer brush [17–19].

The lubrication mechanism is not sufficiently clear, but it is probably caused by oil exudation due to compression of the adsorbed polymeric FM layer during friction testing. Figure 12b shows an image of the same surface area 2 hours after a second heating at 100°C. The deformation in the 2 × 2 μm area evident in Fig. 12a disappeared as the reheating at 100°C, completely recovered the area due to reswelling of the adsorbed polymeric FM layer. Since the segment-segment interactions of polymeric FM should be stronger than the solvent-segment ones at 23°C, the Gr. III oil was easily exuded so that the adsorbed polymeric

FM layer was compressed by the applied load and friction. Since the solvent-segment interactions were strengthened by heating, the Gr. III oil penetrated the adsorbed polymeric FM layer, causing it to swell again.

These results demonstrate that the adsorbed layer of the developed polymeric FM can maintain low-friction characteristics and protect surfaces from wear for a sufficiently long time even in an environment where the temperature changes drastically.

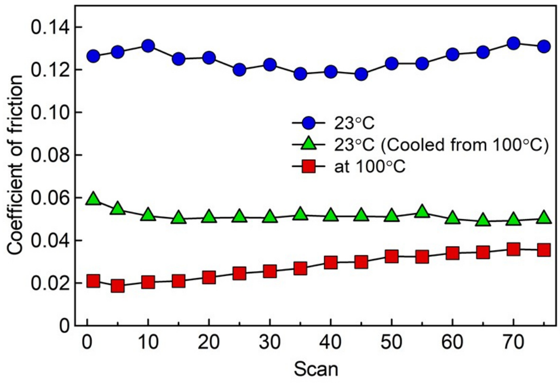
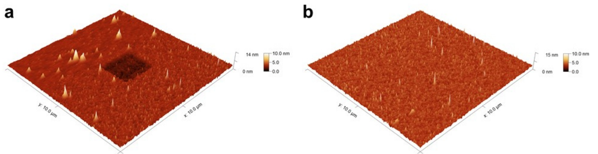


Fig. 11 Coefficient of friction measured by AFM (75-times-repeated friction test) performed 2 hours after cooling from 100°C; for comparison, results for 23°C and 100°C (shown in Fig. 9) are also plotted.



Deformation in 2 × 2 μm; -1.6 nm

No deformation in 2 × 2 μm

Fig. 12 Surface images of same area where 75 friction scans were applied after being cooled from 100°C and left at 23°C for 2 hours, observed (a) before and (a) after second heating at 100°C.

## 6. Discussion

Figure 13 shows the relationship between the CoF measured in the MTM friction test (Figs. 2ab) and the minimum oil film thickness in the MTM test calculated using the Hamrock-Dowson equation [30]. The pressure-viscosity coefficient used in that equation was calculated by ASTM-Walther equation and Wu-Klaus equation [31]. In the measurement with polymeric FM, the thickness of adsorbed polymeric FM layer on both disk and ball surfaces during the MTM friction test with polymeric FM is unknown. Therefore, compressed thickness of the polymeric FM layer calculated in neutron reflectometry at each temperature (Fig. 8) was regarded as the thickness during the friction measurement using MTM. The total thickness of the oil film (Gr. III oil plus adsorbed polymeric FM layer on disk and ball surfaces) was calculated by adding the twice value of the compressed thickness to minimum oil film thickness calculated under without polymeric FM condition by Hamrock-Dowson equation. Since the polymeric FM concentration was sufficiently low and the viscosity of the lubricant was close to that of the Gr. III base oil alone, there was almost no difference in the CoF when the oil film was thicker than 30 nm.

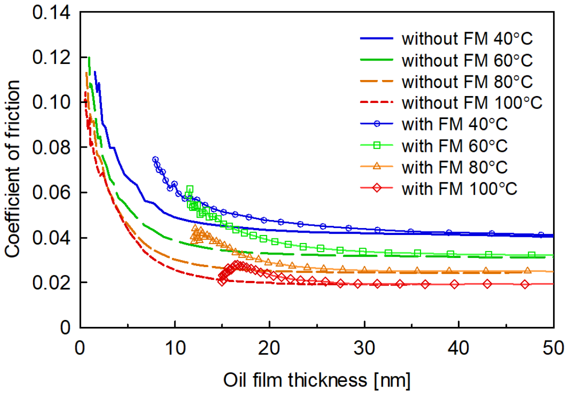


Fig. 13 Relationship between the CoF measured by MTM test at various temperatures and the calculated oil film thickness.

In the measurement without polymeric FM, the CoF gradually increased when the oil film was less than 15 nm thick at all temperatures; hence, the transition from an EHL regime to a mixed lubrication regime was estimated to occur when the film thickness was 10–15 nm. However, since the MTM friction test was performed with steel-steel contact (not glass-steel), the oil film thickness was not able to be measured directly. Therefore, the oil film thickness at which the CoF begins to rise is defined as the oil film thickness at the transition from an EHL regime to a mixed lubrication regime. In this study, the transition thickness was determined as the film thickness at which the inclination of the CoF against oil film thickness dropped below -0.01, which is low enough to correspond to 'negative' inclination. As a result, the thickness for all temperatures was 11.0–11.4 nm.

As the thickness of the oil film dropped below this transition value, a much greater number of asperities on the steel surfaces directly contacted each other, which increased boundary friction and thereby increased the CoF to 0.12. In contrast, in the measurement with polymeric FM, the total thickness of the oil film (Gr. III oil plus adsorbed polymeric FM layer) at the transition of the inclinations of CoF below −0.01 was 19.4–20.5 nm for all temperatures. However, as shown in Fig. 13, the CoF gradually increased when the total oil film thickness was much larger, especially at 40 and 60°C. This increase in CoF when the total oil film thickness was 20–30 nm was due to the effect of thin-film lubrication (TFL), which is one of the lubrication states between

EHL and mixed lubrication. With TFL, shear resistance is stronger due to the flow of lubricant molecules (base oil and polymeric FM) interacting with an adsorbed polymeric FM layer, and shear resistance increases when the polymeric concentration at the interface is high [11, 32]. This viscous boundary layer tends to form when the interaction between the polymeric FM dissolved in the base oil and the adsorbed polymeric FM layer is strong. As discussed in Section 4.3, the polymeric FM had stronger segment-segment interaction at lower temperatures, which also indicates stronger interaction between the polymeric FM dissolved in the base oil and the adsorbed polymeric FM layer. Therefore, the effect of TFL at lower temperatures was larger than that at higher temperatures.

In the measurement with polymeric FM at 100°C, the CoF decreased when the total thickness of the oil film was below 16 nm. Basically, in the mixed lubrication regime without any additives, the friction force is determined by the boundary friction caused by direct contact of the asperities on the surfaces of both the steel ball and disk and by the shear resistance caused by the flow of Gr. III base oil. With the polymeric FM, it is determined by the boundary friction of the adsorbed layer on both steel surfaces and by the higher shear resistance caused by TFL.

In the MTM friction test with the polymeric FM at 100°C, since asperities on steel surfaces should be covered with a highly swollen rigid adsorbed polymeric FM layer, as shown in the AFM measurements, direct contact of the asperities on a steel surface were prevented. Additionally, the boundary friction of the adsorbed polymeric FM layers on both the disk and ball surfaces at 100°C should be low since low friction was demonstrated even in the contact between the polymeric FM layer and silica probe in the AFM friction test (as described in Section 5.2).

As the total oil film thickness decreased, the area of boundary friction of the adsorbed polymeric FM layers became larger, so the area of the TFL state became smaller. At higher temperatures (such as 100°C), the effect of the TFL was basically small due to the weaker segment-segment interaction, and the polymeric FM was characterised by lower boundary friction than at lower temperatures. Therefore, the effect of the low-friction characteristic of polymeric FM overwhelmed the effect of TFL at 100°C, so extremely low friction was obtained when the total thickness of the oil film was less than 16 nm.

## 7. Conclusion

An oil-soluble polymeric friction modifier (FM) has been developed that changes its structure with a rise in temperature and provides excellent tribological properties. Its low-friction mechanism at higher temperatures was clarified by associating the temperature with the layer thickness. The results are summarized as follows.

- Neutron reflectometry measurement revealed that the polymeric FM adsorbed on a Cu surface and quickly formed a layer with a thickness of 6.0 nm, which became about three times greater at 100°C.
- The polymeric FM layer exhibited low friction, especially at 100°C in both measurements using a mini traction machine (MTM) tribometer and an atomic force microscope. This tendency was evident not only in the contact between polymeric FM layers but also in the contact between the polymeric FM layer and silica colloidal probe.
- The adsorbed polymeric FM layer retained its swollen state even after cooling from 100°C and exhibited lower friction than before heating. The layer was deformed by repeated friction testing, but the deformation was recovered by reheating.
- In the frictional measurement with the MTM tribometer at high temperature, the increase in shear resistance due to the effect of thin-film lubrication was suppressed since the interactions between the adsorbed polymeric FM layer and polymeric FM dissolved in the base oil became smaller. With a much thinner oil film under low-speed conditions, substantially lower friction was achieved due to an increase in the contact area of the swollen-state polymeric FM layers, which had extremely low boundary friction properties.

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Table 1 Viscosities of lubricants used in friction tests.

Table 2 Conditions for macroscale friction test using MTM tribometer.

Fig. 1 Schematic illustration of oil-soluble polymer-type friction modifier.

Fig. 2 Temperature and entrainment speed dependence of coefficient of friction measured in macroscale friction test (a) without FM, (b) with polymeric FM, and (c) with GMO dissolved in Gr. III oil.

Fig. 3 Schematic illustration of neutron reflectometry and SLD values used in fitting analysis.

Fig. 4 Neutron reflectivities measured at 23°C for evaluating time dependence of polymeric FM adsorbed layer formation and optimum fitting line for each result. Solid lines are optimized fitting results.

Fig. 5 SLD profiles obtained from optimum fitting analysis of results shown in Figure 4.

Fig. 6 Neutron reflectivities measured for evaluating temperature dependence of thickness of adsorbed polymeric FM layer and optimum fitting line for each result. Solid lines are optimized fitting results.

Fig. 7 SLD profiles obtained from optimum fitting analysis of results shown in Figure 6.

Fig. 8 Compressed thickness of adsorbed polymeric FM layer on copper surface.

Fig. 9 75-times repeated friction measurement by AFM with or without polymeric FM at 23°C and 100°C.

Fig. 10 Typical surface profiles observed after 75-times-repeated friction test without polymeric FM (a) at 23°C, (b) 100°C, and with polymer FM (c) at 23°C, (d) 100°C.

Fig. 11 Coefficient of friction measured by AFM (75-times-repeated friction test) performed 2 hours after cooling from 100°C; for comparison, results for 23°C and 100°C (shown in Fig. 9) are also plotted.

Fig. 12 Surface images of same area where 75 friction scans were applied after being cooled from 100°C and left at 23°C for 2 hours, observed (a) before and (a) after second heating at 100°C.

Fig. 13 Relationship between the CoF measured by MTM test at various temperatures and the calculated oil film thickness.