## ナノ隙間における高分子添加潤滑油のずり粘弾性計測

Measurement of shear viscoelasticity of polymer-added lubricants in nanogaps

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## 1. Introduction

Lubricants are becoming increasingly low-viscosity to enhance the energy efficiency of automobiles<sup>1)</sup>. Furthermore, electric vehicle (EV) fluids are expected to be utilized for lubricating reduction gears and cooling motors in the future, necessitating low-viscosity fluids to improve cooling efficiency<sup>2)</sup>. As the viscosity of the lubricating oil decreases, the load capacity diminishes, and the sliding gap narrows, potentially leading to wear and seizures. Consequently, the development of low-friction technology in the boundary lubrication state while achieving a low-viscosity lubricating oil is a critical issue. Previous studies have reported that the addition of polymers to lubricating oil reduces friction in the boundary lubrication state<sup>3,4)</sup>. Polymer additives are known to function as viscosity index improvers that alter the temperature dependence of the viscosity. However, the lubricity exhibited by polymers adsorbed on surfaces is not yet fully understood, and the quantification of their mechanical properties and elucidation of their adsorption morphology are essential for lubrication design. In our previous study, we successfully quantified the mechanical properties (shear viscoelasticity) of lubricating oils in nanoscale sliding gaps by applying the fiber wobbling method (FWM)<sup>5)</sup>, a nanorheological measurement method that we originally developed. We also developed a sample heating stage for FWM and successfully measured the temperature dependence of the shear viscoelasticity of polyalkylmethacrylate-added lubricating oil in the nanogaps<sup>6)</sup>. In this report, we review the representative results of shear viscoelasticity of lubricants in nanogaps, where the adsorption film of polymer additives is dominant, as well as the measurement method.

# 2. Shear viscoelasticity measurement of lubricating oils in nanogaps

A schematic of the FWM measurement system is shown in Figure 1. FWM employs an optical fiber with a spherical tip as the sliding probe. The radius of the sphere at the tip of the probe was approximately 100 µm and the length of the probe was approximately 2 mm. The fiber probe was sinusoidally vibrated using a piezoelectric actuator to induce shear in the lubricant on the substrate. The amplitude and phase changes of the tip were optically detected to measure the shear viscoelasticity of the lubricant in the nanogap between the probe tip and substrate. The shear gap can be measured with an accuracy of approximately 1 nm using optical interferometry. A piezoelectric stage is used to adjust the gap. The sample stage was equipped with a heating apparatus to measure the temperature dependence of the sample from room temperature to the maximum temperature of 100°C. A lubricant droplet was deposited on the substrate, and the probe tip was inserted into the lubricant. The volume

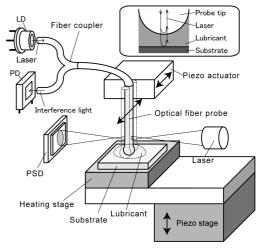


Fig. 1 Schematic of fiber wobbling method equipped. Inset shows the schematic of light interference at sliding interface for the gap measurement<sup>4,5)</sup>.

of the lubricant was adjusted so that only the spherical portion of the probe tip was fully immersed. After the temperature increased in the heating stage and reached the set temperature, the shear gap was reduced at a constant rate (approximately 10 nm/s). The vibration amplitude and phase delay of the probe tip during this process were measured by using a lock-in amplifier to obtain shear viscoelasticity of the oil, which is complex viscoelasticity  $\eta' - i\eta$ ". The real component  $\eta'$  of complex viscoelasticity represents viscosity, whereas the imaginary component  $\eta$ " represents elasticity. The mechanical model employed to calculate  $\eta'$  and  $\eta$ " can be found in Ref. 5).

#### 3. Results and discussion

The lubrication sample used in this study was base oil (Gr. III mineral oil) to which polyalkyl methacrylate (PAMA) was added at a concentration of 2 wt%. The molecular weight of PAMA was 60,000. The substrate was a silicon substrate sputter-coated with a thin stainless steel film (approximately 60 nm thick). The roughness of the stainless steel surface was 0.2-0.3 nm. In this study, the frequency and amplitude of probe excitation were set to 1 kHz and 50 nm, respectively.

Figures 2 (a) and (b) show the temperature dependence of complex viscosity  $\eta' - i\eta''$  measured at 25, 40, 60, 80, and 100°C. For reference, the results obtained at 25°C using only the base oil, which does not contain PAMA, are also shown in Fig. 2. With the PAMA additive, both the viscosity  $\eta'$  and elasticity  $\eta''$  increased sharply when the gap narrowed to less than 10 nm. These results can be attributed to the adsorption of PAMA on the substrate surface. An increase in the viscoelasticity was observed in almost the same gap region at all heating temperatures, indicating that the adsorbed film did not desorb from the surface at 100°C. It is said that PAMA added to lubricating oil in the bulk state swells as the temperature increases. In contrast, the gap region where the shear viscoelasticity increased was independent of temperature. This suggests that the deformation of the polymer chain is suppressed by surface adsorption, and the adsorption film does not swell, even when heated.

Viscosity  $\eta'$  and elasticity  $\eta''$  at representative gaps are plotted against temperature in Fig. 3(a) and (b), respectively, based on the results of Fig. 2. The temperature dependence of viscosity shows that the decrease in viscosity with increasing temperature was suppressed in the 5 nm gap compared to the results for a relatively wide gap of 100 nm. In other words, the viscosity index increased in the gap region, where the adsorption layer was dominant. The elasticity increased in proportion to the temperature. This result suggests that the polymer chains adsorbed on the surface have a part that can move freely, which may be stretched by shear and express entropic elasticity (rubber elasticity). An increase in elasticity may lead to an increase in surface coverage during friction.

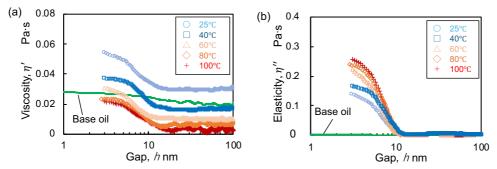


Fig. 2 Shear-gap dependence of (a) viscosity  $\eta'$  and (b) elasticity  $\eta''$  measured at various heating temperatures for lubricants containing PAMA with a molecular weight of 60,000. For comparison, the measurement results of the base oil at room temperature (25 °C) are indicated by the solid lines<sup>6</sup>.

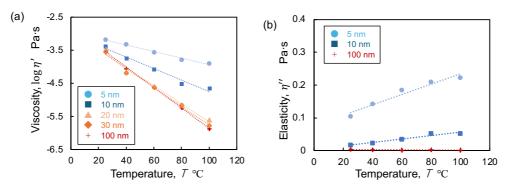


Fig. 3 Temperature dependence of (a) viscosity  $\eta'$  and (b) elasticity  $\eta''$  for lubricants with PAMA with a molecular weight of 60,000 at typical gaps of 5 to 100 nm<sup>6</sup>).

#### 4. Summary

The temperature dependence of the shear viscoelasticity of a polymer-doped lubricant in a nanogap was successfully measured using the FWM. Even at a heating temperature of 100°C, a polymer adsorption film formed on the surface, and its mechanical properties were significantly different from those of the base oil alone. It is suggested that the viscosity of the polymer adsorption film has a small temperature dependence and that its elasticity may have entropy elasticity.

### References

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