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ポリアルキルメタクリレート（PAMA）系高分子添加剤の極性が摺動時の油膜形成能力に及ぼす影響

Effects of polarity of polyalkylmethacrylate (PAMA) polymer additives on film formation ability during sliding

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1. Introduction

Adding polymer additives into lubricant oil has been used as an effective method to improve the lubrication performance of boundary and mixed lubrication regime. By adsorbing on metal surfaces, polymer could help separate related sliding surfaces and thus to reduce wear and friction. In previous studies, it was found that the higher polarity of the polymer, the thicker the lubricating film during sliding would be generated. However, the reason was still unclear, especially for the random copolymers and homopolymers whose adsorbed film thicknesses were just few nanometers.

In this study, without the pressure applied on the adsorbed film, we estimated the thicknesses and conformations of adsorbed films formed by polyalkylmethacrylate (PAMA) polymers with different polarities using neutron reflectometry (NR). Also, with vertical-objective-type ellipsometric microscopy (VEM), we measured the thicknesses of adsorbed films under pressure. The gap changes with sliding cycles were also measured by VEM. It was found that with increase in the polarity of polymer, the conformation of the adsorbed film will be changed from single-layer structure to double-layer structure. In addition, higher the polarity of the polymer, thicker lubricating films were produced during sliding, which was believed to be due to the temporarily trapped polymers by the previously adsorbed film on the surfaces.

2. Experimental samples

The base oil used in this study is the group Ⅲ mineral oil. The polymer additive is the polyalkylmethacrylate (PAMA) with the molecular weight of ~20,000 (20 k) g/mol. The concentration of the PAMA polymer additive is 2.0 wt%. Two kinds of PAMA polymers with different polarities was used in this study. The polymers are poly (2-ethylhexyl methacrylate) (PMA-EH), and poly (lauryl methacrylate) (PMA-LA). The polarity of PMA-EH is higher than that of PMA-LA.

3. Experiment methods

3.1 Adsorbed film thickness and sliding gap measurement by VEM

The schematic setup for measuring thickness of adsorbed film thickness under pressure with VEM is shown in Fig. 1. This method is based on ellipsometry. By analyzing the intensity image of the reflected polarized light captured by the CMOS camera, the gap between the glass substrate and the slider can be obtained. The details for obtaining thickness of adsorbed films can be find in Ref. (1), which is summarized as follows: The slider was first separated from the substrate to allow additive to adsorb on surfaces. The separation was kept for a certain periods (~ 10 s, 30 s, 60 s and 120 s). Then, by pressing the slider with load of 25.5 mN and squeezing base oil out from the gap between the surfaces, the adsorbed film was isolated. Since only the adsorbed film remains in the gap, the measured gap by VEM between the surfaces is then equal to the adsorbed film thickness. By repeating the procedures of separation and pressing, the temporal changes in thickness of adsorbed films during adsorption were measured. In addition, the glass substrate was attached on the x-piezo stage that could do reciprocating movements, using strobe imaging, the changes in gaps with sliding cycles were also measured.

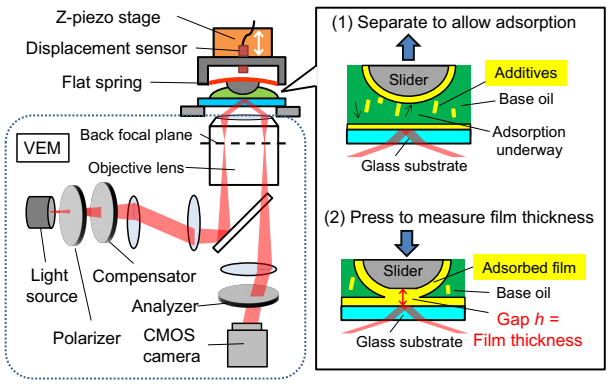

Fig. 1 Schematic setup for adsorbed film thickness and sliding gaps measurement with VEM

The glass with the refractive index of 1.93 was used as the substrate, and its thickness is 0.8 mm. The slider is the plano-convex glass lens, which was coated by the 53-nm thick stainless-steel through sputtering. Its radius is 15.6 mm. The roughness in Rq of the slider surface and the glass substrate was 1.1 nm and 0.4 nm, respectively.

3.2 NR measurement

To measure the thickness without pressure and the density profile of the adsorbed film, NR experiments were conducted using the Soft Interface Analyzer (SOFIA) horizontal-type neutron reflectometer at the Materials and Life Science Experimental Facility in the J-PARC facility. The 30-nm-thick Fe film sputtered on a mirror polished silicon block (50 × 50 × 10 mm) by KUR-IBS was used as the substrate. The solvent of the polymer solutions was replaced by deuterated hexadecane. The measurements were carried out 15 mins after the solutions were injected into the sample holder. The NR profiles were analyzed using GenX software. The experiments were conducted at 25 ℃.

4. Results and discussions

The reflectivity and scattering length density (SLD) profiles measured by NR are shown in Fig. 2, and Fig. 3, respectively. Without pressure applied on the adsorbed film, the 1.8 nm-thick PMA-LA adsorbed film was found on the Fe surface with the density of 99%. On the other hand, the PMA-EH adsorbed film showed double-layer conformation, where the thickness of the bottom layer was around 3.0 nm (density: 99%) and the thickness of the top layer was around 4.3 nm (density: 24%). The low density of the top layer indicated that there were more loops and tails in the top layer of the adsorbed film.

With VEM, the temporal changes in thickness of adsorbed film during adsorption under the 25.5 mN loads are shown in Fig. 4. Under 25.5 mN load, the saturation thickness of PMA-EH adsorbed film was around 3.0 nm, indicating that only the bottom layer of adsorbed film can endure the load. The thickness of PMA-LA measured by VEM is 1.5 nm, similar to that measured by NR.

The measured gap changes of PMA-LA and PMA-EH with sliding cycles under different sliding loads are shown in Fig. 5, and Fig. 6, respectively. With increase in sliding cycles, the gap between the slider and the glass substrate with the PMA-LA kept stable. The higher the sliding load, the smaller the gap was measured. On the other hand, measured gap of PMA-EH increased with sliding cycles. Interestingly, the measured gaps under different sliding loads reached at same level after around 300 cycles of sliding. Since more loops and tails existed in the top layer of the adsorbed film formed by PMA-EH, the increase in the sliding gap could be due to the temporarily trapped polymers by the tails and loops of the top layer of adsorbed film on the surface.

5. Summary

By measuring thickness of adsorbed film formed by polymer with different polarities and the gap changes with sliding cycles, the effects of polarity on film forming ability were investigated. The higher the polarity of the polymer additive, the more likely it is to produce thicker lubricating films during sliding.

Acknowledgments

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References

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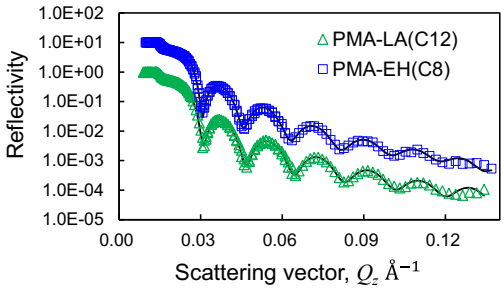

Fig. 2 Neutron reflectivity profiles

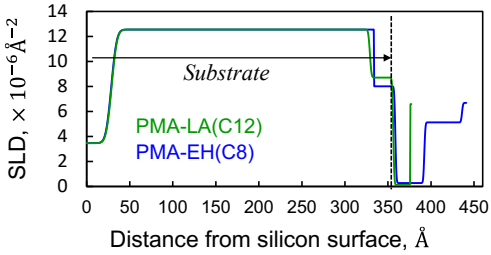

Fig. 3 SLD profiles

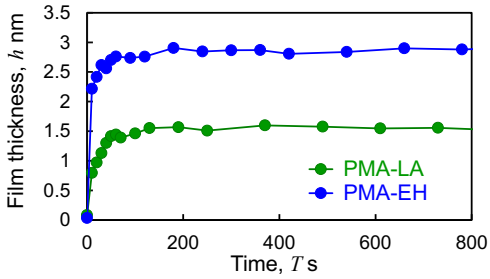

Fig. 4 Thickness of adsorbed film under 25.5 mN load by VEM

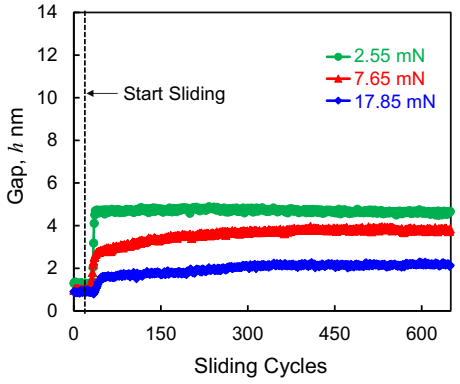

Fig. 5 Gap changes of PMA-LA with sliding cycles under different sliding loads

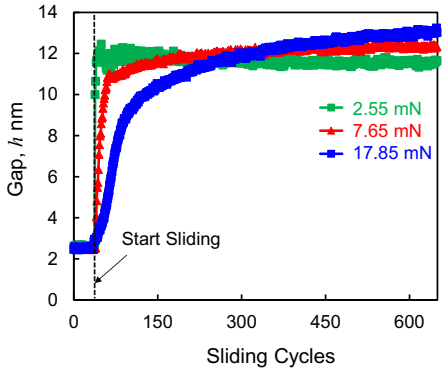

Fig. 6 Gap changes of PMA-EH with sliding cycles under different sliding loads