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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吸着膜の厚さと耐久性に及ぼす影響

Effects of polarity of polyalkylmethacrylate (PAMA) polymer additives on adsorbed film's thickness and durability

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1. Introduction

The need for higher energy efficiency has led to significant reduction in the viscosity of lubricant oils. However, the lower the viscosity of the lubricant oil, the more difficult it is for the mechanical systems generate sufficient hydrodynamic forces to separate the relative sliding surfaces, resulting in higher friction. It was found that oil soluble additives such as polyalkylmethacrylate (PAMA) polymers can adsorb on the surfaces and thus to prevent the direct contact during sliding, which could help reduce the friction. Nevertheless, the conformation of the adsorbed film and how it affects the friction reduction performance have not been clarified yet[1)].

In this study, the thicknesses of adsorbed films formed by PAMA polymers with different polarities were measured by vertical-objective-type ellipsometric microscopy (VEM). It was found that with increase in the polarity of polymer, the thickness of formed adsorbed film also increased, indicating the different conformation of the adsorbed film. In addition, the results with atomic force microscopy (AFM) indicated that the adsorbed films formed by higher polarity polymer has higher durability.

2. Experiment methods

2.1 Adsorbed film thickness measurement by VEM

The schematic setup for measuring thickness of adsorbed film thickness 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. (2), 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 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.

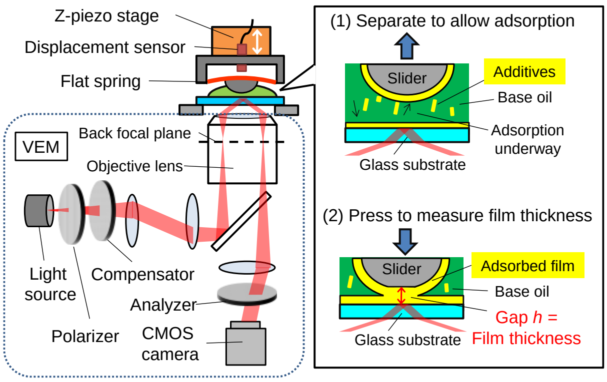

Fig. 1 Schematic setup for thickness measurement of adsorbed film with VEM

2.2 Friction and durability test

Friction tests were carried out using an atomic force microscope (AFM, SPM-9700, Shimadzu), as shown in Fig. 2. The probe was a chip less cantilever (TL-FM, Nanosensors) with an 8 μm diameter SiO_2 sphere attached to the tip. The experiment procedures are as follows:

(1) Drop 200 μl lubricant with PAMA additives on substrate and wait for 30 minutes.

(2) Measure the transition of the friction coefficient during 40 consecutive observations of a 2 × 2 μm area (Area A in Fig. 2) at 8 $\mu m/s$ under a contact surface pressure of about 300 MPa.

(3) Measure the profile of a 10 × 10 μm area (Area B in Fig. 2) under a

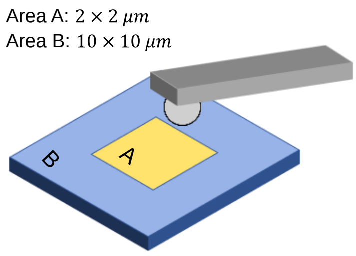

Fig. 2 Schematic setup for friction and durability test with AFM

contact surface pressure of about 100 MPa to evaluate the durability of the adsorbed film.

3. Materials

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%.

Three kinds of PAMA polymers with different polarities was used in this study. The polymers are poly (2-ethylhexyl methacrylate) (PMA-EH), poly (lauryl methacrylate) (PMA-LA), and poly (stearyl methacrylate) (PMA-ST). Among these polymers, PMA-EH has the highest polarity, followed by PMA-LA, and PMA-ST.

In the adsorbed film thickness measurement experiments 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.

In the friction and durability test with AFM, the 53-nm thick stainless-steel coated glass was used as the substrate, whose surfaces roughness in Rq was 0.4 nm.

4. Results and discussions

The temporal changes in thickness of adsorbed film during adsorption formed by 2.0 wt% PAMA solutions are shown in Fig. 3. It can be seen that thicknesses for all adsorbed films saturated at a high speed. The saturation thicknesses of adsorbed films formed by PMA-ST, PMA-LA, and PMA-EH were around 1 nm, 1.5 nm, and 3 nm, respectively. With increase in the polarity of polymers, the thickness of formed adsorbed films also increased.

The profiles of surfaces after 40 cycles rubbing using AFM were shown in Fig. 4. It can be seen that after sliding, the deformation of surface with PMA-EH was almost unobservable, indicating the adsorbed film formed by the PMA-EH has high durability. On the other hand, the deformations of surfaces after 40 cycles rubbing with PMA-LA and PMA-ST were tangible, indicating their lower durability.

The thinner thickness of film formed by PAMA with lower polarity indicates a flatter film. On the other hand, more "loop" and "tail" structures were expected in the adsorbed film formed by PMA-EH because of its thicker thickness. As a result, entanglement between polymers in the adsorbed films formed by PMA-EH on the surface should be more likely occur. The entanglement between polymers leads to stronger interactions between polymers, making the adsorbed film harder to be removed during rubbing, which interprets the higher durability of PMA-EH adsorbed film.

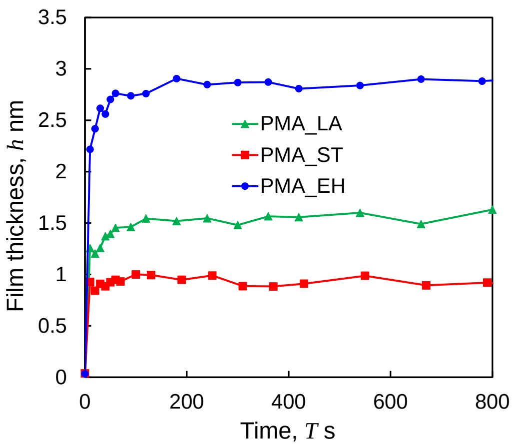

Fig. 3 Measured thickness of adsorbed film formed by PAMA polymers with different polarities.

5. Summary

By measuring the thicknesses and surface deformations after rubbing of adsorbed films formed by PAMAs with different polarities, the influence of polarity of polymer on adsorption and durability of adsorbed film was investigated.

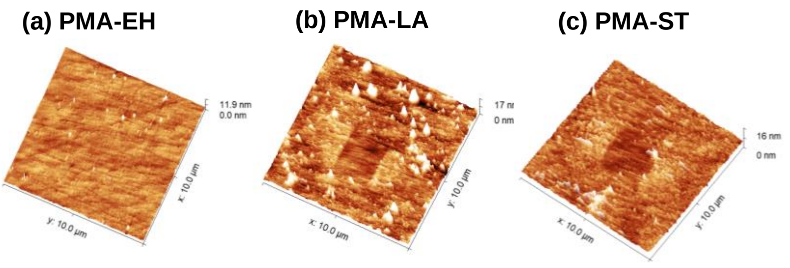

Fig. 4 Surface profiles after 40 cycles rubbing using AFM with (a) PMA-EH, (b) PMA-LA, (c) PMA-ST

Acknowledgments

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