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Effect of Liquid Viscosity on the Internal Fluidity of a Droplet Sliding on a Fluoroalkylsilane Coating

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The effect of liquid viscosity on the internal fluidity of droplets during sliding on an inclined Si surface treated with fluoroalkylsilane (FAS) was investigated for water–glycerin mixture using particle image velocimetry (PIV). Increasing viscosity remarkably decreases the slipping motion on the solid–liquid interface and overall sliding acceleration. It affects the rolling motion, but its degree of influence is smaller than that on slipping. The viscosity had different contributions to slipping and rolling motions of the droplets.

Hydrophobic coatings are widely used for water-repellent treatment of solid surfaces. The static contact angle has commonly been used for evaluation of surface hydrophobicity. However, recognition of the importance of dynamic hydrophobicity, such as sliding acceleration and velocity, is growing for assessment of water-shedding properties of hydrophobic solid surfaces.[1]

Recent studies have revealed two components in the liquid droplets' sliding behavior on a solid surface: rolling and slipping.[2,3] The dominant component during sliding depends on the chemical composition and surface state of solids.

Recently, we developed a new particle image velocimetry (PIV) system for direct observation of the internal fluidity of a liquid droplet during sliding.[4] Using this facility, we investigated the effect of surface roughness on the internal fluidity of a water droplet during sliding with constant acceleration on an inclined Si surface treated with fluoroalkylsilane (FAS).[5] Results showed that a water droplet can slide down by rolling with or without slipping on a solid–liquid interface. The slipping/rolling ratio on the sliding acceleration depends on the surface roughness; the droplet advances on the rough surface mainly by the rolling mechanism.

Not only solid surface characteristics, properties of liquid such as viscosity and surface energy will also affect the overall sliding behavior. However, fundamental understanding of the effect of these factors is still insufficient. In the current study, we examined the effect of liquid viscosity on the sliding acceleration and the dominant sliding mode through direct observation of internal fluidity of water–glycerin mixture using the PIV system.

A Si plate ((100), $15 \times 40\,\mathrm{mm}^2$) was precleaned using sonication in ethanol and acetone for 7 min each. Then, the surface was irradiated with vacuum ultraviolet light for complete decomposition of remaining organic compounds. For this study, 1*H*,1*H*,2*H*,2*H*-perfluorodecyltrimethoxysilane (FAS17, $CF_3(CF_2)_7(CH_2)_2Si(OCH_3)_3$) was used as the hydrophobic agent. Smooth FAS17 coatings were prepared using chemical vapor deposition (CVD). The Si plate was heated with 0.02 mL of FAS17 (TSL8233; GE Toshiba Silicones, Tokyo, Japan) in a Petri dish in flowing N_2 at 150 °C for 1 h. Then, the surface was rinsed with toluene, acetone, and water and dried at 80 °C for 30 min.

Surface roughness was evaluated in a 5-μm^2 area using atomic force microscopy (AFM) with a Si cantilever. Static contact angles of 4-μL liquid droplets were measured using a contact angle meter (Dropmaster 500; Kyowa Interface Science Co., Ltd., Saitama, Japan) by sessile drop method. The sliding angle (SA) was evaluated for 30-μL water droplets using an automatic measurement system (SA-20; Kyowa Interface Science Co., Ltd.).

For this study, we used water–glycerin mixture as the test liquid. Although the surface energies of these two liquids are similar (water, $72.8\,\mathrm{mJ{\cdot}m^{-2}}$; glycerin, $63.4\,\mathrm{mJ{\cdot}m^{-2}}$ at 293 K),[6] their viscosities differ greatly (water, 1.01 mPa·s; glycerin, 1412 mPa·s at 293 K).[7] We changed the glycerin concentration from 0 to 85%, and kinematic viscosity was calculated by dividing the practical viscosity value (measured using an E-type viscometer: TV22; Toki Sangyo Co., Ltd.) of each liquid by liquid density.

The PIV analysis was performed for a 35-μL liquid droplet with 0.06 mass% fluorescent particles (R0300; Duke Scientific Corp., CA, USA) on a sample surface tilted at 35°. Sequential images of the droplet were taken using a high-speed camera. A sheet-shaped Ar laser beam was passed vertically into the center of the droplet as a light source. The Graphical Abstract includes a schematic illustration of this system; details are also described in refs 4 and 5. For this study, we set a meshed image (10 pixels) with ca. $3.0 \times 10^4\,\mu m^2$ and the time separation of 0.33–1.00 ms. The velocity vectors were evaluated using commercial software (DIP-Flow; Ditect Inc., Tokyo, Japan) for PIV pattern matching using the correlation factor of 0.65 or greater.

Figure 1 presents an AFM image of the Si surface coated with FAS-17. The average surface roughness values (*R*a) were 0.30 nm. The coating was smooth; heterogeneous agglomerations were not observed. The water contact angle was 106° (average) ±1° (standard deviation); the sliding angle was $9 \pm 1°$. Figure 2 depicts the dependence of the contact angle and kinematic viscosity on the glycerin concentration. The contact angle does not change remarkably throughout the entire

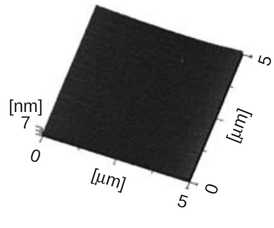

Figure 1. AFM image of the Si surface coated with FAS-17.

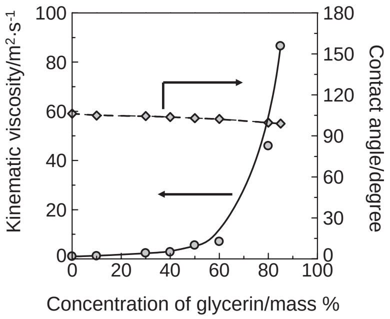

Figure 2. Dependence of contact angle and kinematic viscosity on the glycerin concentration.

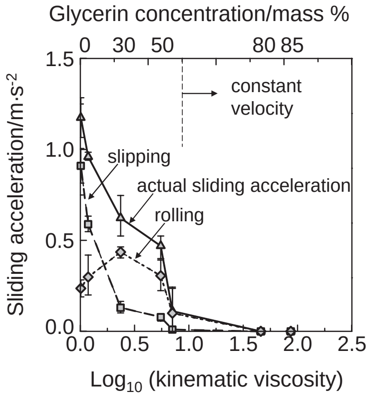

Figure 3. Dependence of sliding acceleration on the kinematic viscosity.

concentration range. However, the kinematic viscosity value increases rapidly when the glycerin concentration becomes greater than 50%. Practical images taken from the center of glycerin 0 and 85% liquid droplets were sufficiently clear for analysis of internal fluidity using the PIV system.[8] Moreover, shape deformation during sliding was almost negligible in this measurement when liquid droplets were sliding with constant accelerations. Furthermore, for all observed liquid droplets sliding with constant accelerations, the flow velocity for the sliding direction increased linearly with droplet height.[8] Therefore, the model used in the previous study[5] to evaluate rolling and slipping components in sliding acceleration from the PIV image is also applicable to results in this study.

Figure 3 shows the dependence of sliding acceleration on the kinematic viscosity. The actual sliding acceleration measured from the sliding distance at the advancing edge of the liquid droplets is nearly equal to the sum of the acceleration by rolling motion and that by slipping motion. This result suggests that effects of surface curvature of droplets and scattering or reflection of emitted light are negligible. The acceleration by slipping motion decreases rapidly when the kinematic viscosity increases. The acceleration by rolling motion increases initially with increasing kinematic viscosity; once the kinematic viscosity reaches $2\,\mathrm{m^2 \cdot s^{-1}}$ (glycerin concentration becomes greater than 30%), it starts to decrease. Both components are almost zero when the kinematic viscosity is greater than $10\,\mathrm{m^2 \cdot s^{-1}}$ (glycerin concentration is greater than 60%), suggesting sliding with constant velocities.

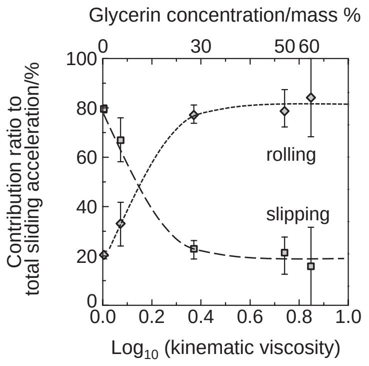

Figure 4. Contribution ratio of rolling and slipping components to entire sliding acceleration in the range of constant sliding acceleration.

Figure 4 presents the contribution ratio of rolling and slipping components to the overall sliding acceleration in the range of constant sliding accelerations (namely, the kinematic viscosity $<10\,\mathrm{m^2 \cdot s^{-1}}$). The contribution of slipping decreases with increasing kinematic viscosity; this trend is opposite from that of rolling. Although the acceleration component by rolling decreases when kinematic viscosity is more than $2\,\mathrm{m^2 \cdot s^{-1}}$ (see Figure 3), this result implies that the effect of kinematic viscosity on the acceleration component is different.

In the previous study, we showed that the rolling mechanism is advantageous to avoid large friction drag imparted by slippage at the water–solid interface for the droplet's sliding on a rough surface.[5] Shear stress at the interface is described by the product of viscosity and velocity gradient against the droplet height. Since the rolling motion is likely to Rankin's vortex from the velocity gradient with respect to droplet height,[8] shear stress on this region will be small. Thus, when glycerin concentration increases from zero to 30%, the contribution of slipping to entire sliding acceleration decreases and rolling becomes dominant. It is inferable that the dependence of velocity gradient upon viscosity is different between rolling and slipping in this concentration region, and thus, entire sliding acceleration will be governed by the velocity gradient. When glycerin concentration is more than 30% (and less than 50%), entire sliding acceleration decreases with decreasing both slipping and rolling components. The sliding acceleration of this region will be governed by the viscosity.

Results of this study directly demonstrated that the liquid viscosity had different contributions to slipping and rolling motions of the droplets. Increasing viscosity decreases the slipping motion on the solid–liquid interface and decreases the entire sliding acceleration remarkably. It also affects the rolling motion, but its degree is smaller than slipping. The dominant sliding mode in acceleration depends on the liquid viscosity. These results are obtained on the water–glycerin mixture, and detailed analyses on the relationship between internal fluidity and surface state of solid for other liquids are addressed in future studies.

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