Sliding Behavior of Water Droplets on Smooth Hydrophobic Fluoroalkylsilane Coatings with Different Surface Coverage Ratio

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Abstract

Smooth fluoroalkylsilane (FAS17) coatings ($R_a < 0.2$ nm) with different surface coverage ratios were prepared on a Si substrate by changing the deposition time. Then the internal fluidity of water droplets sliding on the coatings was evaluated using particle image velocimetry (PIV). The water droplets slid downward with acceleration by a caterpillar-like rotation with slippage on the solid-liquid interface. The sliding acceleration of the advancing contact line decreased concomitantly with the decreasing surface coverage ratio. However, the slipping/rolling ratio to the overall sliding acceleration was almost constant against surface coverage ratio. This result suggests that physical roughness and chemical composition contributed differently to slipping and rolling motions of the droplets.

Key-words: Hydrophobicity, Droplet, Sliding acceleration, Particle image velocimetry, Fluoroalkylsilane

1. Introduction

For improved performance of water-repellent coatings, the motion of a liquid droplet on a hydrophobic solid surface has been investigated frequently as an important subject in various industrial fields such as vehicle development, architecture, and electronics. The sliding angle (a critical angle at which a droplet starts sliding down an inclined surface by gradual tilting), and contact angle hysteresis (the difference between the receding and advancing contact angles of a sliding droplet on an inclined surface) are often evaluated as criteria for assessing water-shedding properties from a hydrophobic surface.

However, these values are insufficient to represent water-shedding kinetics such as sliding acceleration and the velocity of water droplets. For surface materials' design, information related to how fast the droplet can be removed from the surface at a certain tilt angle is becoming more important than information related to the lowest tilt angle at which the droplet slides downward. Recognition of the importance of a droplet’s water-shedding kinetics is growing gradually; several studies have been made using direct observation.

Water droplets are known to slide down on the hydrophobic solid surface by a caterpillar-like rolling motion with or without slippage at the solid-liquid boundary. Very recently, we developed a particle image velocimetry (PIV) system for direct observation of the internal fluidity of a water droplet during sliding. Using this system, we investigated the effect of surface heterogeneity on the internal fluidity of a water droplet during sliding. Results show that the slipping/rolling ratio on the sliding acceleration depended on the surface heterogeneity; the droplet advanced on the rough surface mainly by the rolling mechanism. The surface roughness value ($R_a$) of the smoothest coating tested in the study was less than 0.2 nm. However, the heterogeneous surface used in the study had roughness of more than 3 nm and presented both a chemical composition difference (several hydrophilic parts were distributed in the hydrophobic matrix) and physical surface
roughness. Separation of the effects of physical surface roughness from chemical composition on the slipping/rolling ratio of sliding acceleration was not attained.

Several factors exist in the chemical composition difference of the chemical composition itself, and size, number and distribution of different parts (hydrophilic parts) in the surface. In this study, we treated a Si surface with the same fluoroalkylsilane by changing the deposition time and prepared several smooth coatings with different surface coverage ratios. Using this method, the entire surface composition depends on the deposition time. The surface topography was observed using atomic force microscopy (AFM, JSPM-4200; JEOL, Tokyo, Japan).

Then, the internal fluidity during sliding of water droplets on these coatings was evaluated using our PIV system. The initial accelerations of slipping and rolling motions were measured experimentally. Their relation is discussed herein.

2. Analysis Model of Internal Fluidity with Rolling and Slipping Motions

Fig. 1 presents a schematic illustration of the PIV system and a conceptual model of the internal fluidity for the droplet descending on an inclined plane by caterpillar-like rotation flow with slipping motion, as suggested by Sakai et al.\(^\text{17}\). This model is appropriate when the droplet shape deformation is negligible during sliding. For a caterpillar-like rotation flow, the rolling velocity for the \(x\) (slope) direction \(v_{\text{roll}}\) is 0 at the bottom position. The \(z\) line is described vertically for the \(z\) (normal to slope) axis passing the top position and the bottom position. The rolling velocity at the top position of the droplet is expected to be \(2v_{\text{roll}}\) when the center of the \(z\) line has a rolling velocity of \(v_{\text{roll}}\) in the \(x\) direction. In this model, the slipping velocity \(v_{\text{slip}}\) is assumed to be identical in the droplet above the boundary layer, under which region the slipping velocity decreased gradually toward the solid wall. In this study, the effect of the boundary layer was considered to be slight for evaluation of the macroscopic (> 100 \(\mu\)m) droplet’s slippage. The sliding velocity at the bottom position \(v_b\) evaluated macroscopic PIV was determined as the slipping velocity of the droplet as Eq. (1) in this study.

\[
v_b = v_{\text{slip}}
\]

With the linear progression of rolling velocity for \(z\) direction in the droplet, the sliding velocity at the center of \(z\) line \(v_c\), at the top position \(v_T\) can be evaluated as shown by Eqs. (2) and (3).

\[
v_c = v_{\text{slip}} + v_{\text{roll}}
\]

\[
v_T = v_{\text{slip}} + 2v_{\text{roll}}
\]

Using Eqs. (1) and (3), \(v_{\text{roll}}\) can be estimated from \(v_b\) and \(v_T\) as shown below.

\[
v_{\text{roll}} = (v_T - v_b) / 2
\]

Sakai et al. confirmed that the terminal constant velocity of the advancing contact edge for the \(x\) direction \(v_{\text{AD}}\) became almost identical to \(v_c\), suggesting that the \(v_c\) (around the center of the droplet) represents the whole droplet’s advancing velocity. This result suggests that the evaluations of respective components and modeling presented in Fig. 1 were appropriate for representing the dynamic motion of the droplet. In this study, the velocity change of each motion was evaluated using this model for a water droplet, which slides down with the constant acceleration on the inclined hydrophobic surface.

3. Experimental

3.1 Sample Preparation

The surface of a Si (100) wafer (n-type; Aki Corp., Miyagi, Japan) was cut into a 15 × 50 mm plate and cleaned using ethanol and acetone. Vacuum ultraviolet (VUV) light was irradiated (\(\lambda = 172\) nm with power density of approximately 7 mW cm\(^{-2}\), UEM20-172; Ushio Inc., Tokyo, Japan) to the cleaned wafers for 10 min in air to form a homogeneous oxide layer (terminated by SiOH)\(^\text{19}\). The plate was then treated with fluoroalkylsilane using chemical vapor deposition. The plate was set into a glass container with 0.02 m\(^2\) of 1\(H\)1\(H\)2\(H\)2\(H\)-perfluorodecyltrimethoxysilane (FAS17, CF\(_3\)\(CF_2\)\(_7\)(CH\(_2\)\(_2\))\(_2\)Si(OCH\(_3\))\(_3\), TSL8233; GE Toshiba Silicones, Tokyo, Japan) and sealed with a glass lid under dry N\(_2\) conditions. Then, the container was heated in an oven from room temperature to 423 K (5 \(^{\circ}\)C/min) and kept at that temperature for 0, 40, and 60 min with flowing dry N\(_2\) (Fig. 2). In this study, these samples are designated respectively as FAS17 (a), FAS17 (b), and FAS17 (c). After heat treatment, the plate’s surface was rinsed with flows of acetone, toluene, and water. Then it was dried at 353 K in air for 20 min.

3.2 Evaluation

The surface topography was observed using atomic force microscopy (AFM, JSPM-4200; JEOL, Tokyo, Japan).
The sample was set on the sample stage tilted at 35°. The static water contact angle (WCA) was evaluated for the area with 5 µm². Using Pt-Ti coated probes (NSC36-b; µ-mash Ltd., Narva mmt., Estonia), the contact surface potential distribution (CPD) of samples was evaluated using Kelvin force microscopy (KFM) mode with the same system (JSPM-4200).

The static water contact angle (WCA) was measured using the sessile drop method with 4-mg distilled water droplets and a contact angle meter (Dropmaster 500; Kyowa Interface Science Co. Ltd., Saitama, Japan). The sliding angle (SA) was evaluated for 30-mg water droplets using a commercial system (SA-20; Kyowa Interface Science Co. Ltd.). Each measurement was performed at five points (WCA) or three points (SA); then the measurements were averaged.

The sample was set on the sample stage tilted at 35° from horizontal position. The sliding distance of the advancing and receding contact line of a water droplet was measured from the sequential photographs observed using a high-speed camera system (1024 PCI; Photron Co. Ltd., Tokyo Japan) and commercial software (DIP-Motion, and DIP-Macro; Ditect Co. Ltd., Tokyo, Japan and KAST, Kanagawa, Japan).

Fig. 3 portrays an example of sequential images obtained from a high-speed camera at the side position for a sliding water droplet on an inclined sample surface (herein the camera lens was in a horizontal position). The dynamic advancing and receding contact angles (θa, θr) were also measured during sliding. The droplet mass was 35 mg. By calculating the deviation of sliding distance against time, the sliding velocity of the contact lines was evaluated. The sliding acceleration was estimated as the slope of the changing of the sliding velocity against the time using a root mean square method. The standard deviation of the sliding acceleration was estimated as more than three times according to measurements.

For PIV analyses, the water droplet contained 0.06 mass % fluorescent particles (mainly polystyrene; diameter, 3 µm; density, 1.05 cm³ g⁻¹; excitation wavelength, 542 nm; emission wavelength, 612 nm, R0300; Duke Scientific Corp., CA, USA). This suspension is designated as the test fluid. The respective surface energy and viscosity of the test fluid were 70 mJ m⁻² and 1.05 mPa s. A droplet of the test fluid weighing 35 mg was prepared using a microsyringe on the sample surface inclined at 35°. A sheet-shaped laser beam (Ar ion type; intensity, 1000 mW; wavelengths, 488 and 514 nm; width, ca. 200 µm; Seika Corp., Tokyo, Japan) was emitted vertically to the droplet and was set to the center of droplet during sliding. After gently moving the microsyringe tip upward, dynamic images of the excited particles were taken using a high-speed camera rotated at 35° (slope inclination). The internal velocity vectors were evaluated using PIV software (DIP-Flow-KAST; Ditect Co. Ltd., Tokyo, Japan). A previous report described detailed techniques. For this study, we estimated the velocity vectors on each meshed cell region of about 136 × 136 µm² in the entire dynamic image of sliding droplets using the time separation of ca. 0.33 ms. Pattern matching for PIV analysis was performed for the correlation factor of 0.65 or greater. Then the velocity vectors were smoothed using software (DIP-Flow). The sample surface position was judged directly from the images.

4. Results and Discussion

The values of WCA, SA, θa, θr, and Re of FAS17 (a) – FAS17 (c) are presented in Table 1. The averaged CPD values for 5 µm² are also listed. Observations made using AFM revealed that the surface roughness (Re) of a prepared sample was less than 0.2 nm; no particulate aggregates were observed (Fig. 4). The WCA increased and saturated around 108° with increased deposition time. The θa also increased and saturated within 40 min, whereas the θr continued increasing concomitantly with increasing deposition.
Table 1 WCA, SA, \( \theta_a \), \( \theta_b \), \( R_s \), and CPD evaluated for the coatings of FAS17 (a), FAS17 (b), and FAS17 (c).

<table>
<thead>
<tr>
<th>Sample</th>
<th>WCA (deg)</th>
<th>SA (deg)</th>
<th>( \theta_a ) (deg)</th>
<th>( \theta_b ) (deg)</th>
<th>( R_s ) (nm)</th>
<th>CPD (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FAS17 (a)</td>
<td>101 ± 1</td>
<td>23 ± 1</td>
<td>109 ± 1</td>
<td>90 ± 2</td>
<td>0.15</td>
<td>133 ± 6</td>
</tr>
<tr>
<td>FAS17 (b)</td>
<td>108 ± 1</td>
<td>15 ± 1</td>
<td>120 ± 2</td>
<td>101 ± 1</td>
<td>0.17</td>
<td>67 ± 6</td>
</tr>
<tr>
<td>FAS17 (c)</td>
<td>108 ± 1</td>
<td>11 ± 1</td>
<td>120 ± 2</td>
<td>104 ± 1</td>
<td>0.19</td>
<td>97 ± 6</td>
</tr>
</tbody>
</table>

Fig. 4 AFM images of coating surfaces: (a) FAS17 (a), (b) FAS17 (b), (c) FAS17 (c).

Fig. 5 Schematic diagram of the state of FAS17 molecules at the surface of FAS17 (a) — FAS17 (c).

Fig. 6 Sliding acceleration of each component \( a_{AD} \), \( a_{slip} \), \( a_{roll} \) evaluated for a 35-mg test-fluid droplet on FAS17 (a) — FAS17 (c). Here, \( a_{slip} \) shows the estimated value for \( a_{AD} \) from the summation of \( a_{slip} \) and \( a_{roll} \).

Based on previous reports, Si plates covered by FAS17 molecules are expected to have lower surface potential than the Si surface (SiOH and SiO\(_2\)). The decrease of the CPD values with increasing deposition time suggests that the coverage of FAS17 on the Si surface increased. The CPD values were possibly positive and negative locally in the surface because the KFM image and CPD value were obtained by averaging the surface potential values at each position (the resolution was 256 \( \times \) 256 counts for a 1-\( \mu \)m square) in this study. Moreover, it is expected that the CPD value became positive when the CH moieties of FAS17 molecules were exposed by tilting the graft chain at the surface with low packing density of silane. Fig. 5 portrays a schematic illustration of the state of FAS17 molecules grafted on the Si surface for FAS17 (a) — FAS17 (c). On the surface with low surface coverage of silanes, polar groups such as SiO\(_2\) and SiOH might be exposed at the surface, which provides chemical heterogeneities for the sample surface. Assuming that FAS17 molecules align parallel and stand with the same direction, the surface coverage ratios for FAS (a)/FAS (c) and FAS (b)/FAS (c) are calculated respectively as 0.74 and 0.97 from CPD values\(^{23}\). No simple and standard evaluation methodology with reliable accuracy exists for the average distance and its deviation among self-organized monolayer FAS17 molecules on the solid Si substrate. This evaluation should be addressed in future studies.

The results in Table 1 show that \( \theta_b \) is more sensitive to chemical heterogeneity than WCA and \( \theta_a \), probably because of the pinning droplet at the receding edge. The SA is proportional to the difference between \( \theta_a \) and \( \theta_b \) (contact angle hysteresis). On the smooth surface \( R_s \) less than 0.2 nm, the chemical heterogeneity governs the SA.

During sliding of the test-fluid droplet on the sample surface tilted at 35°, a region was found in which the droplet slid down with constant acceleration. In that region, the dynamic contact angle and sliding velocity of the contact edge of a test-fluid droplet were almost constant and equal to those for a pure water droplet. Moreover, droplet deformation (such as changes of droplet height and length) during the measurement of sliding behavior was ignorable.

Fig. 6 shows the sliding acceleration of each advancing contact edge \( a_{AD} \) observed for a 35-mg test-fluid droplet on the surface of FAS17 (a) — FAS17 (c) tilted 35°. The \( a_{AD} \) increased concomitantly with increased deposition time. These \( a_{AD} \) values evaluated for a test-fluid droplet were almost equivalent to those observed for a pure water droplet in this observed condition, implying that the effect on the sliding velocity and acceleration of adding a small amount of fluorescent particles was negligible.

Assuming the retentive force for droplet’s sliding \( F_R \), the equation of motion for droplet’s sliding was readily derived as
shown below.

\[ m_{\text{AD}} = m g \sin 35° - F_R \]  

Therein, \( m \) is droplet mass and \( g \) represents gravitational acceleration.

Carre et al. derived \( F_R \) acting on the three-phase contact line from the balance of surface tensions for a circular contact line of a droplet as

\[ F_R = \pi r \gamma_{LV} (\cos \theta_R - \cos \theta_A) / 2 \]  

where \( r \) is the contact radius of the droplet and \( \gamma_{LV} \) is the surface energy of the liquid. For FAS17 (a) - FAS17 (c), the \( \cos \theta_R - \cos \theta_A \) values were evaluated respectively as about 0.33, 0.31, and 0.26. Based on Eqs. (5) and (6), \( a_{\text{AD}} \) is inferred to increase concomitantly with decreasing the \( \cos \theta_R - \cos \theta_A \) values. This trend corresponds to the \( a_{\text{AD}} \) values evaluated for FAS17 (a) - FAS17 (c).

Before starting PIV analysis, it was confirmed that the vertical velocity distribution for slope direction is linear against droplet height. Moreover, \( v_{\text{calc}} \) \( (= v_{\text{slip}} + v_{\text{roll}}) \) obtained from \( v_{\text{slip}} \) and \( v_{\text{roll}} \) almost corresponded to the practical \( v_{\text{AD}} \), suggesting that the modeling and evaluation of each velocity were appropriate for the observed region in this study, as confirmed in Ref. 7, and that effects of surface curvature of droplets and scattering or reflection of emitted light at the particle-water or water-air interface were almost negligible in the observed region.

From time dependence of \( v_{\text{slip}} \) and \( v_{\text{roll}} \), the sliding acceleration of each motion \( a_{\text{slip}} \) and \( a_{\text{coll}} \) was estimated for FAS17 (a) - FAS17 (c). Those estimates are depicted in Fig. 6 with the \( a_{\text{calc}} \) \( (= a_{\text{slip}} + a_{\text{coll}}) \). As portrayed in Fig. 6, \( a_{\text{calc}} \) values were almost equal to the practical values \( (a_{\text{AD}}) \), implying that the practical sliding acceleration of the advancing edge on the smooth silane coatings was expressed using caterpillar-like rotation flow and slippage at the solid-liquid boundary.

With increasing deposition time, the slipping and rolling accelerations increased. Consequently, the sliding acceleration of the advancing edge of a droplet increased. The slipping/rolling ratios on sliding acceleration \( (R = a_{\text{slip}} / a_{\text{coll}}) \) were almost constant among FAS17 (a), FAS17 (b), and FAS17 (c) by considering error bars. These results suggest that the increase of the uncoated area in the surface decreases the overall sliding acceleration; however, it does not decrease slipping/rolling ratios in this composition range when \( R_c \) is less than 0.2 nm. It is noteworthy that the droplet’s shape might affect the rotating flow dynamics in the droplet. Actually, the droplet on FAS17 (c) was more spherical than the droplets on either FAS17 (a) or FAS17 (b) (as inferred easily from the dynamic contact angles presented in Table 1). In this case, experimental results suggest that surface coverage difference affects both slipping and rolling almost equivalently. Not only the difference of solid-liquid interface energy, but also the possibility of rolling movability difference by droplet deformation might contribute to this result.

In previous studies using the same material (FAS17) coating with physical surface roughness \( (R_c \text{ of } 3.1 \text{ nm}) \), the overall sliding acceleration decreased to less than 0.2 ms\(^{-2}\) and the slipping/rolling ratio decreased to around 1.0, although WCA was higher than FAS17 (c) \(^{10}\). Based on the result obtained from the present study, it was deduced that the chemical composition and physical roughness made different contributions to slipping and rolling motions of the droplets. Both the chemical composition and physical roughness decreased the sliding acceleration of the water droplet. However, the slipping/rolling ratio was not affected remarkably by chemical composition when the \( R_c \) value was less than 0.2 nm in this chemical composition range. It was decreased by physical nanometer-scale roughness as was expected from the rigid body mechanics. Moreover, SA of FAS17 (b) and that of FAS17 coating with physical surface roughness of 3.1 nm are almost identical \((15°)\). These results indicate that sliding acceleration is more sensitive to the surface state than it is to SA.

Furthermore, the static contact angles were almost equal between FAS17 (b) and FAS17 (c). However, their sliding accelerations differed, suggesting that dynamic hydrophobicity is more sensitive to the chemical composition than it is to static hydrophobicity. For a sufficiently smooth surface \( (R_c \text{ of } 0.2 \text{ nm}) \), a chemically homogeneous surface is expected to provide a low sliding angle and large sliding acceleration \((\text{velocity})\) to the water droplet on the surface.

### 5. Conclusion

This study measured the internal fluidity in the sliding of a water droplet on various smooth \((R_c < 0.2 \text{ nm})\) FAS17 coatings. The water droplets slid downward with acceleration by a caterpillar-like rotation with slippage on the solid-liquid interface. The sliding acceleration of the advancing contact line decreased concomitantly with the decreasing surface coverage ratio. However, the slipping/rolling ratio was not affected remarkably by chemical heterogeneity. The contribution of chemical composition to the slipping/rolling ratio differs from that of physical roughness at the nanometer level.

### References

表面被覆率の異なる平滑和水性フルオロアルキルシランコーティング上での水滴の転落挙動

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要　旨
傾斜した被水表面上での水滴の転落性能は、輸送機械分野を中心にその重要性が高まっている。この性質は固体表面内の均質性が高いことが指摘されているが、均質性の中で、組成と物理的な粗さが水滴の転落挙動に及ぼす影響が明確化されている。本研究ではフルオロアルキルシランを用い、蒸留水を制御して、表面粗さ（Ra）を0.2 nm以下のレーザー微細研削によって作製した。そしてその表面に水滴を転落させ、粒子画像流速解析により水滴の内部流動を可視化し測定した。その結果、水滴の転落速度は、表面の被覆率の低下とともに低下したが、転落時の滑り/回転の比率はほとんど変化しないことが明らかになった。この傾向は、同一材料で表面に物理的な粗さ（Ra = 3.1 nm）をもつ水滴の転落挙動に影響を及ぼす影響は異なる可能性が示されました。