Wetting Transition Characteristics on Microstructured Hydrophobic Surfaces

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Hydrophobicity and wetting transition behavior of water droplets were investigated on microstructured hydrophobic rough surfaces with pillar arrays, fabricated by self-replication with hydrophobic polydimethylsiloxane(PDMS) together with the use of CNC machine. The surfaces consist of microscale pillars(diameter: 105 μm , height: 150 μm) with varying spacing-to-diameter ratio (s/d) ranging from ~ 1.0 to ~ 3.3 . A de-ionized(DI) water droplet of 4.3 μl was placed on hydrophobic surfaces and contact angles(CA) were measured by the digital image processing algorithm. A wetting transition from the Cassie state to the Wenzel state was demonstrated depending on the values of s/d , from ~ 1.81 to ~ 2.95 . In the transition regime, a partial penetration of liquid meniscus which moves downward in the groove formed by four pillar posts was observed. It was also found that the contact angle prediction using the Cassie-Baxter equation showed fairly good agreement with experimental data, whereas in the transition regime, the rapid decrease in CA was found. [doi:10.2320/matertrans.M2010118]

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1. Introduction

Since hydrophobic surfaces have considerable technological potential due to their extreme water repellent properties, surface fabrication and wetting characteristics are of increasing interest in a variety of fields such as film coating, MEMS/BioMEMS, tribology, and microfluidics.¹⁻⁴⁾ As one of the most important surface properties, wettability has been studied vigorously to control the contact angle by using surfaces roughness for variety of fields, such as in mechanical, electronic, and bio-technology.⁵⁻⁸⁾ Generally, wetting regimes have been classified into three distinct states such as the Cassie state, the Wenzel state, and the intermediate state.⁹⁾ The Wenzel state describes the situation where a liquid drop penetrates into the corrugation of the surface whereas the Cassie state describes the situation where a drop rests on the surface without penetration state, and the transition state represents that the droplet partially penetrates between the pillars.^{9,10)} Bico *et al.* studied hydrophobic surfaces with controlled surface roughness to identify solid fraction effect, and verified that the Cassie-Baxter theory by solid fraction is good agreement with the measured contact angle.^{11,12)} Onda *et al.* reported the synthesis of an artificial superhydrophobic surface by using alkyl ketene dimer (AKD) wax, and showed that contact angle can be predicted well by the Wenzel theory for various rough surfaces.^{13,14)} Recently, some researchers have studied on the transition state where Cassie and Wenzel states are present simultaneously.^{1,9,15)} Studies of transition from Cassie state to Wenzel state have been carried out and some important factors, affecting the occurrence of transition, such as contact line density, energy barrier, and spacing factors have been discussed.¹⁶⁻¹⁹⁾ Moulinet and Bartolo studied the droplet equilibrium state deposited on hydrophobic rough surfaces by using the real-time 3D imaging technique for different droplet sizes.²⁰⁾ Erbil and Cansoy estimated the droplet penetration between the pillars by suggesting the modified Cassie-Baxter equation based on the geometry of square and cylindrical pillar patterns.⁹⁾ Although a number of studies

have reported some important physics behind droplet wetting behavior on hydrophobic surfaces on the basis of experiments and modeling, clear understanding of transition wetting phenomena showing penetration of liquid between pillars is required for designing and controlling hydrophobic surfaces effectively.

This article reports the experimental study on transition wetting behavior of water droplet on microstructured hydrophobic surfaces manufactured by CNC machining process and self-replication way with hydrophobic polydimethylsiloxane(PDMS). Measurement of contact angles was conducted by using the digital image process algorithm and a wetting transition from CB state to Wenzel state was demonstrated depending on different pillar spacing ratio.

2. Fabrication and Measurement Technique

2.1 Fabrication of micro-structured surfaces

Micro-holes in square-patterned array were machined on an acrylic plate by a micro CNC machine (EGX-350, Roland). Each cylindrical hole has dimensions of 105 μm in diameter, which corresponds to the drill diameter, and 150 μm in depth. The height can be adjusted as needed by the software control. However, the dimensions were kept the same throughout the machining since wetting characteristics would be not easily determined if the aspect ratio is very small or large. Moderate rotational speed of spindle was used because a high speed rotation, e.g., over 10,000 rpm, would cause thermal damage of the acrylic. Also, low rotational speed would deteriorate machinability of the acrylic and would result in failure of the micro drill. It should be noted here that the travel speed of the spindle, especially when approaching to the sample along z-axis, was maintained very low, 0.6 mm/s, to avoid abrupt failure of micro drill by sudden contact to the sample surface. Compressed air was also sprayed to remove chips and burrs formed during machining. It also reduced interference occurring between the drill and chips during machining.

Aside from the CNC machining conditions, to investigate the effect of micro-pillar structures on wetting characteristics, nine micro-pillar structures having different pillar

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Fig. 1 SEM images of PDMS replica surface. The diameter and height of each pillar are 105 μm and 150 μm , respectively.

density on the acrylic plates were made by polydimethylsiloxane (PDMS, Sylgard, 184, Dow Corning) replicas. To make the PDMS replicas, PDMS was first mixed with a curing agent, where the ratio of PDMS to the curing agent was 10. Then, the PDMS was placed in a vacuum chamber for 1 to 2 h to get rid of air bubbles. Curing was next done at 65°C for 6 h. The variation in pillar density was made by changing the interval which is the distance of two adjacent holes. The distance varied from 100 to 340 μm with 30 μm increments.

Surface morphology of PDMS replicas was examined by SEM (S-3400N, Hitachi) and it is shown in Fig. 1. For each density, 10 arbitrary pillars were selected to measure the dimensional distribution. The results revealed that the dimensions of the PDMS pillars were about the same as those of holes on the acrylic plates. That is, the difference in the dimensions between machined and measured structure is within $\pm 2 \mu\text{m}$ and it can be thus said that the reliability of the CNC machining is pretty high.

2.2 Measurement technique

For characterization of wetting state, we generated a water droplet on the fabricated hydrophobic surfaces by using the injection system which consists of a flat-tipped metal hub needle (Gage 33, HAMILTON) and the syringe pump (LSP01-1A, LongerPump). A de-ionized (DI) water droplet of 4.3 μl was measured by the micro balance (AC 121 S, Sartorius) for 10 times under the controlled environmental condition. The needle tip was mounted at the center of pillar arrangement and located at 3 mm from the top surface of the pillars. As shown in Fig. 2, we used the telecentric lens (TEC-M55, Computar) and high-speed camera (Hotshot 1280, NAC) including Field of View (FOV) of $24.4 \times 18.2 \text{ mm}$ with a resolution of 17 μm to one pixel and with 0.6% distortion angle. For the side view imaging of the droplet, we utilized Macro Lens (EF 100 mm MACRO, Canon) and DSLR camera (EOS 7D, Canon) with computer-live mode for needle positioning. The digital images acquired at the front and side views were modified for getting accurate outlines of droplets by the well-known Laplacian function method which was included in the free open source multiplatform Java image-processing program (ImageJ).^{21,22)}

Fig. 2 Schematic of the optic system used in this study for contact angle measurement.

Fig. 3 Comparison of drooping depth as a function of wetting state. S is the distance between pillars and d is the pillar diameter.

Using this program, we estimated the maximum drooping depth and the contact angles together with the use of drop-snake method for contact angle measurement method involved in ImageJ.²³⁾

3. Results and Discussion

According to the observation of Jung and Bhushan,¹⁹⁾ as the droplet hits the surface at velocity, the liquid-air interface below the droplet is formed as seen in Fig. 3 when the dynamic pressure is less than the Laplace pressure. They reported that an equilibrium (or maximum) drooping depth δ of the droplet in the center of the square formed by four pillars can be defined as the ratio of droplet radius to droplet area as follows:

$$\delta = \frac{\sqrt{2P} - D}{8R} \quad (1)$$

where R , P , and D denote the droplet radius, the pitch of pillars, and the pillar diameter, respectively. As illustrated in Fig. 3, it was observed that there are three regimes, i.e., the Cassie state, the Wenzel state, and the transition state for different spacing ratio. In Fig. 3, we can see that under a spacing ratio of 1.81, droplet wetting behavior follows the Cassie state, and at larger than the spacing ratio s/d of ~ 2.95 ,

Fig. 4 Comparison of the measured contact angle on pillars with the theoretical predictions based on Cassie-Baxter and Wenzel models.

the droplet goes to the Wenzel state. Thus, in the range of s/d from ~ 1.81 to ~ 2.95 , there is the transition state where the meniscus is moving inside the groove between two pillar posts and the shape of the meniscus is curved to satisfy the equilibrium CA on the side walls of the posts. In particular, Fig. 3 shows the comparison of the equilibrium drooping depth δ using eq. (1) with the measured data. There exists a substantial difference in the transition regime because eq. (1) originally suggested by Jung and Bhushan¹⁹⁾ cannot describe the partial penetration of liquid meniscus downward, observed in the present experiments. Physically, it was thought that the partial penetration of liquid meniscus shown in Fig. 3 occurs because of the decrease in adhesive forces as the pillar sizes decrease up to sub-millimeter scales. The reason why a partial penetration occurs can be deduced from the force balance between gravitational force and capillary force. Hence, we further need more elaborate expression for eq. (1) by modification including the partial penetration of liquid meniscus in the groove.

Figure 4 shows the measured contact angle (CA) with respect to the normalized spacing ratio by the pillar height H . In general, the Cassie-Baxter and Wenzel equations can be expressed by

$$\cos \theta_W = \left(1 + \frac{\pi d H}{(s+d)^2} \right) \cos \theta_0 \quad \text{for Wenzel state}^{24)} \quad (2)$$

$$\cos \theta_{CB} = \frac{\pi d^2}{4(s+d)^2} (\cos \theta_0 + 1) - 1 \quad \text{for Cassie-Baxter state}^{25)}. \quad (3)$$

Here, θ_0 , s , d and H are the equilibrium contact angle on a flat PDMS, spacing, diameter and height of pillar, respectively. As seen in Fig. 4, the measured contact angles are fairly in good agreement with the Cassie-Baxter equation when s/d is less than 1.81, whereas for higher value of $s/d \sim 1.81$, rapid decrease in CA can be observed. It suggests the existence of transition regime affected by the pillar spacing. In this state, the increase of surface area due to the partial penetration causes the decrease in contact angle.

4. Conclusions

We have reported experimentally the wetting behavior of microstructured hydrophobic surfaces with different pillar spacing sizes. The values of CA and the drooping depth which exists in the transition regime were measured and their characteristics were discussed. The conclusions of the present study can be drawn as follows: First, droplet wetting state changes the Cassie state to the Wenzel state by increasing the spacing ratio, and the transition state was observed. In the transition state, there exists the droop of droplet inside the groove formed by four pillars and the liquid meniscus moves downward because of the force balance between gravitational force and capillary force. Some deviation of measured data from the previous relationship is present because of such a partial penetration of meniscus downward. Second, the contact angle prediction using the Cassie-Baxter equation showed fairly good agreement with experimental data, whereas in the transition regime, the rapid decrease in CA was found. Moreover, as the spacing ratio increases, the droplet state goes to the Wenzel state that the water droplet prefers from a thermodynamic standpoint.

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