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Controlling droplet shape and water repellency by Micro-Structured Precision Surface

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Water repellency of solid surfaces is caused by chemical or structural effects. This property control by chemical effects has been applied to a variety of products, but it requires repeated reapplication, which poses a cost issue. For this reason, the attention has been focused on the structural effect of this property manifested by the micro-structured surface. However, it is unclear that the microstructure suitable for achieving the desired water repellency. The purpose of this study is to investigate microstructures suitable for controlling droplet shape and water repellency, and to clear the mechanisms of droplet shape and microstructure. In this study, we fabricated various microstructures on solid surfaces and experimentally evaluated their water repellency when a droplet is dropped on them. In addition, I considered how the shape and arrangement of the microstructure affects the droplet's water repellency. In general, concavo-convex microstructures exhibit water repellency because air enters the concave areas and surface tension is generated between the air and the liquid. The array of microscopic convexities creates concavities and water repellency. When a drop of water is dropped on a linear microstructure, the capillary action continues to occur in the direction along the line, resulting in a large ratio of contact area to droplet volume, which may not fully demonstrate the water repellency effect. Therefore, we predicted that it would be possible to control the surface water repellency by arranging the shape of the micro-cylinders. To evaluate the droplet shape and water repellency of the fabricated microstructures, we investigated the angle of fall and investigated the microstructures suitable for controlling water repellency. Then, I observed the relationship between the surface of the microstructure and the water repellency of the droplets.

NOMENCLATURE

γ_{SG} =Surface tension of a solid
γ_{LG}=Surface tension of a liquid
γ_{SL}=Interfacial tension between solid and liquid
θ=Contact angle
θ'= Apparent contact angle
r=Ratio of surface to projected area of a droplet
f=Ratio of air to surface on which droplets are dripping

1. Introduction

Controlling droplet shape and water repellency are the technology needed in many fields, and it is expected to be applied to a wide variety of products by increasing water and dirt resistance(1). Water repellency of solid surfaces is caused by chemical or structural effects. This property controlled by chemical effects has been applied to a variety of products, but it requires repeated reapplication, which poses a cost issue. In general, chemical water-repellent processing has the advantage of being easy to process, but unevenness and peeling may occur. In comparison, structural water-repellent processing is more expensive, but it is less prone to unevenness and peeling, and its water repellency can be finely controlled by designing the structure at the micrometer level. For this reason, the attention has been focused on the structural effect of this property manifested by the micro-structured surface. However, it is unclear that the microstructure suitable for achieving the desired droplet shape and water repellency. The purpose of this study is to investigate microstructures suitable for controlling droplet shape and water repellency, and to clear the mechanisms of droplet shape and microstructure. In addition, we considered how the shape and arrangement of the microstructure affects the droplet's water repellency. In this paper, we investigated the contact angle and the fall angle of droplets dropped on the microstructure fabricated by photoresist and discussed the influence of the microstructure on the droplet's water repellency from the measurement results and the change in droplet shape.

2. Evaluation of water repellency

2.1 Contact angle

The water repellency of a solid surface can be evaluated by measuring the contact angle and fall angle when a drop of water is dropped on it. A contact angle is the angle between the solid/liquid boundary and the liquid side of the liquid/gas boundary for a droplet on a solid surface. The contact angle of less than 90 degrees is called hydrophilic, while the contact angle of greater than 90 degrees is called hydrophobic. In an uneven microstructure, air enters the recesses and surface tension is generated between the air and the liquid. When a droplet is dropped onto a solid surface, the droplet curls up due to its own surface tension, and Young's formula is valid[2]. Young's model diagram is shown in Fig. 1.

$$\gamma_{SG} = \gamma_{LG}\cos\theta + \gamma_{SL} \#(1)$$

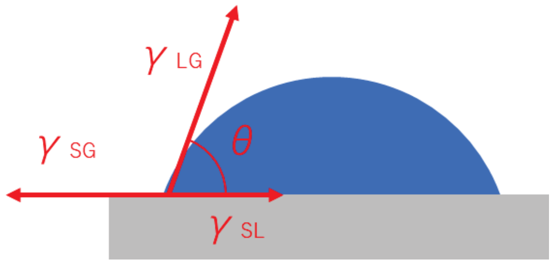


Fig. 1 Young's model diagram.

Wenzel's theory or Cassie-Baxter's theory is the theory that takes roughness into account in Young's theory. If the ratio of the area of the rough surface to the projected area of the droplet is less than a certain criterion, the liquid flows into the concave area, the contact area is increased, and the hydrophilicity is increased Wenzel's equation is valid[3].

$$\cos\theta' = r\frac{\gamma_{SG} - \gamma_{SL}}{\gamma_{LG}} = r\cos\theta \#(2)$$

In contrast, if the ratio is greater than a certain level, the Cassie equation holds that air stays in the recesses and water repellency increases[4].

$$\cos\theta' = f(r\cos\theta + 1) - 1\#(3)$$

The value of f is in the range between 0 and 1. When $f = 1$, the entire solid surface is wet and the Wenzel equation holds.

On the other hand, if the solid surface is tilted after a drop is placed on it, the droplet begins to slide on the surface. The angle of inclination at the moment the droplet begins to slide is called the fall angle. The greater the adhesion force between the droplet and the solid, the larger the tilt angle needs to be. Therefore, the fall angle is an indicator for evaluating water repellency.

2.2 Fabrication of microstructures

In general, concavo-convex microstructures exhibit water repellency when air enters the concave areas and surface tension is generated between the air and the liquid. The array of microscopic convexities creates concavities and water repellency. When water droplets are dropped on the linear microstructure, capillary action occurs in the direction along the line, which may result in insufficient effect of water repellency. Therefore, we expected that the surface repellency could be controlled by arranging the shape of the cylinders. The sample is composed of microcylinders arranged in the shape of an arrow vane.

Microstructures for testing in this study are fabricated by a microfabrication method called photolithography. OAP (HMDS) treatment was used to improve adhesion between the silicon substrate and the photolithography, and SU8-3025 was used as the photoresist. We fabricated several arrays of cylinders with different diameters, array spacing, and array angles. The reason for fabricating multiple arrays is to confirm the effect of array parameters on droplet repellency. The image of the array is shown in Fig. 2. Vertical spacing was set at half the diameter. Linear arrays with different line widths, array spacing, and array angles were also fabricated. Photoresist was fabricated with a thickness of 70 µm.

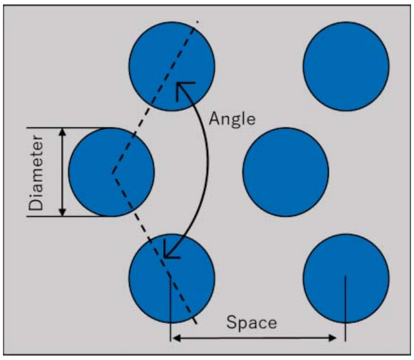


Fig. 2 Image of the designed array.

2.3 Measurement of water repellency

To evaluate the water repellency of the prepared samples, the contact angle and tumble angle were measured when a drop of liquid was dropped on them. Measurements were also taken on surfaces without microstructure, and the differences between surfaces with and without microstructure were observed.

Measurements were carried out by using a contact angle meter (KYOWA, DMs-401). This equipment can measure the contact angle and the tilt angle when tilted up to 90 degrees from the camera by placing a sample on it and dropping a drop of liquid on it.

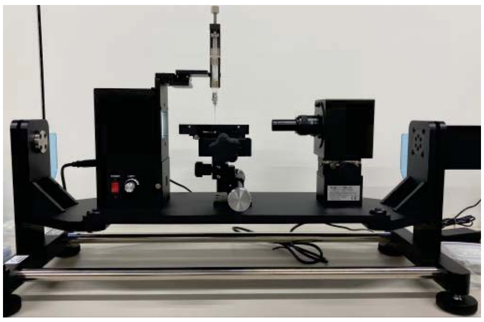


Fig. 3 Contact angle meter (KYOWA, DMs-401).

3. Water repellency of the prepared samples

3.1 Measurement results of fall angle

The water repellency of the prepared samples was evaluated. The droplet with 0.3 µL was dropped on the surface and the angle of fall was measured when the sample was tilted up to 90 degrees.

Microstructure measurements may be unstable due to surface contamination or photoresist degradation. Therefore, we measured the contact angle on the patterned surface where the contact angle could be measured stably. The parameters of the sequences for which measurements were made are listed in Tables 1 and 2.

Table 1 Parameters of the microcylinder array.

No.	Diameter[μm]	Space[μm]	Angle[°]
1	20	20	100
2	20	40	120
3	20	20	160

Table 2 Parameters of the micro linear array.

No.	Width[μm]	Space[μm]	Angle[°]
4	10	20	100
5	10	20	140

The results of five measurements on each surface are shown in Table 3. Measurements were taken every other day to allow the surface to dry sufficiently. The shaded lines in the table indicate that no droplets fell.

Table 3 Fall angle of a droplet dropped on a microstructure.

No.	Fall angle[°]					AVG (Average)	SD (Standard Deviation)
	1st	2nd	3rd	4th	5th		
1		79	43	57		59.7	14.8
2	40	34	30		54	39.5	9.1
3							
4	19	54				36.5	17.5
5			72			72	0

In the sample No. 2, a stable value was observed with a large number of droplets tumbling down. The sample No. 1 and No. 3, where no droplet tumbling was observed, are arrays of microcylinders, but the values of spacing and the angles of the arrays are different from No. 2. Therefore, we investigated the difference in water repellency in samples with different diameters and spacing of microcylinders and different angles of alignment. The parameters of the surfaces measured are shown in Table 4.

Table 4 Parameters of the array of microcylinders that differ only in the angle of the array.

No.	Diameter[μm]	Space[μm]	Angle[°]
2	20	40	120
6	20	40	100
7	20	40	140
8	20	40	160

The results of five measurements for each surface are shown in Table 5. Measurements were taken every other day. The shaded lines in the table indicate that no droplets fell.

Table 5 Fall angle of a droplet dropped on a microstructure

No.	Fall angle[°]					AVG	SD
	1st	2nd	3rd	4th	5th		
2	39	37	40	37	37	38.0	1.3
6	43	36	42	44	38	40.2	3.5
7	38	44	39	40	38	39.8	2.2
8							

The results of contact angle measurements are shown in Table 6. L in Table 6 indicates the arrowhead side of the arrays, and R indicates the arrowhead side of the arrays.

Table 6 Contact angle of a droplet dropped on a microstructure

No.	Contact angle[°]										AVG		SD	
	1st		2nd		3rd		4th		5th					
	L	R	L	R	L	R	L	R	L	R	L	R	L	R
2	136	127	142	145	143	144	142	142	143	140	141	140	2.4	6.6
6	137	135	143	142	136	136	139	142	148	148	141	141	4.2	4.7
7	140	142	135	137	140	141	143	139	131	139	138	140	4.2	1.5
8	134	134	144	142	139	139	143	141	145	137	141	138	4.1	2.7

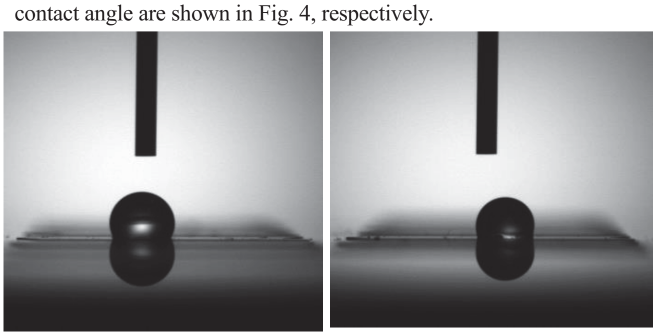
Finally, water repellency was evaluated on a photoresist-coated surface with no microstructure. The contact angle measurement results are shown in Table 7. The sample was tilted up to 90 degrees, but no droplets fell.

Table 7 Contact angle of a droplet on a surface without microstructure.

Contact angle[°]										AVG		SD	
1st		2nd		3rd		4th		5th					
L	R	L	R	L	R	L	R	L	R	L	R	L	R
83.4	83.4	81.4	81.4	79.8	79.8	87.6	85.2	82.8	83.4	83.0	82.6	2.6	1.9

3.2 Observation of droplet shape

Droplets dropped on the microstructure changed shape along the microstructure alignment. The shapes of the droplets taken at the contact angle are shown in Fig. 4, respectively.



(a) Contact angle 116.4° (b) Contact angle 108.3°

Fig.4 Droplet shape photographed by contact angle meter.

The two shapes and contact angles were not very different, but the difference in shape could be seen when each was photographed from directly above. The results are shown in Fig. 5 and Fig.6.

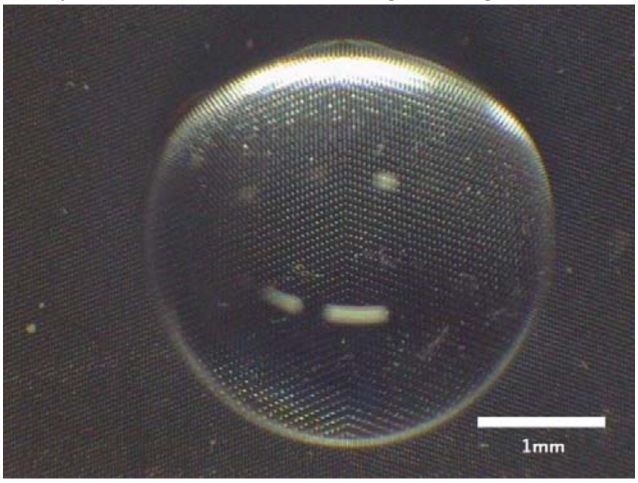


Fig. 5 Droplet photographed from directly above (116.4°).

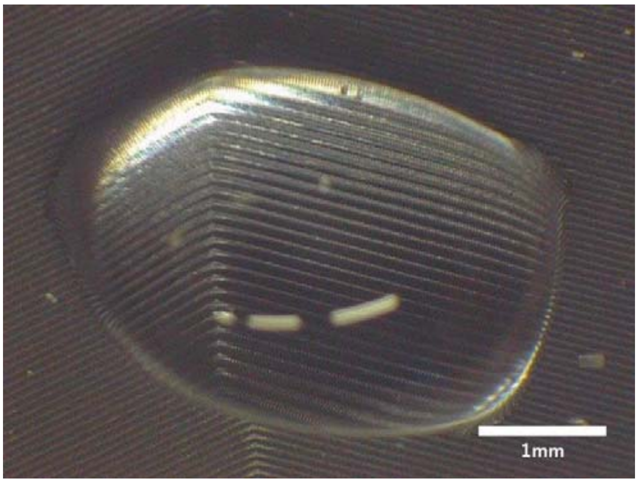


Fig. 6 Droplet photographed from directly above (108.3°).

In Fig. 5, the droplet shape was close to a new circle, but in Fig. 6, the droplet shape appears to change according to the arrangement of microstructures. The reason for the change in droplet shape is thought to be that the spacing between the arrays is different in the direction along the arrowhead and in the horizontal direction, and the water repellency is different in each direction.

4. Discussions

It was thought that linear shapes could not exhibit sufficient water repellency due to capillary action, but Table 3 shows that even the microstructure arrangement has lower water repellency than linear shapes depending on the parameters.

In Table 5, No. 8, which had a large array angle, did not fall, and No. 6, which had a small angle, had a large fall angle and standard deviation. Therefore, it can be said that the difference in the angle of alignment of the microcylinders affects the water repellency. It can be seen that to increase water repellency, it is not always enough to increase the spacing and the area where the droplet is in contact with air.

The contact angle did not exceed 90° on surfaces without microstructure, whereas it exceeded 90° on surfaces with microstructure, even on surfaces where no droplets fell. Therefore, it can be seen that the microstructure expresses water repellency.

Even though the magnitude of contact angle is close, the magnitude of fall angle is different. From this, it can be said that both the contact angle and the fall angle need to be considered when evaluating water repellency.

5. Conclusion

In this study, to evaluate the water repellency due to structural effects on solid surfaces, microstructures were fabricated and the fall angle and contact angle were measured. Measurements were taken on microstructures fabricated by photolithography.

When the fall angles were compared for different microstructure parameters, surfaces with a diameter of 20 μm, spacing of 40 μm, and angle of 120 ° were found to have a lower fall angle and a smaller standard deviation. The contact angle measurements also showed that the presence of microstructure affected the water repellency.

The droplet shape was found to depend on the water repellency of each direction in the microstructure array.

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