Evaluation of Oil Repellent Effect by Metamaterial Structure

Tomoki Nishino¹*, Hiroshi Tanigawa², Atsushi Sekiguchi²,³, and Hiroyuki Mayama⁴

¹ College of Science and Engineering,
² The Research Organization of Science and Technology,
Ritsumeikan University, Kusatsu, Shiga 525-8577, Japan
³ Litho Tech Japan Corporation, Kawaguchi, Saitama 332-0034, Japan
⁴ Department of Chemistry, Asahikawa Medical University,
2-1-1-1 Midorigaoka-Higashi, Asahikawa, Hokkaido 078-8510, Japan

*rits0108@fc.ritsumei.ac.jp

The snail shell has a 200 nm porous structure and oil repellency in water. The nano-porous structure of 200 nm was found to have an oil repellent effect, but the oil repellent behavior on various micro surfaces was not reported, so the oil repellent evaluation of the micro-surface and the nano-surface was performed. The nanosurface showed excellent oil repellency rating, but it was found that the state of oil repellency is different even at the same nanosize. In order to consider the wetting of oil droplets in water, based on surface morphology, the relationship between super water repellency in air and water super water repellency was discussed. These results are useful for designs that add oil repellent technology to the structure. In the near future, oil repelling effect is expected in view of medical use. Therefore, we will promote oil repellent evaluation and production based on the structure.

Keywords: Biomimetics, Repel oil and water, Porous materials, Antifouling technology

1. Introduction

Living organisms are known to be efficient for survival in nature. These have unique features and functions. In particular, there are many studies that focus on the surface effect of living things [1-6]. For example, it is an oil repellent effect in a snail shell having a porous structure with a size of 200 nm. It has been reported that a fine porous structure forms a hydrophilic surface and produces an oil repellent effect [7-9].

In this study, we report how water and oil work on fine surfaces. The nano-porous structure reported to be oil repellent in water [10-13]. The 200 nm nano-porous structure has been found to have an oil repellent effect, but oil repellent behavior on various micro surfaces is not reported. In order to convert to applied technology, evaluation was carried out because it is necessary to have an oil repellent effect on micro surfaces and nano surfaces.

2. Oil repellent effect in structure

As shown in Fig. 1, the structure of the snail shell has an oil repellent effect in water. The equipment for oil repellent experiment is composed of a CCD camera, a stand of vertical and horizontal mechanism, a spectroscopic cell for observation, and a fine needle for measurement. When oil droplets are pressed against the snail shell at a constant speed, no oil droplets adhere to the shell. The oil repellency results were confirmed over time, but no oil droplets were deposited.

Fig. 1. Oil repellent evaluation device and observation.
Next, helium ion microscope (HIM) was used to observe the snail shell with high resolution (Fig. 2). Like a SEM apparatus for scanning electron beams and an FIB apparatus for scanning gallium ions, it is a microscope that can observe helium ions and observe the surface from a secondary electron image obtained from a sample. Moreover, since it is a noble gas, there is little contamination of the sample. Furthermore, by irradiating e\(^-\) simultaneously with He\(^+\) ions, charge-up can be canceled, so it is strong in observation of insulators. The depth of field is five times deeper than the SEM because of the point light source.

![Fig. 2. Snail shells HIM photos: (a) snail shell, (b) whole shells, and (c) enlarged shells.](image)

As shown in Fig. 3, a quartz mask (micro-structure) was produced, and contact exposure was performed to produce a sheet (micro-structure). Although the oil repellency was evaluated, oil droplets did not adhere to the side of the Si substrate to cause oil repellency. It can be seen that structures similar to snail shells do not provide the same function at larger sizes.

![Fig. 3. Oil repellent evaluation device and observation.](image)

Therefore, 200 nm size comparable to a snail shell was examined by the nano-pattern which is further refinement. Figure 4 shows oil repellency evaluations for various nano-surface structures. From the results of the nanopillars aligned with the nano-porous structure, it was found that the oil-repellent state is different even for the same 200 nm-sized structure. It is necessary to discuss the balance of forces at the nano-surface. The contact angle of the surface and the surface energy in air have long been debated for a long time [14-17].

![Fig. 4. Oil repellent in water: (a) no repellent on 2-10 micro-pillar molded PAK, (b) repellent on nano-porous ZrO\(_2\) molded PAK, (c) repellent on black silicon, and (d) repellent on 200 nm-pillar molded PAK.](image)

3. Wetting of water droplets in air: balance between interfacial tensions

Figure 5 illustrates schematic representations of wetting of a water droplet in air (upper panels) and that of an oil droplet in water (lower panels). Let us discuss the relationship between the super water-repellency in air and the super oil-repellency in water based on the surface morphologies.

![Fig. 5. Schematic representations of wetting on flat PAK (a), nano-porous ZrO\(_2\) molded PAK (b) and 200 nm-pillar molded PAK (c), Wetting of a water droplet onto the surfaces in air (upper panels) and wetting of an oil droplet onto the surfaces in water (lower panels).](image)
tension $\gamma_w$ and the solid-water interfacial tension $\gamma_{s-w}$ along horizontal direction as shown in the upper panel of Fig. 5(a). This is described by the following equation (Young’s relation).

$$\cos \theta_{\text{flat}} = \frac{y_s - y_{s-w}}{\gamma_w}$$ (1)

On the other hand, the wetting state on the rough surface of nano-porous ZrO$_2$ molded PAK as shown in the upper panel of Fig. 5(b) is the Wenzel state in which water penetrates into space between surface structures completely. In this case, the air-water interfacial tension and the air-solid interfacial tension are enhanced by $r_\tau$ times due to rough surface structure. The contact angle on rough surface in the Wenzel state, $\theta_W$, is described by Eq. 2 [18].

$$\cos \theta_W = \frac{r_\tau (y_s - y_{s-w})}{\gamma_w}$$ (2)

where $r_\tau$ is roughness factor. This is the ratio of effective surface area to apparent surface area and $r_\tau \geq 1$. The wetting on periodic surface structure is explained by Eq. 3 due to the Cassie-Baxter state. The ideal contact angle in the Cassie-Baxter state $\theta_{\text{CB}}$ is described by the following relation [19].

$$\cos \theta_{\text{CB}} = f_1 \cos \theta_1 + f_2 \cos \theta_2$$ (3)

where $\theta_1$ and $\theta_2$ are the contact angles of flat surfaces of material 1 and 2, respectively, $f_1$ and $f_2$ are the area fractions of material 1 and 2 in apparent surface area, respectively, $\cos \theta_1$ and $\cos \theta_2$ means the wetting on flat surfaces of material 1 and 2, respectively.

Table 1 summarizes the calculation results of the flat PAK, nano-porous ZrO$_2$ molded PAK and multi-pillar PAK.

| Surface | Flat PAK | Nano-porous ZrO$_2$ molded PAK (Periodic surface structures) | Multi-pillar PAK (Periodic surface structures) |
|---------|----------|-------------------------------------------------------------|------------------------------------------------|
| Contact angle (deg.) | $\theta_{\text{flat}} = 62.2^\circ$ | $38.7^\circ$ | $82.7^\circ$ |
| Ratio | 0.66 | 0.63 | 0.64 |
| $r_\tau$ | 1.00 | 1.30 | 1.18 |
| $\theta_{\text{CB}} = \cos^{-1}[(f_1 \cos \theta_1 + f_2 \cos \theta_2)]$ | - | $50.7^\circ$ (exp.) | $52.0^\circ$ (exp.) |
| $f_1$ | 0.65 (iron CA) | 0.26 (exp.) | 0.26 (exp.) |
| $f_2$ | - | 0.90 (iron CA) | 0.90 (iron CA) |
| $\theta_W$ | - | $50.0^\circ$ (exp.) | $52.0^\circ$ (exp.) |
| Wetting state | Usual | Usual | Cassie-Baxter state with pinning effect |

Table 1 summarizes the calculation results of $r_\tau$, experimental and theoretical values of $\theta_W$, $f_1$, $\theta_{\text{CB}}$ and corresponding wetting state. As a result, the wetting on nano-porous ZrO$_2$ molded PAK is explained by the Wenzel state, while that on multi-pillar can be understood by both the Wenzel state and the non-ideal Cassie-Baxter state. In the non-ideal Cassie-Baxter state, the contact line is pinned by the edges of pillars. This is the reason why the actual wetting state is deviated from the ideal Cassie-Baxter state.

4. Wetting of oil droplets in water: balance of Laplace pressures

Next, let us discuss the wetting of oil droplets in water. In this case, the oil-water interfacial tension $\gamma_{o-w}$ and the solid-water interfacial tension $\gamma_{s-w}$ take the places of $\gamma_w$ and $y_s$ in air, respectively. There are three factors to understand the wetting in water. One is Laplace pressure of oil droplet in water $P_{L,\text{oil in w}}$ due to its radius $R_{\text{oil}}$. $P_{L,\text{oil in w}}$ is described by the following relation.

$$P_{L,\text{oil in w}} = \frac{2\gamma_{o-w}}{R_{\text{oil}}}$$ (4)

where $\gamma_{o-w}$ is the oil-water interfacial tension.

Second is Laplace pressure due to surface structure $P_{L,\text{surf}}$. This is due to the curvature radius of the oil droplet when it touches the basement between the surface structures as shown in Fig. 6(c). Assuming the arrangement of the square lattice of cylindrical pillars, $P_{L,\text{surf}}$ is expressed by Eq. 5.

$$P_{L,\text{surf}} = \frac{16\gamma_L H}{(\sqrt{2}p - D)^2}$$ (5)

where $\gamma_L$ is the surface tension of liquid, $H$ is the height of pillars, $p$ is the pitch of pillars and $D$ is the diameter of pillars. Now, Laplace pressure in water $P_{L,\text{surf in w}}$ is

$$P_{L,\text{surf in w}} = \frac{16\gamma_{o-w} H}{(\sqrt{2}p - D)^2}$$ (6)
Roughly, the condition of the adhesion of the oil droplet onto the surfaces is $P_{L,\text{surf in w}} < P_{L,\text{oil in w}}$. Third is Laplace pressure $P_{L,\text{fric}}$ corresponding to friction energy originating from fluids. One fluid is droplet and other is the fluid on surface, air or liquid. This is described by Eq. 7.

$$P_{L,\text{fric}} = \frac{\eta_{\text{fluid1}}v^2\tau}{(\sqrt{2p-D})^2} + \frac{\eta_{\text{fluid2}}v^2\tau}{(\sqrt{2p-D})^2} \quad (7)$$

where $\eta_{\text{fluid1}}$ and $\eta_{\text{fluid2}}$ are the viscosities of fluid 1 and 2, $v$ is the velocity of the droplet in touch to surface, and $\tau$ is the characteristic time scale to remove water in the space between the surface structures. It should be noted that $P_{L,\text{fric}}$ can be neglected in the conditions of larger $p$, however, this can not be neglected in the conditions of smaller $p$. The fluids are water and air in the case of wetting of the water droplets in air, while these are oil and water in the case of wetting of the oil droplets in water. Now, Eq. 7 becomes Eq. 8.

$$P_{L,\text{fric in w}} = \frac{\eta_w v^2\tau}{(\sqrt{2p-D})^2} + \frac{\eta_oil v^2\tau}{(\sqrt{2p-D})^2} \quad (8)$$

From Eqs. 4, 7, and 8, let us discuss the condition of wetting (adhesion) of oil droplets onto the surfaces in water. The wetting of oil droplets in water occurs in the following conditions.

$$P_{L,\text{oil in w}} > P_{L,\text{surf in w}} + P_{L,\text{fric in w}} \quad (9)$$

In the case of flat PAK surface, $P_{L,\text{surf}} = 0$, $P_{L,\text{fric}} = 0$ because of the conditions of flat surface are $H = 0$, $p = \infty$ and $D = 0$. Therefore, $P_{L,\text{oil}} > 0$ and Eq. 9 is maintained and the wetting of the oil droplets is explained. In the case of nano-porous ZrO$_2$ molded PAK surface, the small amount of oil adhered. This means that it is possible to touch the surface between the random surface structures. This is easy to understand when the situation as shown Fig. 6(c) is valid. The conditions of the local surface are $H > 0$ and $p < R_{oil}$. $P_{L,\text{surf}} > 0$ and $P_{L,\text{fric}} > 0$. Therefore, the relation of $P_{L,\text{oil}} < P_{L,\text{surf}} + P_{L,\text{fric}}$ is maintained in the local surface. In the case of multi-pillar PAK surface, the conditions are $H = 200 \text{ nm} > 0$ and $p = 200 \text{ nm} \ll R_{oil}$. Therefore, the relation of $P_{L,\text{oil}} \ll P_{L,\text{surf}} + P_{L,\text{fric}}$ is maintained in the surface. The non-wetting of the oil droplet is thus explained. Table 2 summarizes the conditions of the surfaces of flat PAK, nano-porous ZrO$_2$ molded PAK and multi-pillar PAK and these Laplace pressures.

### 5. Balance of Laplace pressures in wetting of water droplets in air

In the above discussion, we discussed the contact angles in the wetting of water droplets in air based on the balance between the interfacial tensions first, and then we discussed the wetting of oil droplets in water based on the balance between the Laplace pressures. Now, we go back to the wetting of water droplets in air and try to understand it along the scenario of the balance between Laplace pressures. The significant differences can be found in Laplace pressures due to the surface tensions of droplet and friction between fluids. The Laplace pressure of the water droplet (surface tension $\gamma_w$ and radius $R_w$) in air $P_{L,w}$ is described by Eq. 10.

Table 2 Conditions of the surfaces of the flat PAK, nano-porous ZrO$_2$ molded PAK and multi-pillar PAK and these Laplace pressures.

| Surface | Flat PAK | Nano-porous ZrO$_2$ molded PAK (Random surface structure) | Multi-pillar PAK (Periodic surface structure) |
|---------|----------|---------------------------------------------------------|------------------------------------------|
| $H$     | 0        | $> 0$                                                   | $\leq 200 \text{ nm} < R_{oil}$              |
| $p$     | $w$      | $< R_{oil}$                                            | $200 \text{ nm} < R_{oil}$            |
| $\eta_{oil}$ | $> 0$ | $> 0$ (Local)                                         | $> 0$                                   |
| $\eta_{\text{air}}$ | $0$ | $\leq 0$ (Local)                                     | $> 0$                                   |
| Relation | $P_{\text{L,air in w}} > P_{\text{L,oil in w}} + P_{\text{L,fric in w}}$ | $P_{\text{L,air in w}} > P_{\text{L,oil in w}} + P_{\text{L,fric in w}}$ | $P_{\text{L,air in w}} < P_{\text{L,oil in w}} + P_{\text{L,fric in w}}$ | $P_{\text{L,air in w}} < P_{\text{L,oil in w}} + P_{\text{L,fric in w}}$ |
| Water wetting | Local Wetting | Non-Wetting | Wet |
| $P_{\text{L,oil}}$ | $> 0$ | $> 0$ | $> 0$ |
| $P_{\text{L,fric}}$ | $0$ | $> 0$ | $> 0$ |
| Relation | $P_{\text{L,oil}} > P_{\text{L,fric}}$ | $P_{\text{L,oil}} > P_{\text{L,fric}}$ | $P_{\text{L,oil}} > P_{\text{L,fric}}$ | $P_{\text{L,oil}} > P_{\text{L,fric}}$ |
| Water in air | Wet | Wet | Wet |

$$P_{L,w} \frac{2\gamma_w}{R_w} > P_{L,\text{oil in w}} \quad (10)$$

The Laplace pressure due to surface structures in air is

$$P_{L,\text{surf}} = \frac{16\gamma_w H}{(\sqrt{2p-D})^2} > P_{L,\text{surf in w}} \quad (11)$$

The Laplace pressure due to friction in air is

$$P_{L,\text{fric}} = \frac{\eta_{\text{air}} v^2 \tau}{(\sqrt{2p-D})^2} + \frac{\eta_w v^2 \tau}{(\sqrt{2p-D})^2} \sim \frac{\eta_w v^2 \tau}{(\sqrt{2p-D})^2} \quad (12)$$

$P_{L,\text{fric}}$ is expected to be several tens percent of
As a result, the experimental results explain the following relation.

\[ P_{L,w} > P_{L,\text{surf}} + P_{L,\text{fric}} \]  (13)

In air, the Laplace pressure due to friction decreases. This is the driving force of the penetration of water in air. Table 2 summarizes the Laplace pressures and these relations in water and air.

6. Conclusions

The oil repellency of the micro-surface and the nano-surface was evaluated. The nano-surface showed excellent oil repellency rating, but it was found that the state of oil repellency is different even at the same nano size. In order to consider the wetting of oil droplets in water, we first discussed the contact angle in the wetting of water droplets in air based on the balance of interfacial tension. Next, we discussed the wetting of oil droplets in water based on the balance of Laplace pressure. The major differences are seen in the surface tension of the droplets and the Laplace pressure due to friction between the fluids. In the future, we will investigate the effects of oil repellency and structures such as height, width and radius of curvature. We will also proceed with the preparation of medical products using oil repellent technology.

References

1. K. Watanabe, T. Hoshino, K. Kanda, Y. Haruyama, and S. Matsui, Jpn. J. Appl. Phys., 44 (2005) L48.
2. A. Finnemore, P. Cunha, T. Shean, S. Vignolini, S. Guldin, M. Oyen, and U. Steiner, Nat. Commun., 3 (2012) 966.
3. K. Autumn, Y. A. Liang, S. T. Hsieh, W. Zesch, W. P. Chan, T. W. Kenny, R. Fearing, and R. J. Full, Nature, 405 (2000) 681.
4. B. Bhushan, Philos. Trans. R. Soc., 367 (2009) 1445.
5. B. Bhushan and Y. C. Jung, Nanotechnology, 17 (2006) 2758.
6. Z. Burton and B. Bhushan, Ultramicroscopy, 106 (2006) 709.
7. A. G. Domel, M. Saadat, J. C. Weaver, H. H. Hariri, K. Bertolodi, and G. V. Launder, J. R. Soc. Interface, 15 (2018) 1742.
8. J. Knippers, K. G. Nickel, and T. Speck, “Biomimetic Research for Architecture and Building Construction” Springer International Pub. Co., Switzerland, (2016) 408.
9. M. Shimomura, “Biomimetics” Tokai university Pub. Co., Tokai, (2016) 16.
10. T. Nishino, H. Tanigawa, and A. Sekiguchi, J. Photopolym. Sci. Technol., 31 (2018) 129.
11. A. Sekiguchi, Y. Matsumoto, H. Minami, T. Nishino, H. Tanigawa, K. Tokumaru, and F. Tsumori, J. Photopolym. Sci. Technol., 31 (2018) 121.
12. A. Sekiguchi, Y. Matsumoto, H. Minami, T. Nishino, H. Tanigawa, K. Tokumaru, and F. Tsumori, Proc. SPIE, 10728 (2018) 107280L.
13. T. Nishino, H. Tanigawa, and A. Sekiguchi, Proc. SPIE, 10728 (2018) 1072804.
14. C. W. Extend, Langmuir., 18 (2002) 7991.
15. J. Kijlstra, K. Reihs, A. Klami, Colloids Surf., 206 (2002) 521.
16. B. Bhushan and Y. C. Jung, J. Phys.: Condens. Matter, 20 (2008) 225010.
17. Y. C. Jung and B. Bhushan, J. Microsc., 229 (2008) 127.
18. R. N. Wenzel, Ind. Eng. Chem., 28 (1936) 988.
19. A. Cassie and S. Baxter, Trans. Faraday Soc., 40 (1944) 546.