Study of Nanoimprinting Plant Structures with Super Water Repellency

Atsushi Sekiguchi1,2*, Tomoki Nishino2, Hiroshi Tanigawa2, Hiroko Minami1, Yoko Matsumoto1, and Hiroyuki Mayama3

1 Litho Tech Japan Corporation, 2-6-6-201, Namiki, Kawaguchi, Saitama 332-0034, Japan
2 The Research Organization of Science and Technology, Ritsumeikan University, 1-1-1 Noji-higashi, Kusatsu, Shiga 525-8577, Japan
3 Asahikawa Medical University, Midorigaoka-Higashi 2-1-1-1, Asahikawa, Hokkaido 078-8510, Japan
*Sekiguchi-pdg@ltj.co.jp

The leaves of plants belonging to the Araceae family and to the Nelumbonaceae family, represented by the lotus leaf, are known to exhibit water repellency, a property attributed to a double roughness structure having nanostructures on the surface of the leaves. Past research efforts have examined biomimetic structures modeled on the structure of the lotus leaf. The present report presents the results of investigations of a lotus leaf structure transferred onto acrylic resin, made using a live plant as the original material instead of an engineered imitation. The results confirmed that the super water repellency derives from this structure.

Keywords: Lotus leaf, Taro leaf, Super water repellency, Biomimetics, Nanoimprinting, PDMS, UV-cured acrylic resin

1. Introduction

The leaves of plants belonging to the Araceae family and to the Nelumbonaceae family, represented by the lotus leaf, are known to exhibit water repellency [1], a property attributed to double roughness nanostructures [2,3]. Past research efforts have examined biomimetic structures modeled on the structure of the lotus leaf [4,5]. The study reported on here used a live plant as the source of the structure, which was transferred onto PDMS [6] by the nanocasting method [7,8]. The PDMS transcript was subsequently used as a mold for retransferring the structure onto acrylic resin by the nanoimprinting method [9,10]. This paper reports on investigations carried out to determine whether water repellency is reproduced in the acrylic resin transcript and whether the water repellency derives from the structure itself.

2. Structures and water repellency of plant leaves

Figure 1 presents photos showing the appearance, SEM observations of leaf surfaces, and water repellency (contact angles) of the plants studied.

The plants selected were three species of water repellent plants (Colocasia esculenta 'Black Magic,' Colocasia esculenta var. Aquatillis, and Nelumbo nucifera 'Mamukala') and three species of non-water repellent plants (Colocasia esculenta 'Coffee Cups,' Alocasia odora, and Nymphaea 'General Pershing'). The round projections located in indentations or on projections and the fine fibers covering the entire surface of the leaves are common features of the leaf surfaces of water repellent plants. All exhibit angles of contact with water exceeding 150°, making them super water repellent. In contrast, the leaf surfaces of non-water repellent plants lack such projections and fine fibers. Angles of contact with water were 60° for the Nymphaea leaf and 90° for the leaves of the Araceae family. Of particular interest is the significant difference observed in water repellency between Colocasia esculenta 'Black Magic' and Colocasia esculenta 'Coffee Cups,' both of which belong to the same family (Araceae) and genus (Colocasia). While the shapes of the leaves are similar, the difference in
Fig. 1. Photos of leaf appearance, SEM observations of leaf surfaces, and water repellency of the plant leaves studied.

(a) Water repellent plants

Colocasia esculenta
'Black Magic'

Colocasia esculenta
Var. Aquatilis

Nelumbo nucifera
'Mamukala'

Water repellent
Contact Angle
CA>150°

(b) Non-water repellent plants

Colocasia esculenta
'Coffee Cups'

Nymphaes Mexicana
'Mexicana'

Alocasia odora
'Alocasia odora'

Water repellent
Contact Angle
CA=92.2°
CA=59.3°
CA=94.8°
The surface structures of these leaves were transferred from the six species of plants onto PDMS by the nanocasting method, then transferred to light-curable acrylic resin by the PDMS transcript produced as the mold to allow measurements of contact angles.

3. Experimental
3.1. Patterning by nanocasting and nanoimprinting methods

Figure 2 illustrates the nanocasting method [5,6]. First, a plant leaf is fixed inside a Petri dish, onto which an Si-based resin PDMS is poured [9]. Before the resin is poured, a mold release agent was sprayed onto the leaf and allowed to dry. The mold release agent is DURASURF DS-800 (Harves Co., Ltd.). The PDMS is the SILPOT 184 (Dow Corning Toray Co, Ltd.). The resin was placed in a vacuum chamber for 24 hours, then heated to 60 °C and allowed to stand for two hours to cure. At this point, the PDMS was released from the leaf and ready to use as a transcript mold.

Figure 3 shows the scheme of the nanoimprinting method [9,10]. First, a mold release agent was sprayed onto the PDMS transcript mold obtained in
the previous step and allowed to stand to dry. A UV-curable acrylic resin (PAK-01) was the dripped over a quartz substrate [11] and the PDMS mold pressed onto the resin from above. This process was performed using the LTNIP-5000 nanoimprint equipment [12], with stamping pressure set to 1.5 MPa. Once the PAK-01 completely filled the mold, the resin was exposed to UV light to cure (wavelength and illuminance of 365 nm and 10 mW/cm², respectively). After the PAK-01 was cured, the PDMS mold was released, at which point the acrylic resin transcript of the original plant leaf was ready.

Figure 4 are photos showing the results of nanocasting and nanoimprinting transfer.

This method was used to transfer the structures of three water repellent plant species and three non-water repellent plant species to acrylic resin. Figure 5 shows the transfer results.

All water repellent plants exhibit a double roughness structure on their surface. This is also observed on the acrylic resin transcripts. In contrast, the double roughness structure is absent from the surfaces of non-water repellent plants and from their acrylic resin transcripts.

3.2. Evaluation of contact angles

Figure 6 shows the results of investigations of the water repellency of acrylic resin transcripts of three water repellent plant species and three non-water repellent plant species.

The contact angles of PAK-01 transcripts of the water repellent plants were about 110°; the contact angles of PAK-01 transcripts of the non-water repellent plants were about 70° to 90°; and the contact angle of a flat PAK-01 substrate was 65.7°. Without exception, the contact angles of the PAK-01 transcripts of water repellent plants exceeded those of the non-water repellent plants. This confirms that PAK-01 transcripts with the double roughness structure transferred from water repellent plants demonstrate enhanced water repellency. However, no instances were observed of super water repellent contact angles exceeding 150° recorded in the real leaves.

The subsequent section discusses this failure to achieve super water repellent contact angles exceeding 150° in the PAK-01 transcripts.

4. Results and discussion

The discussions here will focus on the *Colocasia esculenta* 'Black Magic' leaf. Figure 7 presents SEM photos of a *Colocasia esculenta* 'Black Magic' leaf.

The surface of the *Colocasia esculenta* 'Black Magic' leaf features fine nanostructures on top of large projections. The nanostructures measure approximately 100 nm. Hence, the leaf can be regarded to have a double roughness structure. These fine nanostructures are believed to trap air and create water repellency. Figure 8 shows the results of laser scanning microscope observations of a *Colocasia esculenta* 'Black Magic' leaf, the PDMS transcript mold, and the acrylic resin transcript. The PDMS transcript mold exhibits an inverted pattern relative to the original leaf; the concave/
Fig. 5. Transfer results (SEM photos) for plant leaf surfaces, PDMS, and acrylic resin (PAK-01).

(a) Transfer results for water repellent plants

Colocasia esculenta
'Black Magic'

Colocasia esculenta
Var. Aquatilis

Nelumbo nucifera
'Mamukala'

(b) Transfer results for non-water repellent plants

Colocasia esculenta
'Coffee Cups'

Nymphaes Mexicana
'Mexicana'

Alocasia odora
'Alocasia odora'
Fig. 6. Evaluations of water repellency of PAK-01 transcripts (contact angle measurements).

Fig. 7. SEM photos of the surface of the *Colocasia esculenta* 'Black Magic' leaf.

Fig. 8. Results of laser scanning microscope observations of *Colocasia esculenta* 'Black Magic' leaf, PDMS transcript mold, and acrylic resin transcript.
convex structures in the image are reversed for the sake of comparison.

Microscopic observations of the Colocasia esculenta 'Black Magic' leaf show fine nanostructures on the upper parts of the projections and in surrounding areas (areas within the circle). These are absent from the PDMS transcript mold and thus from the acrylic resin transcript. The failure of the contact angle in the PAK-01 transcript to achieve contact angles greater than 110° appears to be attributable to the absence of the double roughness structure. Nevertheless, the water repellency of the single roughness structure still exceeds that of a flat pattern-free PAK-01 substrate. The contact angle of the PAK-01 transcript exceeds the 65.7° of the flat PAK-01 substrate.

The following is a theoretical consideration of the water repellency of the double roughness structure. A lotus leaf completely repels raindrops, as shown in Fig. 9(a); these drops roll down a slightly tilted leaf, a phenomenon called the lotus effect [13-17] and considered among the most important topics in biomimetics. In current studies of wetting phenomena, the lotus effect is explained by the double roughness structure surface on the lotus leaf.

Here, the double roughness structure surface is defined as a surface covered by both large-scale and small-scale structures, wherein the large-scale structures are further covered by small-scale structures, as shown in Fig. 9(b). The lotus effect has two aspects of interest: super water repellency (contact angle $\theta \geq 150^\circ$) and the phenomenon of water droplets sliding down slightly tilted lotus leaves. The focus here is on the bouncing behavior of raindrops on a lotus leaf, as shown in Fig. 9(b), the mechanism of which is not fully explained by the physics of double roughness structure surfaces. The super water repellency of the lotus effect has conventionally been explained by the Cassie–Baxter state (Fig. 9) [17-19]: as a water droplet slides over a super water repellent surface in a Cassie–Baxter state, it touches only the heads of the pillars along the normal direction and does not infiltrate into the spaces between them. As a result, air occupies this space between the pillars. The contact angle in the Cassie–Baxter state, $\theta_{CB}$, is given by Eq. (1):

$$\cos \theta_{CB} = f_1 \cos \theta_1 + f_2 \cos \theta_2$$  \hspace{1cm} (1)

where $f_1$ and $f_2$ are area fractions of Species 1 and 2, respectively; $f_1 + f_2 = 1$; and $\theta_1$ and $\theta_2$ are contact angles of Species 1 and 2, respectively. That is, $\theta_{CB}$ is the contact angle for the mixed surface of Species 1 and 2. If Species 1 and 2, respectively are a hydrophobic material and air, Eq. (2) for the mixed surface of Species 1 and air can be derived from Eq. (1): \[17-19\]

$$\cos \theta_{CB} = f_1 (1 + \cos \theta_1) - 1$$  \hspace{1cm} (2)

Upon careful observation, the shiny surface of a lotus leaf is visible under water droplets due to the reflection of sunlight from the air–water interface, as shown in Fig. 10. The Cassie–Baxter state occurs on single roughness structure surfaces as well as on double roughness structure surfaces.

The sliding phenomenon of water drops on a lotus leaf is explained by the local pinning effect of small-scale structures on large-scale structures, as shown in Fig. 11 [20,21]. Generally, the pinning effect means that the contact line of a water droplet is pinned by pinning points such as surface structures (physical defects) and contaminants (chemical defects) and that the surface area of the pinned droplet increases due to its deformation [18,22]. The energy required for the deformation corresponds to the pinning energy [22].
Subsequently, a droplet slides down when its potential energy between two large-scale structures on a lotus leaf exceeds the local pinning energy of small-scale structures.

Fig. 10. Schematic drawing of Cassie–Baxter state on multi-pillar surface.

The super water repellency induced by the Cassie–Baxter state and the sliding phenomenon can be explained by the double roughness structure. Taking the above into consideration, super water repellency appears reproducible by forming a double roughness structure on the acrylic reprinted material [23].

5. Summary

Based on the original of a live plant leaf, the leaf surface structure was transferred onto PDMS by the nanocasting method. This PDMS pattern served as the transcript mold. The structure was then retransferred onto an acrylic resin by the nanoimprinting method to create an acrylic resin transcript. Experiments were performed to determine whether super water repellency can be reproduced with the structure on the acrylic resin transcript. The resulting contact angles of the acrylic resin transcripts of super water repellent plants and non-water repellent plants were approximately 110° and 70° to 90°, respectively. The contact angles were greater for the transcripts of super water repellent plants. Contact angles greater than 150° on the leaf itself could not be reproduced, indicating that the double roughness structure was not successfully transferred to the acrylic resin transcript. Since the contact angle of acrylic resin is 65.7°, this confirms water repellency is attributable to this structure. Future studies will seek to determine whether super water repellency can be reproduced by forming the double roughness structure on the acrylic resin transcript.

Acknowledgements

We are grateful to Ms. Natsuko Koike of the Kawaguchi Green Center Botanical Garden and Park and Mr. Kazuyoshi Yamamoto of the Kyoto Botanical Gardens provided the plants used in this study.

References
1. M. Shimomura, “Biomimetics, National Science Museum16”, Tokai University Press, 2 (2016) 2.
2. R. N. Wenzel, Ind. Eng. Chem., 28 (1936) 988.
3. Y. C. Jung and B. Bhushan, J. Microsc., 229 (2008) 127.
4. H. Nishikawa, J. Surf. Finish. Soc. Jpn., 49 (2011) 458.
5. H. Nishikawa, J. Surf. Finish. Soc. Jpn., 67 (2016) 482.
6. T. Hasegawa, Jpn. Soc. Microgravity Appl., 25 (2008) 161.
7. H. Takegami, M. Fuji, and M. Takahashi, Ann. Rep. Ceram. Res. Lab. Nagoya Inst. Technol., 5 (2005) 33.
8. K. Sogo, M. Nakajima, and Y. Hirai, J. Photopolym. Sci. Technol., 19 (2006) 647.
9. K. Suzuki, S. W. Youn, and H. Hiroshima, J. Photopolym. Sci. Technol., 31 (2018) 295.
10. A. Miyauchi, J. High Press. Inst. Jpn., 44 (2006) 341 (in Japanese).
11. N. Sakai and T. Hirasawa, Kobunshi Ronbunshu, 66 (2009) 88 (in Japanese).
12. A. Sekiguchi, Y. Kono, and Y. Hirai, J. Photopolym. Sci. Technol., 18 (2005) 543.
13. W. Barthlott and C. Neinhuis, *Planta*, **202** (1997) 1.
14. C. Neinhuis and W. Barthlott, *Ann. Bot.*, **79** (1997) 667.
15. L. Feng, Y. Zhang, J. Xi, Y. Zhu, N. Wang, F. Xia, and L. Jiang, *Langmuir*, **24** (2008) 4114.
16. J. Lv, Y. Song, L. Jiang, and J. Wang, *ACS Nano*, **8** (2014) 3152.
17. B. Bhushan, “Biomimetics – Bioinspired Hierarchical-Structured Surfaces for Green Science and Technology”, 2nd ed., Springer, (2016).
18. P. G. de Gennes, F. Brochard-Wyart, and D. Quéré, “Capillarity and Wetting Phenomena: Drops, Bubbles, Pearls, Waves”, Springer, New York, 2004 (translated by A. Reisinger).
19. A. B. D. Cassie and S. Baxter, *Trans. Faraday Soc.*, **40** (1944) 546.
20. K. Uchida, R. Nishimura, E. Hatano, H. Mayama, and S. Yokojima, *Chem. Eur. J.*, **24** (2018) 8491.
21. M. Yamamoto, N. Nishikawa, H. Mayama, Y. Nonomura, S. Yokojima, S. Nakamura, and K. Uchida, *Langmuir*, **31** (2015) 7355.
22. H. Mayama and Y. Nonomura, *Langmuir*, **27** (2011) 3550.
23. H. Mayama, *J. Photopolym. Sci. Technol.*, **35** (2018) 543.