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HYDROPHOBICITY OF FEATHER-INSPIRED, 3D-PRINTED, POLYMERIC MATERIALS

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ABSTRACT

Feathers can vary hydrophobicity through differences in their microstructure geometry. These microstructures, known as barbs and barbules, can be emulated through 3D-printed materials at an enlarged scale to probe how different parameters of feather-like ridges influence hydrophobicity. The design includes five three-millimeter-wide circular samples featuring barbule-like ridges with different widths and angles. To characterize hydrophobicity, a two-microliter drop of water is placed on a sample surface, and a goniometer measures the mean contact angle (MCA), where higher mean contact angles indicate greater hydrophobicity. Wider ridges decreased hydrophobicity quadratically, with a leading coefficient of $(-2.37 \pm 0.92)\times10^{-3}$ °/µm^2, while steeper angles increased hydrophobicity linearly, with a slope of $(7.0 \pm 3.8)\times10^{-1}$, which is consistent with the theory behind feather hydrophobicity.

Keywords: barbules, feather structure, hydrophobicity, contact angle

INTRODUCTION

Feathers exhibit a range of affinity to water, and this property is thought to be determined mainly by the width and spacing of barbs and barbules, illustrated in figure 1. They're arranged in such a way that minimizes contact between a water drop and a feather [1].

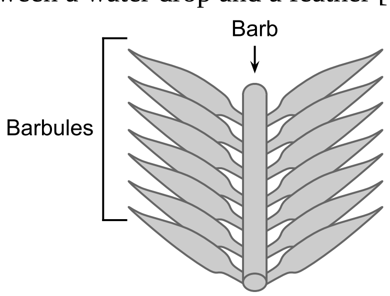

Figure 1: General schematic of a barb and barbules from a bird feather [1].

The male mallard flight feather in figure 2 shows how generally, wider-spaced and thinner barbules are more hydrophobic. Iridescent feathers have closer-spaced and wider barbules to reflect more light, but with the detriment of typically being more hydrophilic [2].

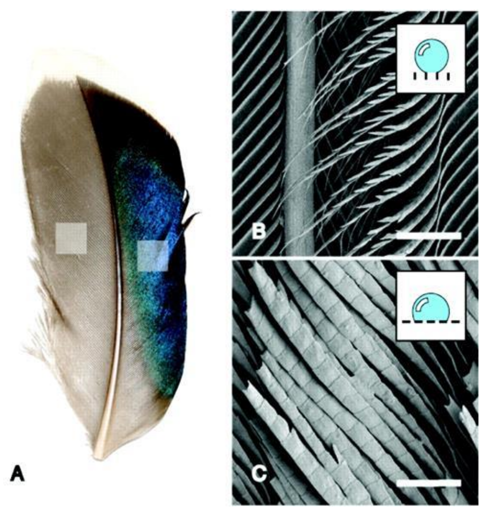

Figure 2: Secondary flight feather showcasing the iridescent and non-iridescent parts of a feather from a male mallard (A). Scanning electron microscope (SEM) images that show the wide variance in barbule geometry between the iridescent (B) and non-iridescent (C) parts of the feather [2].

However, the gorget (iridescent throat) feathers of the male hummingbird are simultaneously hydrophobic and iridescent. Figure 3 shows how the barbules of the gorget feathers are quite close together and wide, but the side view shows the angles of the barbules. Generally, feathers largely depend on thinner barbules to maintain hydrophobicity, so this structure is atypical among bird species and may offer a different way to maintain hydrophobicity [2].

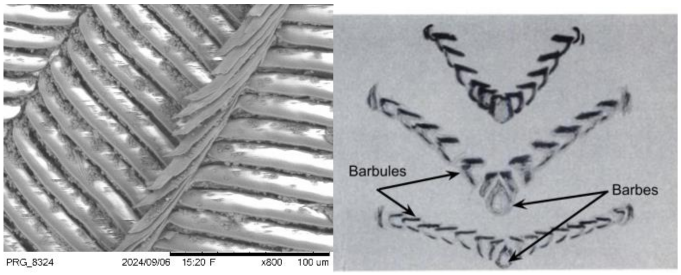

Figure 3: Personal SEM image taken of gorget feather from male ruby-throated hummingbird (left) and side view of the barbule angles from the same feather type (right). The side view images provides an atypical way to vary hydrophobicity of feathers [3, 4].

Referencing these different feather types offers two ways to possibly vary the hydrophobicity of feather-like materials: through ridge width and angles of a material. A method of necessary abstraction is developed from a literature review to provide the scaling and geometry to CAD and 3D-print samples with varying parameters within the range of real feather-like geometry. Second, a goniometer measures the static contact angle of water drops set to a constant volume, with higher contact angles correlating with higher hydrophobicity. The hydrophobicity can then be compared to varying widths and angles of the samples. This project is an extension of a larger project for a SuperUROP specifically studying how gorget feathers from the ruby-throated hummingbird can be simultaneously hydrophobic and iridescent, which explains why some design choices take more inspiration from hummingbird feathers.

BACKGROUND THEORY

Previous literature on the hydrophobicity of feathers allows the development of a methodology for how to design feather-like materials and characterize the hydrophobicity of these complex surfaces.

BARBULE STRUCTURE

SEM images of barbules from different bird species can be used to find different appropriate ridge widths and spacing to test. Figure 4 reveals that barbules tend to be spaced 16-20 micrometers apart, and visually, the barbules appear to take up between a sixth to almost all the space from the top view, observed between the American robin and the ruby-throated hummingbird back feathers. The side view image in figure 3 offers an idea of the appropriate angles to test, which are approximately 15º, 30º, and 45º relative to the horizontal axis. A ratio of roughly 1:5 for the center-to-center spacing to the length of the barbules can be observed from figures 3 and 4, which can act as a good constant for the sample design.

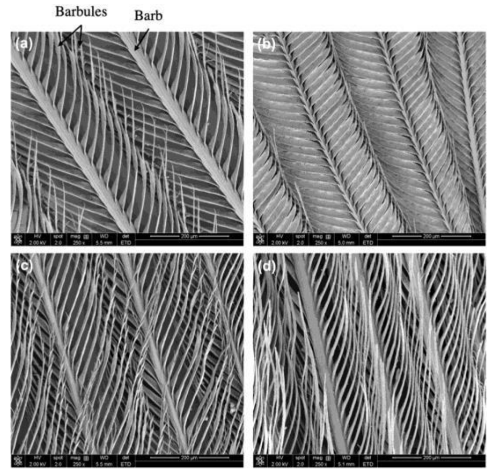

Figure 4: SEM images of feathers from the backs of: American robin (a), ruby-throated hummingbird (b), common tern (c), and the thick-billed murre (d). Comparing the geometries confirms how generally, hydrophobic feathers tend to minimize surface area exposed through more perpendicularly aligned barbules, which can be seen among the common tern's and the thick-billed murre's feathers. The common tern and thick-billed murre are aquatic bird species, which tend to have more hydrophobic feathers. Referencing different feathers from a variety of species is necessary for determining an acceptable range of geometry for the 3D-printed samples [1].

Referencing these values from the images enables the computer-aided designing and 3D-printing of small circles with varying parameters based off similar proportions observed from these images. For faster and easier design and prints, the design was scaled up sixfold from the actual feathers. For the necessary resolution, an UpNano two-photon polymerization 3D-printer was used with UpPhoto resin. A sample CAD is shown in figure 5. The five printed samples are circular with diameters of three millimeters and vary either ridge width or angle. The main valley lines are akin to barbs from real feathers. Also, the 120 μm center-to-center ridge spacing, 600 μm ridge-length spacing, and the 65º branching of the ridges from the middle ridge will not change, with the length proportions discussed before, and the 65º determined from the SEM image in figure 3, chosen so that the samples somewhat emulate hummingbird feathers.

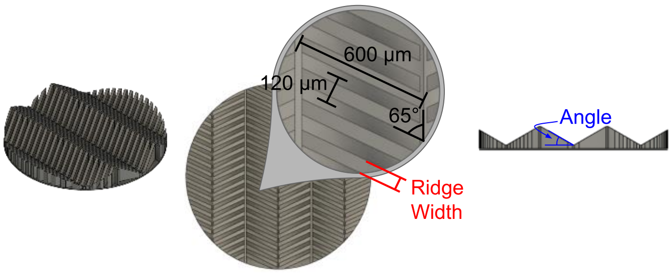

Figure 5: Sample CAD with isometric view (left), top view (middle), and side view (right), showcasing the different parameters, which are ridge width and angle.

CHARACTERIZING HYDROPHOBICITY

For a flat surface, it is rather simple to quantify hydrophobicity through correlating it with the contact angle measurements from the goniometer. According to figure 6, a surface can be considered wettable, or hydrophilic, if the contact angle is less than 90º, and conversely, non-wettable, or hydrophobic, if the contact angle is greater than 90º. Following this model, a surface can be considered more hydrophobic with higher average contact angles.

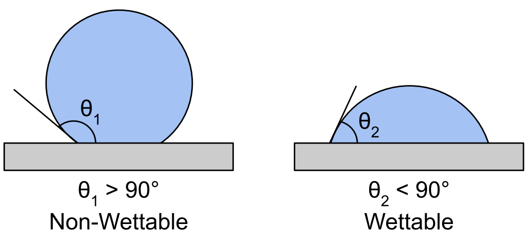

Figure 6: Diagram that shows how contact angle measurements look on a smooth, simple surface. In this case, $\theta_1 > \theta_2$, indicating that the left surface is more hydrophobic [1].

WETTING STATES

For more complicated textured surfaces, such as with feathers, there are different wetting states, with two main stable configurations: Cassie-Baxter and Wenzel states, as portrayed in figure 7. Feathers must maintain a Cassie-Baxter state to stay hydrophobic, with Cassie-Baxter states signaling that there is less surface in contact with the drop [5]. A lower energy Wenzel state would lead to lower contact angles, where gravitational forces overtake surface tension forces of the water [5]. Interestingly, the samples in figure 5 could have both Cassie-Baxter and Wenzel states simultaneously since the angles and ridges of them present two different levels of textured surfaces.

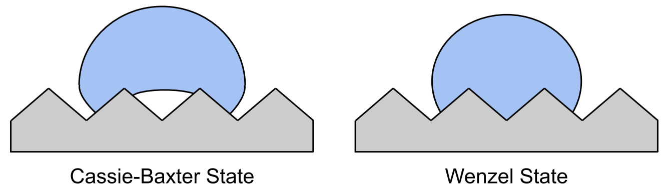

Figure 7: Diagram of different wetting states. A Cassie-Baxter state would require the sample to sustain an air pocket within the valley. This provides a way to classify how feather-like the 3D-printed structures are since feathers prefer the more hydrophobic Cassie-Baxter wetting state [1].

EXPERIMENTAL DESIGN

To measure contact angles, a ramé-hart 590-F1 goniometer took images of the side view of two-microliter drops of water on the samples, and ImageJ's contact angle plug-in was used to calculate the contact angles remotely due to the goniometer software occasionally malfunctioning with contact angle measurements. The images would be taken immediately after pipetting the water drop since the drops evaporate quickly. The samples would be oriented such that valley lines were perpendicular to the goniometer camera to avoid difficulty in calculating the contact angle for the plug-in, pictured in figure 8; however, images with the valleys pointed into the camera also offer key insight into the wetting states of the drops. For repeated testing, the samples would be dried with an air duster since a wet surface may yield lower contact angles.

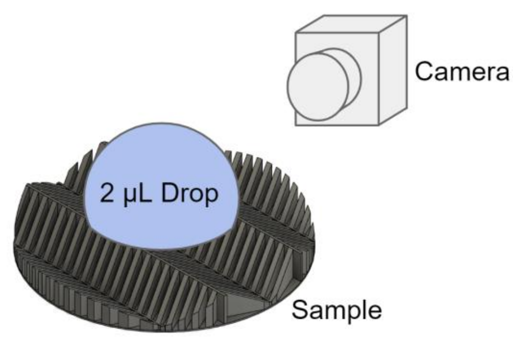

Figure 8: Diagram of set up used for the experiment. The "barbs," or valley lines, are directed perpendicular to the camera for easier quantifying of the horizontal surface for determining the contact angles for the ImageJ plug-in.

RESULTS AND DISCUSSION

Figure 9 showcases sample images from the goniometer of separate attempts of drops on the same sample at different angles. The drops tended to be quite volatile, varying much based on whether they would extend past the middle valley of the sample.

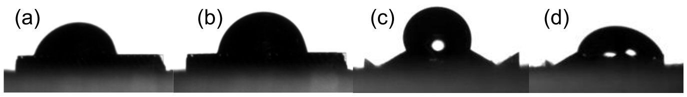

Figure 9: Images of separate attempts of the same sample with the valley lines perpendicular (a, b) vs. parallel (c, d) to the camera. Only images like (a) and (b) were used to measure the contact angles. Images like the (c) and (d) were used to reveal the wetting states of the samples, which show that they were unable to sustain an air pocket, indicating a Wenzel wetting state.

Decreasing the ridge width and increasing the angles increased hydrophobicity, according to the data shown in figures 10 and 11.

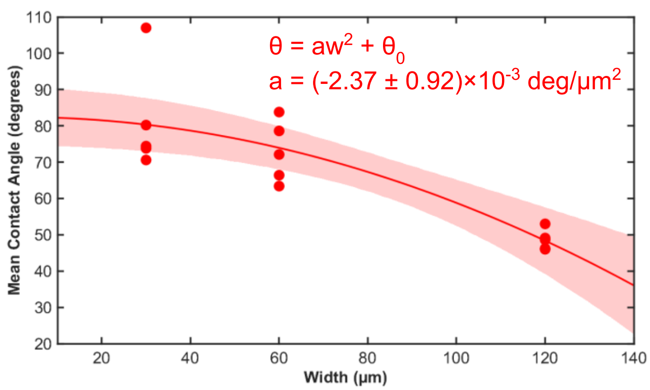

Figure 10: Plot of MCA vs. ridge width including least squares (LSQ) fit and 95% confidence interval. An LSQ quadratic fit of $\theta = aw^2 + \theta_0$ was applied to the data with values $a = (-2.37 \pm 0.92)\times10^{-3}$ °/μm² and $\theta_0 = (8.25 \pm 0.79)\times10°$. A linear fit was not used since the values had larger uncertainties. Since the center-to-center spacing of the ridges was 120 μm, the sample with the "width" of 120 μm didn't have ridges and just had angles. Since the LSQ fit is a concave-down, centered quadratic function, the predicted max angle would occur when the width is zero, where MATLAB's predint function predicted a maximum angle of 82.5 ± 22.3°.

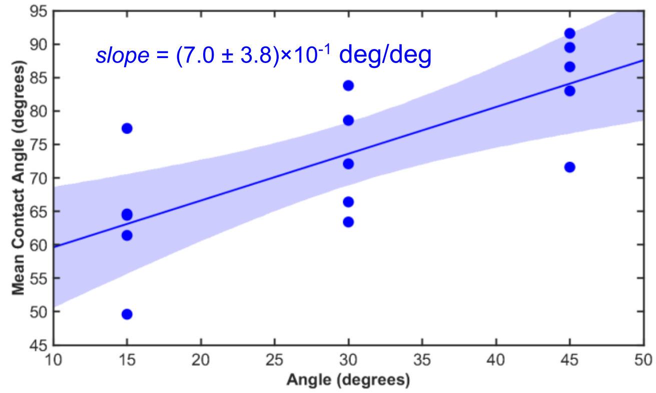

Figure 11: Plot of MCA vs. angle including LSQ fit and 95% confidence interval. An LSQ linear fit of $\theta = cd + \theta_0$ was applied to the data, with values $c = (7.0 \pm 3.8)\times10^{-1}$ and $\theta_0 = (5.2 \pm 1.2)\times10°$.

Because determining whether the water drop seeped between the ridges is not possible through the goniometer images, only the wetting state in relation to the angles can be observed. Figure 8 shows that the samples did not present the Cassie-Baxter state, which feathers generally exhibit; they overwhelmingly tended to gravitate towards the Wenzel state immediately. This makes sense since the drop size is quite large relative to the spacing of the peaks of the angles, where surface tension forces of the drop are unable to overtake gravitational forces [5]. Actual feathers have features around six times smaller than the ones these samples exhibit, which may explain this discrepancy in the wetting states.

This leads to the main limitation of this project: the samples are too scaled up. To get the Cassie-Baxter state, the angles and ridges must be small enough to sustain air pockets within the structures. A better sample design would have features around the same scale as the ones from the actual feathers, and a more powerful computer for using CAD would be necessary due to attempts to design higher resolution structures leading to the software crashing.

Additionally, the models may only accurately portray the range in which it was tested. For the MCA vs. ridge width plot, the maximum predicted angle was 82.5 ± 22.3° for if the width was zero; however, no width is infeasible, and realistically, the model should dissolve once the width is too small to maintain structural integrity.

CONCLUSIONS

Increasing the ridge width decreased the hydrophobicity of a material quadratically with a leading coefficient of $(-2.37 \pm 0.92)\times10^{-3}$ °/μm², and increasing the ridge angle increased the hydrophobicity of a material linearly with a slope of $(7.0 \pm 3.8)\times10^{-1}$. These results support the theory behind feather hydrophobicity, which suggests that minimizing exposed surface area to a water droplet, either through thinner ridges or steeper angles, will make the surface more hydrophobic to a certain extent [5].

An extension of this project for a SuperUROP will utilize the same geometry but scale them down sixfold through CAD software on a computer that has enough computational power. Creating samples with ridges and angles similar in scale to real gorget feathers from the ruby-throated hummingbird is the next step towards achieving a Cassie-Baxter wetting state, which is optimal for creating a hydrophobic material. This project also signals that feathers offer a unique way for creating surfaces of tunable hydrophobicity.

ACKNOWLEDGMENTS

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