Anisotropic Wetting Behaviour of Modified 3D Printed Micro-Structured Polymer Surfaces for Water Harvesting

M.J. Cook*, J.H. Johnston* and J. Leveneur**

*School of Chemical and Physical Sciences, Victoria University of Wellington
Kelburn Parade, Kelburn, Wellington, New Zealand, michelle.cook@vuw.ac.nz
**GNS Science, New Zealand, j.leveneur@gns.cri.nz

ABSTRACT

This paper presents a novel system to produce patterned hydrophilic/hydrophobic surfaces with directionally dependent wetting behaviour. Specifically, surfaces to direct the flow and movement of water across them preferentially in one direction. The surfaces are attractive in various applications, such as water harvesting. These surfaces were produced using 3D printing to develop an optimal anisotropic surface roughness pattern, followed by a chemical and physical treatment to alter the wettability of the surface. The chemical treatment was found to increase the hydrophobicity of the surface, while the physical treatment was found to decrease the hydrophobicity of the surface and in some cases render the surface hydrophilic. These treatments were developed and tested on an ABS polymer substrate, but it is proposed that the treatments could be extended and applied to other substrates, including other polymers or inorganic materials.

Keywords: wetting, anisotropic, hydrophobic, hydrophilic, micro-structure

1 INTRODUCTION

We present an attractive new technology for the design and fabrication of micro-structured water harvesting surfaces through a unique combination of 3D printing and hydrophilic/hydrophobic surface modification.

For many years, researchers have been examining the wetting behaviours of natural surfaces and applying similar principles to newly created surfaces. For example, the high degree of superhydrophobicity exhibited by the famed "Lotus Leaf" has been replicated several times using novel methods developed in the laboratory [1-3]. The same is true for anisotropic wetting behaviours, such as that which occurs on the back of the *Stenocara gracilipes* beetle [4,5]. Utilising areas of both hydrophilicity and hydrophobicity allows the creature to collect liquid water from the foggy morning air via condensation and directional flow. The beetle's back has hydrophilic bumps to facilitate condensation of water droplets. These droplets then grow and coalesce until they are sufficiently large that they fall into surrounding hydrophobic troughs that channel the water to the beetle's mouth, allowing it to survive in the arid Namib desert. In this work we aimed to simplify the water harvesting process demonstrated by the beetle, using facile manufacturing and processing methods to produce an innovative water harvesting device.

Anisotropic wetting behaviour can be induced in a surface by creating 1-dimensional roughness on the surface. This can be achieved by forming a series of suitably sized lines/channels in the surface that extend in only one direction. This promotes the spreading and movement of water droplets in the direction parallel to these lines/channels and hinders the spreading and movement in the perpendicular direction [6,7]. In our work presented here, 3D printing was used as a method of rapid prototyping to produce polymer surfaces with micro-channels of varying size and shape. These structured surfaces were 3D printed with acrylonitrile butadiene styrene (ABS). The wettability of the surfaces was assessed and the optimum structure was determined, that had hydrophobic contact angles and uni-directional flow properties, to facilitate the movement of droplets in only the direction parallel to the channels. These surfaces were then treated with a fluoroalkyl silane (FAS) to further increase their hydrophobicity. They were then patterned with a novel physical method. The physical treatment caused the hydrophobic nature of the surface to be rendered hydrophilic in the desired patterned areas. This was demonstrated by a contact angle of less than 65° and droplets observed as sitting in a Wenzel state.

The combination of 1-dimensional anisotropic surface roughness and patterned areas of hydrophilicity and hydrophobicity, has led to the creation of a surface with hydrophilic lines surrounded by hydrophobic channels that allow water flow in only the direction parallel to the lines/channels. This surface proved to be an effective water harvesting device. The manufacturing of this device was indeed facile and commercially viable. The 3D printed surface can be easily reshaped and resized to suit different end-use water harvesting requirements and devices, and the post treatments can easily be performed on a small or moderately large scale. As the surface chemistry of the polymer can be altered using FAS surface functionalisation and patterned physical modification, this method can also be extended to metals and other substrates as the structured surface, depending on the particular application.

2 RESULTS

In order to induce anisotropic wetting, 3D printing was used to produce surfaces with designed anisotropic surface roughness. This roughness consisted of lines/channels spanning the surface of each sample with varied size dimensions. Several samples were produced with the width of the lines and channels each varying from 250 µm to 1 mm. The wetting behaviour of these samples was examined. The wetting behaviour was analysed by measuring the static water contact angle (CA) from both a parallel and perpendicular direction, with respect to the lines/channels, and the roll off angle (RoA) again from a parallel and perpendicular angle. All measurements were taken with 10 µL test droplets. While all samples were found to hinder droplet movement in the direction perpendicular to the lines/channels, the sample with the most hydrophobic behaviour in the direction parallel to the lines/channels was selected as the optimised structure. This structure was found to be that with both line and channel width of 500 µm. The computer aided design (CAD) model of the optimised 3D printed structure is shown in Figure 1.

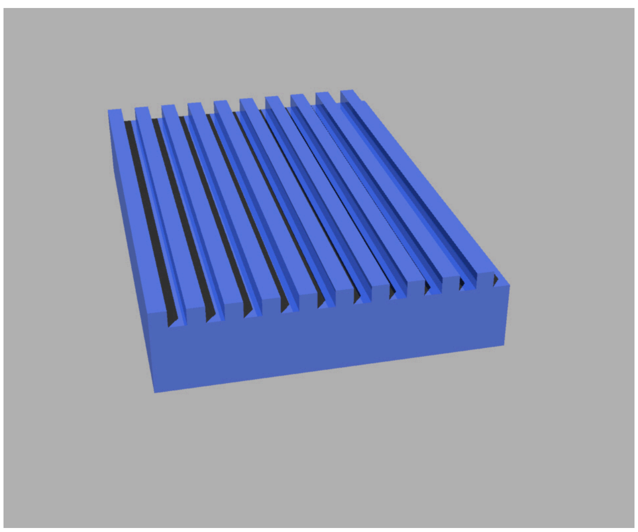

Figure 1: CAD model of optimised 3D printed structure with lines and channels 500 µm wide.

It was found that the width of the lines and channels played a significant role in the wetting behaviour of the samples. The width of the lines had a strong impact on the RoA of the surface as increased line width correlated to increased solid-liquid interfacial area, which led to an increase in adhesion forces, increasing the RoA of the sample. The width of the channels also caused significant changes to the wetting behaviour due to increased solid-liquid interfacial area with decreased channel width. Consequently, the channel width affected the wetting behaviour by controlling whether the test droplets took on a Cassie-Baxter or Wenzel state. When the channel width was small, droplets were precluded from falling into the channels and were held up above a pocket of air, in a Cassie-Baxter state (Figure 2). Whereas when the channel width was large, the droplets fell into the channels and assumed a Wenzel state, eliminating the air pocket and air-solid interface, replacing it with an unfavoured liquid-solid interface, further increasing the adhesion forces. Hence, it was important to maximise the channel width, while still keeping this parameter small enough to preclude the droplets from taking on a Wenzel state.

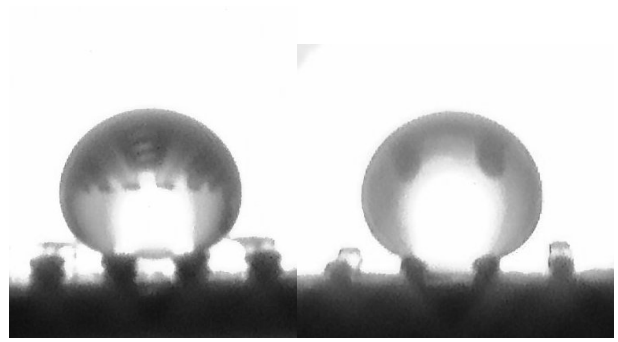

Figure 2: Droplet on surface with narrower channels, assuming a Cassie Baxter state (left). Droplet on surface with wider channels, assuming Wenzel state (right). Both droplets are 10 µL.

This optimised structure was then replicated several times to investigate the effects of the surface treatments. The wettability of each replicate was assessed in order to determine the variation between samples before modification. Two surface treatments were investigated, a chemical surface treatment and a physical surface treatment. The chemical treatment simply involved an aqueous FAS treatment. This treatment was facile and can be applied to many different substrates with ease. Hence, the 3D printed ABS surfaces were successfully modified using this method. It was anticipated that the chemical surface treatment would increase the hydrophobicity of the surface, while the physical treatment was expected to decrease the hydrophobicity of the surface. These expected results were indeed observed. The untreated sample was found to have a parallel CA of 147° and a perpendicular CA of 103°, after the chemical treatment the parallel CA remained approximately the same, but the perpendicular CA was increased to 120°. After the physical treatment, these values were decreased to 124° (parallel) and 85° (perpendicular). Furthermore, when both the chemical and physical treatments were applied to the same surface, the hydrophobicity of the sample was not only reduced, but was rendered hydrophilic. This was seen in a dramatic decrease in perpendicular CA to below 65°, and the droplet no longer assuming a Cassie-Baxter state as it previously had, but assuming a wetted Wenzel state. As the physical treatment used in this work is easily patternable and the surface roughness can be easily altered in the 3D printed model, this system provides a facile method of producing patterned hydrophilic/hydrophobic surfaces with directionally dependent wetting behaviour (Figure 3).

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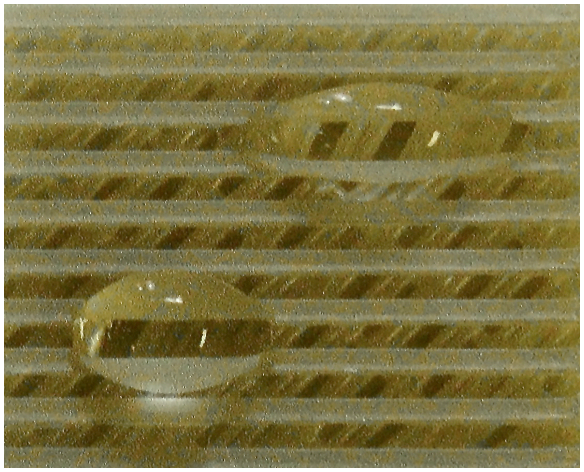

Figure 3: Treated micro-structured surface showing anisotropic wetting behaviour promoting spreading in direction parallel to lines/channels.

3 OTHER SUBSTRATES

The longevity of the effects of the physical treatment was examined and was determined to be diminished within five months of treatment. After this time, the sample recovered it's hydrophobic behaviour, although was not as hydrophobic as the sample before treatment. Other substrates were investigated as a means to create surfaces with greater longevity. Polylactic acid (PLA) was used in place of ABS as it is another commonly available 3D printing material. The untreated line/channel structures printed in PLA were less hydrophobic than those printed with ABS (142° parallel and 91° perpendicular), but still showed directionally dependent wetting behaviours with lower RoA values in the direction parallel to the lines/channels than perpendicular. Even without the addition of the chemical treatment, the PLA samples were rendered hydrophilic after physical treatment. This hydrophobicity was also found to be more robust than that seen in the chemically treated ABS samples as it was found to persist for more than six months after the physical treatment. This provides an avenue for producing patterned hydrophilic/hydrophobic surfaces with directionally dependent wetting behaviours with more longevity than the initial system developed.

While these treatments have only been previously investigated on polymer surfaces, it is possible to apply the same treatments on other substrates, such as steel, aluminium, glass or silicon. As the physical treatment affects only the surface of the sample, when used in conjunction with the chemical treatment, similar effects should be seen, regardless of the initial substrate material.

4 CONCLUSIONS

Micro-structured polymer surfaces were produced using 3D printing and their dimensions optimised to show anisotropic wetting behaviour. The optimised structure showed highly hydrophobic properties in the direction parallel to the one-dimensional micro-structure (high CA and low RoA), but more hydrophilic properties in the direction perpendicular to the micro-structure (lower CA and no movement of water). This allowed for control over the movement of water across the surface which was allowed in only the direction parallel to the micro-structure and promoted spreading in this same direction. The wettability of the surface was then modified using chemical and physical treatments to increase or decrease the hydrophobicity, respectively. In some cases, this decrease in hydrophobicity after physical treatment was found to be so extreme that the surface became hydrophilic.

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