

Superhydrophobic and Superhydrophilic Surfaces

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ABSTRACT

In this research a new generation of materials possessing a wide range of possible consumer applications such as water harvesting, stain resistant self-cleaning and water-repellent breathable surfaces have been fabricated. Based on nature's example of the *stenocara* beetle, superhydrophobic and superhydrophilic woven woollen textile surfaces have been developed, by first creating a hierarchical surface structure in the micro- and nano-range. This surface structure was achieved through layer-by-layer assembly of functionalised silica nanospheres of different diameters, either synthesised in the laboratory via a modified Stöber process or via Klebosol® commercially available colloidal silica suspensions. The resulting surfaces showed superhydrophilic properties. Subsequent chemical surface modification was attained through Dynasylan®, a modified fluoroalkyl siloxane. Static contact angles of 156°, with corresponding contact angle hysteresis and roll-off angles below 15° for a 10 µL droplet have been measured.

Keywords: superhydrophobicity, superhydrophilicity, hierarchical, woollen textiles

1 INTRODUCTION

A superhydrophobic surface is defined as having a static contact angle above 150° [1-3]. Two further criteria have been discussed in the literature that both aim to describe the ease of a water droplet moving across such a surface. First, a low contact angle hysteresis (CAH), the difference between the advancing and the receding contact angle, and second, a low roll-off angle. Valid information can be gained from either of these measurements yet neither has been defined and is therefore not included in our definition of a superhydrophobic surface. Instead we discuss the relationship between all three measurements. A superhydrophilic surface by definition has to have a static contact angle < 5-10° [4, 5]. The main focus of this study is to create both superhydrophobic and superhydrophilic surfaces on wool fibre substrates. In both cases, a sufficiently rough surface is required (equations 1 and 2) in combination with a solid surface with either a low or high surface energy, respectively, to achieve either of these properties. Although Lee *et al.* [6] have shown that the creation of a hierarchical surface structure is not required

for the formation of these surfaces, this was the method of choice here. The Wenzel [7] and Cassie-Baxter (CB) [8] models are often used to describe the wetting behaviour of a rough surface where in the former, the liquid completely fills all the grooves present, effectively creating a homogeneous interface. In the latter, the liquid sits on top of the rough surface entrapping air pockets beneath, which results in the formation of a heterogeneous interface. It has been shown that a superhydrophilic surface requires a fully wetted surface, a Wenzel state, whereas only a CB state leads to a superhydrophobic surface [9, 10].

$$\cos\theta_r^W = r \cos\theta_e \quad (1)$$

Equation (1) defines the apparent Wenzel contact angle, θ_r^W , where r is the roughness factor, the ratio of the actual solid-liquid interfacial surface area and its geometric surface area, and θ_e is the Young's contact angle.

$$\cos\theta_r^{CB} = r_f f \cos\theta_e + f - 1 \quad (2)$$

The rewritten CB equation (2) shows the influence of the surface roughness on the apparent contact angle of a CB surface, θ_r^{CB} , where f is the fraction of the projected area of the solid surface in contact with the water and r_f is the roughness of the portion of the solid that is in contact with water [1].

The surface structure of woven merino wool fibres is modified in this study by creating a hierarchical structure in the micro and nano range via the use of silica nanospheres of different diameters. These were either synthesised in the laboratory via a modified Stöber process [11] or through the use of three different commercially available colloidal silica suspensions (9, 12 and 80 nm particle diameters). Due to the hydrophilic nature of the silica particles, the resulting hierarchical surfaces, which consist of micron sized merino wool fibres and nano sized particles, show superhydrophilic properties. Further chemical modifications, via Dynasylan® a modified fluoroalkyl siloxane, effectively lower the surface energy and should allow the generation of superhydrophobic surfaces.

2 EXPERIMENTAL

2.1 Materials

The woven merino wool fibres with an average fibre diameter of 20 μm were supplied by AgResearch Ltd, Lincoln, NZ. The Klebosol[®] range of monodispersed colloidal silica nanospheres with differing diameters (30R9 (9 nm), 30R12 (12 nm) and 30R50 (80 nm)) was kindly donated by Clariant Ag. Dynasylan[®] F8815 a modified fluoroalkyl siloxane was supplied by Evonik Industries and all other chemicals were commercial from Sigma Aldrich.

2.2 Klebosol[®] Samples

Woven merino wool (0.2 g) was soaked in a 0.1 mol L⁻¹ potassium hydroxide (KOH) in methanol (MeOH) for 30 minutes with gentle agitation. Afterwards the weave was washed with distilled water and dried in an oven for 30 minutes at 80 °C. Klebosol[®] was diluted with distilled water to adjust the solid content. The washed wool was then added to 10 mL of the dilute Klebosol[®] suspension and 100 μL of 1 mol L⁻¹ hydrochloric acid (HCl) was added to adjust the pH to 2.4. The samples were left to react overnight with continuous shaking. Finally, they were dried in an oven for 30 minutes at 80 °C, washed with distilled water and dried again under the same conditions. Half the weave was then soaked in 10 mL of Dynasylan[®] for 20 minutes, which was followed by 30 minutes of drying in an oven at 80 °C. Alternatively, prior to soaking the samples in the Klebosol[®] suspension, they were soaked in 10 mL of a 33.3 % solution of polydiallyl-dimethylammonium-chloride (PolyDADMAC) in distilled water, for 30 minutes to increase the cationic nature of the fibre surface. Afterwards the samples were dried in an oven for 30 minutes at 80 °C. All other reactions and conditions were carried out as described above. A total of three different Klebosol[®] suspensions were used.

2.3 Modified Stöber Process

Normally, the Stöber Process [11] is used to create monodispersed silica nanospheres via the hydrolysis reaction of tetraethylorthosilicate (TEOS), ethanol (EtOH), ammonia (NH₃) and water. Here a modified version was utilised where the TEOS was hydrolysed in the presence of the wool fibres (referred to as *in situ*). 0.2 g of woven merino wool was soaked in a 0.1 mol L⁻¹ KOH in MeOH for 30 minutes with gentle agitation. Afterwards the weave was washed with distilled water and dried in an oven for 30 minutes at 80 °C. Following this step it was soaked in 10 mL of a 33.3 % solution of PolyDADMAC in distilled water, for 30 minutes, after which the samples were dried in an oven for 30 minutes at 80 °C. TEOS, EtOH and NH₃ solution (33%) were added to the weave and the mixture was agitated. The reaction time was varied (2, 4, 6, and 8 hours respectively). Afterwards the samples were again

dried in an oven for 30 minutes at 80 °C, washed with distilled water and dried once more under the same conditions. In the final step, half of the samples were soaked in 10 mL of Dynasylan[®] for 20 min and were then dried in an oven for 30 minutes at 80 °C.

2.4 Contact Angle Measurement

The contact angles of the treated surfaces were measured by using a laboratory designed goniometer. The samples were placed on a level surface and a 10 μL sessile water droplet was placed on top at a constant temperature and pressure. A minimum of four individual measurements were taken, with droplets placed randomly across the sample surface, to obtain the contact angle range. The images were taken using a Panasonic SD900 video camera. The results were verified on a Krüss (DAS 100 Expert with an automatic 4 times droplet dispenser and 7 times optic zoom) and found to be in good agreement.

2.5 Roll-off Angle and CAH measurement

The roll-off angle was determined by placing the sample on a level stage that can be rotated at 1° s⁻¹. Again a 10 μL droplet volume was chosen and placed on the surface. The angle at which the droplet rolled off the surface was recorded. At least three separate measurements were taken randomly across the surface. Simultaneously, the CAH was determined at the first advancing of the solid liquid contact line. In addition, the CAH was also determined on the Krüss (DAS 100 Expert) by increasing and decreasing the droplet volume (10 μL). Four separate measurements were taken to obtain the range across the surface.

2.6 Scanning Electron Microscopy

Scanning electron microscopy (SEM) was used as the characterisation technique to verify particle size, shape and fibre diameter, as well as to study the surface morphology of the modified wool fibres. A JEOL 6500 F field emission gun SEM was used for imaging at 15 kV.

3 RESULTS AND DISCUSSION

Two key factors influence the wetting behaviour of a surface, the surface tension and the roughness. The effect of the latter is similar for a superhydrophilic and superhydrophobic surface and therefore was modified first. In the first steps the naturally hydrophobic nature of the merino fibres had to be altered by removing the 18-methyleicosanoic acid from the surface of the fibres, making them hydrophilic. Initially, it was thought that by simply adding commercially available silica nanospheres to these merino wool fibres, a sufficient coverage of the fibres by silica nanospheres could be achieved. However, the uptake was very limited and an acidic environment (positive surface charge) had to be created for the

electrostatic interactions between the wool fibres and the silica spheres to take place, resulting in good coverage of the fibre (see Fig. 1).

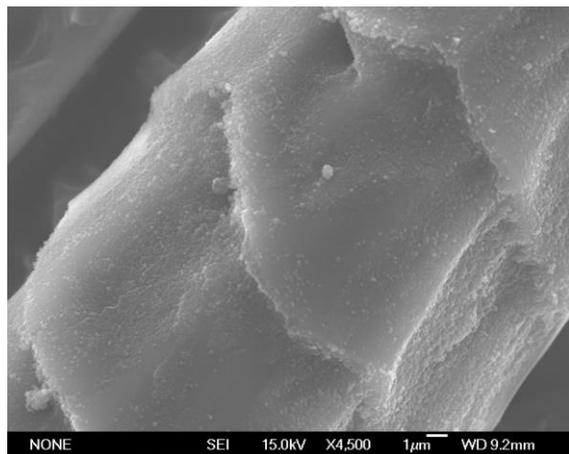


Figure 1: SEM micrograph of 30R50 Klebosol[®] silica nanospheres covering a merino wool fibre.

The uptake of the silica particles could be further increased by soaking the woven merino wool in PolyDADAC, increasing the cationic nature of the weave. As a direct result of this modification a significant increase in silica particle uptake was observed, almost concealing the cuticle edges of the merino fibres (see Fig.2).

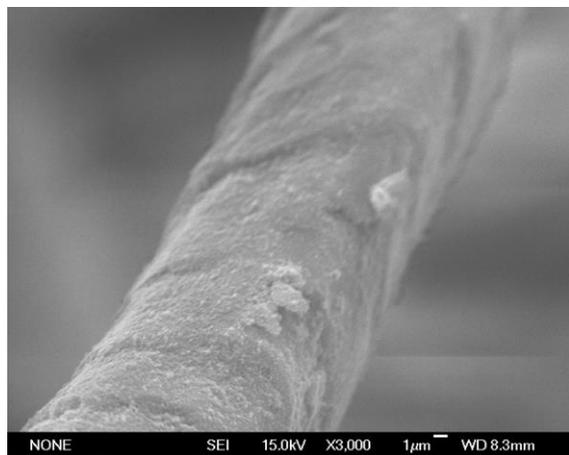


Figure 2: SEM micrograph of PolyDADMAC soaked merino fibre with 30R50 Klebosol[®] silica nanospheres.

These surface modifications allowed the creation of a superhydrophilic surface on the wool fibre with a contact angle of 0°. The subsequent chemical modification via Dynasylan[®] lowered the surface energy significantly and resulted in the expected increase in contact angle. Table 1 shows that the silica particle diameter has an influence on the relative angles. Arguably large uncertainties, due to the challenging nature of the substrate, make it difficult to compare these samples to each other. To be able to compare

the obtained results to a larger data set presented in the literature, three different, yet frequently used methods of determining the dynamic contact angles have been used. It is important to mention here that to the best of our knowledge, there is no known correlation between them.

Table 1: Contact angle, CAH and roll-off angle measurements of a 10 µL water droplet on modified merino weave treated with Dynasylan[®].

Sample	Contact Angle (°)	CAH Krüss (°)	Roll-off Angle (°)	CAH (°)
Wool	131 ± 6	> 90	> 90	> 90
30R9*	149 ± 9	13 ± 6	12 ± 2	7 ± 7
30R12*	148 ± 6	6 ± 4	13 ± 10	10 ± 3
30R50*	152 ± 9	9 ± 7	23 ± 11	13 ± 5

*2.7 wt % Klebosol[®] solutions

The data obtained still portrays that the hierarchical surface structure largely increased the static contact angle from 131° to 152° for 30R50. It can also be seen that the roll-off angle decreases with the decrease in particle size, which is in agreement with Shirtcliffe [12], where lower solid surface fractions improve sliding or rolling. This can also be seen in the CAH measurement but could not be verified by the Krüss measurement. Due to the high static contact angle of the 30R50 samples and acceptable dynamic angles, optimizations were carried out in the hope of improving the performance of the material further. However, Table 2 shows that the decrease in silica nanosphere content resulted in an overall decrease of all angles. While the lowering in roll-off angle has several advantages, particularly in the self-cleaning properties of the material, the decrease in static contact angle is undesirable.

Table 2: Contact angle, CAH and roll-off angle measurements of a 10 µL water droplet on merino weave modified with 30R50 and Dynasylan[®].

30R50 wt %	Contact Angle (°)	CAH Krüss (°)	Roll-off Angle (°)	CAH (°)
0.01	139 ± 3	6 ± 3	11 ± 4	5 ± 6
0.1	143 ± 5	6 ± 5	12 ± 3	8 ± 8
1	147 ± 5	9 ± 5	14 ± 5	9 ± 6

In the second part of this research, a modified Stöber process was used to produce silica nanospheres in the presence of the merino wool fibres, by hydrolysing the TEOS on the surface of the wool fibres. In this way a uniform coating of silica on the wool fibres was achieved. Soaking the weave in PolyDADMAC prior to this reaction allowed the complete coverage of the merino fibres in silica, masking the cuticle edges (see Fig. 3). The modified

surfaces showed superhydrophilic properties with 0° static contact angles. Making a minor change to this experimental procedure by adding some additional water to the reaction mixture caused the TEOS to hydrolyse first, creating discrete silica nanospheres in the 200-300 nm range that then electrostatically attached to the merino fibres. Although a significant difference in surface structure was observed, this change did not affect the superhydrophilic performance of the surface. Altering the chemical nature of both these surfaces with Dynasylan® allowed the formation of a superhydrophobic surface, and in both cases static contact angles of 150° ± 8° with corresponding CAH and roll-off angles below 15° were measured.

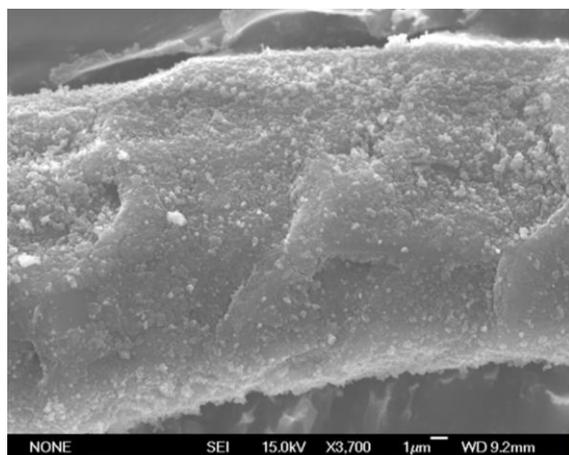


Figure 3: SEM micrograph of silica coated merino wool fibre produced via a modified Stöber process.

Changing the reaction time on the other hand had a more significant effect on both the static and roll-off angles (see Table 3). A longer reaction time resulted in an increase in the static contact angle and a decrease in roll-off angle was achieved. The CAH measurement was unchanged. A maximum reaction time of 8 hours was allowed for the hydrolysis of TEOS to take place, completely coating the merino fibres in silica, which were then chemically modified with Dynasylan®. To portray the superhydrophobicity of this surface an image of the water droplet sitting on top of this merino weave is included (see Fig 4).

Table 3: Contact angle, CAH and roll-off angle measurements of a 10 µL water droplet on top of *in situ* merino weave modified with Dynasylan®.

<i>In situ</i> reaction	Contact Angle (°)	CAH Krüss (°)	Roll-off Angle (°)	CAH (°)
2 h	151 ± 8	4 ± 3	18 ± 8	21 ± 19
4 h	151 ± 9	8 ± 4	19 ± 5	14 ± 8
6 h	147 ± 7	5 ± 3	20 ± 6	24 ± 16
8 h	156 ± 6	7 ± 7	13 ± 3	11 ± 9

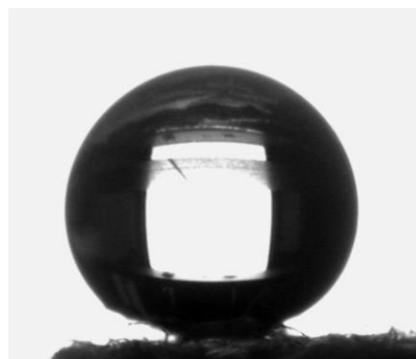


Figure 4: 10 µL water droplet sitting on silica coated merino weave treated with Dynasylan®.

4 CONCLUSION

Two different methods were used to create a hierarchical surface structure on merino wool fibres, effectively creating a Wenzel state that resulted in formation of superhydrophilic surfaces. Subsequent chemical modifications led to a heterogeneous interface, a CB state that allowed the production of superhydrophobic surfaces with contact angles as high as 156°, and corresponding roll-off angles and CAH measurements below 15°. As such, these surfaces show potential for commercial applications.

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