Wool Surfaces Made Superhydrophobic

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ABSTRACT

Wool fibres have been used to fabricate wash-fast nonwoven textile surfaces with superhydrophobic and oleophobic properties, potentially allowing a broad range of consumer applications especially in the upholstery, carpet and textile industries, where surface properties such as water-repellency, yet breathable, self-cleaning and stain resistance are desired.

In this study felting was used to create the specific surface roughness required for a superhydrophobic surface. Fabric samples were prepared in order to study the effect of variations in the degree of felting on the static and dynamic contact angles. The influence of the subsequent chemical modification of the fibre surfaces, using three different surface treatments (A, B and C) on the contact angles of three different test liquids (water, sunflower oil and hexadecane) was investigated. Water vapour transmission rates (WVTR) were determined and water impact penetration studies were performed. Static water contact angles exceeding 140° with corresponding contact angle hysteresis below 15° were achieved for a droplet volume of 10 µL. An oleophobicity of 118° for hexadecane was also measured.

Keywords: superhydrophobicity, oleophobicity, contact angles, woollen textiles

1 INTRODUCTION

The definition of a superhydrophobic surface is to have a static contact angle above 150° [1–3]. Several other criteria have been discussed in the literature, with the view to describing the ease of which a water droplet moves across such a surface. It is argued that a low roll-off angle and/or a low contact angle hysteresis (CAH), which is the difference between the advancing and receding contact angles, are also required for a superhydrophobic surface. Furthermore, compelling arguments have been made in the literature that suggest only advancing and receding contact angles give meaningful information about the wettability of a surface [4–6]. Valid information can still be gained from all these measured angles, yet due to the measurements themselves being not well defined, we exclude these from our definition of a superhydrophobic surface. Instead, we include them as part of the discussion and characterisation of the produced surfaces. Oleophobicity on the other hand is defined to have a static contact angle with oil > 90°.

Two conditions have to be satisfied in order to create a superhydrophobic surface that is also oleophobic: first, the surface structure and morphology has to be properly designed and second it has to have a low surface energy [7]. In this research the surface morphology and structure have been created by using the art of felt making, a process whereby wool fibres are rolled, beaten and pressed to form a compact mass that has even consistency. This technique is considered much older than the art of spinning or weaving and was first documented in Chinese records as far back as the 4th and 3rd century B.C. However its invention and the perfection of the process are believed to date back even further and are attributed to the nomadic tribes of Asia [8].

Wool fibres have been used to create felted surfaces with varying degrees of felting. The resulting surface structures were then chemically altered in a subsequent step by using three different surface treatments (A, B, C). Static and dynamic contact angles were measured using three different test liquids. In addition water vapour transmission rates and water impact repellency measurements were carried out.

2 EXPERIMENTAL

2.1 Contact Angle Measurement

The contact angles of the untreated and 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.

2.2 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.

2.3 Scanning Electron Microscopy

Scanning electron microscopy (SEM) is used as a characterisation technique 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. An energy dispersive X-ray spectrometer integrated with the SEM was also used to show the elemental composition of the surface modified fibres. The elemental mapping function was utilised to verify the chemical nature of the coated fibres and its uniformity.

2.4 Water Vapour Transmission Rate

The Water Vapour Transmission Rate (WVTR) measurement is normally used to determine the amount of water vapour moving through a sheet of paper over time. The measurement of the WVTR has a degree of uncertainty because of the inhomogeneous nature of the paper. In order to ensure consistency and accuracy of the data, the measurement was made according to the Australian Standard (AS 1301.419s-89) for the water vapor transmission rate of paper. This standard provides a gravimetric procedure for determining the rate at which water can pass through a sheet of paper under defined conditions. We adapted this measurement to determine the barrier functionality of our wool samples. The laboratory setup is shown in Figure 1. The samples were placed as a cap into cups of defined size that contain dried and weighed hygroscopic $CaCl_2$ in the bottom section. The prepared cups are then weighed and placed in a plastic box that contains a saturated $MgCl_2$ solution, providing a relative humidity of 45 % at 25 °C. A fan was positioned in the centre of the box to provide a constant movement of air.

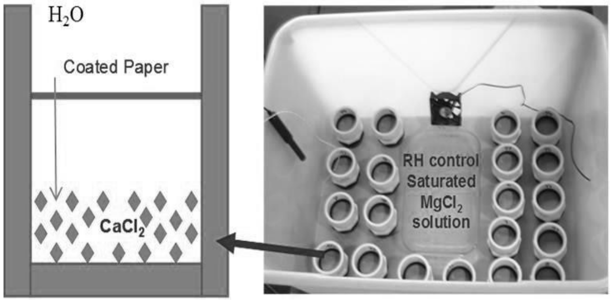

Figure 1: Laboratory setup for the WVTR measurements.

The water molecules in the air can move through the sample into the $CaCl_2$ and the uptake of the moisture is then determined by weighing the cups at the start and the end of the measurement. From the uptake the WVTR can be calculated, as the change in cup-weight indicates how much water vapour has moved through the wool samples. The samples were left in this box for 120 hours and measurements of the water uptake were taken after 24, 72 and 120 hours. The results are expressed in the standard unit of g m^{-2} 24 h^{-1}.

2.5 Water Resistance: Impact Penetration Test

The resistance to water impact was also investigated according to the ACCT test method 42-2007. This method is applicable to any textile surface, treated or untreated, and determines the resistance of the fabric samples to water impact penetration. The test is specific to samples tilted to 45° as can be seen in Figure 2. The volume of water being sprayed onto the sample surface was varied to a maximum of 3 L.

Figure 2: Impact penetration tester

3 RESULTS AND DISCUSSION

Two key factors influence the wetting behavior of a surface, the surface energy and the roughness. The effect of the latter is similar for a superhydrophobic and an oleophobic surface and was therefore modified first. Figure 3 shows the effect of several degrees of felting. The increase in felting assures the formation of a more dense surface structure, where the spaces between the individual fibres have been reduced. This in turn is reflected in an increase in static contact angle from 129° to 137°. The slight decreases in the third and fifth pass are due to the felt being treated more heavily on one side than the other, as compared to the evenly felted two, four and six pass surfaces.

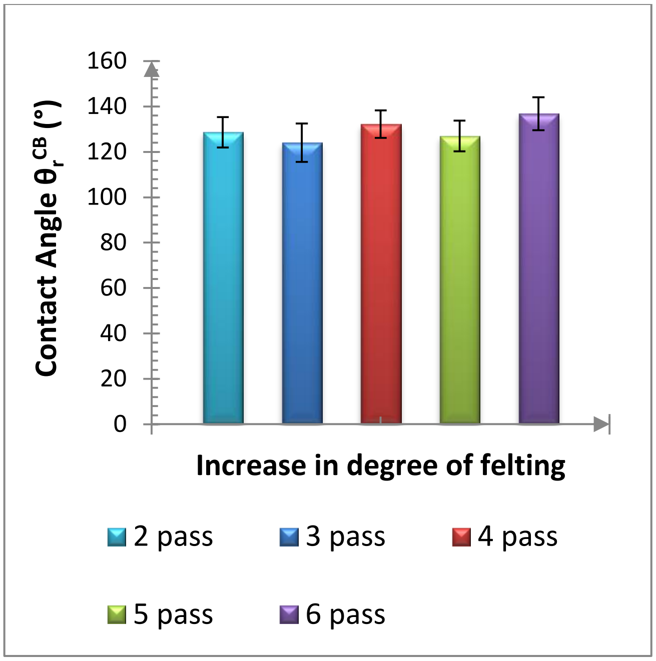

Figure 3: Static contact angle measurements of a 10 µL water droplet on woollen felt with increasing degree of felting. The samples are also chemically modified.

Similar effects can be seen in the WVTR measurements (Table 1). For both the untreated and treated wool surfaces the increase in felting also causes a slight increase in WVTR. This is due to the fact that the increase in felting results in a more dense material, which should in theory result in a decrease in the WVTR, however the felting process also reduces the thickness of the barrier material, effectively shortening the path length that the water vapour has to travel through. In both cases (treated and untreated) the latter appears to be the governing factor, hence an overall increase in WVTR is observed. A difference of around 17 g m^{-2} 24 h^{-1} between the untreated and treated woolen felts was observed and is attributed to the more hydrophobic nature of the material, upon the reduction in the surface energy via the chemical treatment.

The water impact penetration test (Table 2) indicated that the surfaces with a lower degree of felt have a better water resistance. Similar to the WVTR measurements, this is due to an observed decrease in thickness going from a 2 pass to a 6 pass surface. Therefore, the impact of the water droplets cannot penetrate the wool surface fully and displace all the air entrapped within the fibres, unlike those of the 5 and 6 pass surfaces where the water fully wetted the entire sample. It was also confirmed that the successful chemical treatment (verified by SEM and energy dispersive x-ray spectroscopy) increases the hydrophobic nature of the material substantially and a significant improvement in the impact resistance could be made. A maximum of 3 L of liquid were able to be repelled for the less felted surfaces.

Table 1: Water vapour transmission rate of untreated and treated woollen felt

Sample	**WVTR** (g m^{-2} 24 h^{-1}) **untreated**	**WVTR** (g m^{-2} 24 h^{-1}) **treated**
2 pass	92 ± 1	75 ± 2
3 pass	91 ± 3	73 ± 1
4 pass	93 ± 5	76 ± 2
5 pass	95 ± 1	77 ± 1
6 pass	96 ± 5	81 ± 2

Table 2: Water impact penetration test of untreated and treated woollen felt

Sample	**Water penetration** (g) **untreated**	**Water penetration** (g) **treated** [a]
2 pass	0.6 ± 1.1	0 ± 0
3 pass	0.5 ± 1.0	0 ± 0
4 pass	2.7 ± 0.2	0 ± 0
5 pass	5+	0 ± 0 [b]
6 pass	5+	5+

[a] water volume increase from 0.5 L to 3 L

[b] penetration into the felt but not the blotter paper

The chemical nature of the surface material is also important for superhydrophobic or oleophobic surface. In the second part of this research, three different chemical treatments, A, B and C for the felted surfaces were investigated. Table 3 shows the results of a series of contact angle measurements which were performed on the different surfaces. No real trend was observed by looking at the static contact angle or the CAH, yet a material with a high water repellency and a very low CAH has been created, particularly for a 10 µL test droplet size.

Table 3: Contact angle, CAH, advancing / receding contact angle and Roll-off angle measurements (10 µL droplets) of woollen felt using three different chemically modifications; contact angles for sunflower oil and hexadecane included.

Treatment	Contact Angle (°)	CAH (°)	Advancing / Receding Contact Angles (°)	Roll-off Angle (°)	Sunflower Oil (°)	Hexadecane (°)
A	134 ± 8	2 ± 10	137 / 135	80 ± 17	-	-
B	142 ± 13	11 ± 8	138 / 127	44 ± 18	-	-
C	131 ± 9	4 ± 14	141 / 137	31 ± 6	130 ± 2	118 ± 2

Table 3 clearly shows that, with the decrease in surface energy, A > B > C, caused an increase in advancing contact angle, however, the same could not be established for the receding contact angle. This may be explained by the observations made by Dorrer et al. [9] which showed that the receding angle is mainly affected by the surface features present. The decreasing surface energy also shows a significant reduction in roll-off angle from 80° down to 31°.

Only treatment C showed oleophobic tendencies, which does suggest that the surface energy of both treatments A and B is not low enough, allowing the liquid to penetrate the fibre matrix. Comparing contact angles of the three different test liquids, an expected decrease in static contact angle from 131° to 118° can be observed, which is due to the decrease of surface tension going from water to hexadecane.

4 CONCLUSION

Non-woven woollen surfaces have been investigated and the effect of felting on the static and dynamic contact angles has been tested. It was found shown that a higher degree of felting has an increasing effect on the static contact angle. However as a consequence of more felting the water impact penetration and WVTR both increased. While the increase of the former is favored, particularly in terms of breathability of textiles, the latter effect is undesired.

Furthermore, it was shown that only treatment C showed oleophobic tendencies of the three different surface treatments. Based on these findings it is concluded that these surfaces did not perform as well as expected and for nonwoven textiles to have potential future applications considerable further work is required and also their design needs to be tailored to the specific requirements.

ACKNOWLEDGEMENT

We gratefully acknowledge the support given by our collaborators at the Institute of Functional Interfaces, Karlsruhe Institute of Technology in Germany. This research was kindly funded by the FRST TRST UOAX0819 “Materials Accelerator Programme” from The University of Auckland.

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