Controlling the Wetting Behaviour of Wool Fabrics and 3D Printed Polymer Surfaces

by

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Abstract

The wettability of a surface is determined by two factors; the chemistry of the surface, which determines the inherent chemical hydrophilicity or hydrophobicity, and the physicality of the surface, whereby the surface roughness enhances and exaggerates the inherent hydrophilicity or hydrophobicity of the surface. Hence, controlling the wettability of a surface requires manipulation of both the chemical nature of the surface and the surface roughness. This research predominantly investigated controlling the wettability of surfaces through creation and manipulation of surface roughness, but also studied alterations of the chemical hydrophilicity and hydrophobicity of surfaces. These studies were performed using two different substrates, for different potential commercial applications. Wool fabrics were studied, in order to increase their hydrophobicity and produce a stain and water repellent wool fabric. 3D printed polymers were also investigated in order to create surfaces with useful wetting behaviours, including superhydrophobicity and anisotropic wetting.

First, wool fabrics were manipulated through physical processing alone, in order to increase the surface roughness. This relied on altering the arrangement of the micrometre-sized wool fibres in the fabrics and creating a more disordered array. This was achieved through hand-felting of the wool fabrics and was found to successfully increase the surface roughness of the fabrics, and hence increase the hydrophobicity. However, it was found that the increased felting led to detectable increases in the macro-scale roughness of the surface, reducing the soft hand feel of the wool fabrics. This effect is an undesirable property in the textiles industry and another physical process of shearing protruding wool fibres was investigated in order to reduce this macro-scale roughness and increase the softness of the fabric. However, this process was found to also reduce the micro-scale roughness of the surface and hence, the hydrophobicity of the fabrics was also decreased. This decrease in hydrophobicity was exacerbated due to the increased chemical hydrophilicity of the surface due to the exposure of more fibre ends, which are hydrophilic. Hence, the hydrophobicity of the sheared fabrics was reduced to a level lower than the untreated fabrics. Therefore, the use of physical processes to increase the roughness of wool fabrics was found to be successful in increasing the hydrophobicity of the surfaces. However, as the soft texture of the wool fabrics was compromised, the fields of ap-

plication of these fabrics was determined to be somewhat limited.

Subsequently, the hydrophobicity of wool fabrics was increased using chemical modifications to increase the surface roughness, while not compromising the soft texture of the fabrics themselves. In these investigations, the surface roughness was again increased, but on a smaller scale, through the functionalisation of wool fibres with inorganic particles on the micro- or nano-scale. Three types of particles were investigated, gold nanoparticles, Ag/AgCl particles and CaCO_3 particles. The gold nanoparticle functionalisation successfully increased the surface roughness on a very small scale, but the concurrent increase in chemical hydrophilicity was found to outweigh this increased surface roughness and result in a net decrease in hydrophobicity of the functionalised fabrics. The Ag/AgCl and CaCO_3 functionalisations both successfully increased the hydrophobicity of the wool fabrics. Of these treatments, the Ag/AgCl functionalisation was found to have the greatest impact on increasing the hydrophobicity and Ag/AgCl functionalised fabrics showed increased water repellency in practical tests. The Ag/AgCl functionalisation also renders the fabrics antimicrobial, due to the known antimicrobial activity of silver nanoparticles (present as silver nanodomains on AgCl microparticles in Ag/AgCl composites). Hence, these investigations led to the development of water and stain repellent, and antimicrobial wool fabrics with great potential for commercial applications.

Polymer substrates and 3D printing were used in order to create surfaces with specific surface roughness patterns and changeable surface chemistry for the purpose of creating surfaces with controlled wetting behaviours. For these investigations, a fused deposition modelling (FDM) 3D printing process was used to facilitate rapid prototyping of surface roughness pattern designs and allow for optimisation of these designs. These surfaces were printed using acrylonitrile butadiene styrene (ABS). Firstly, a highly hydrophobic surface was designed. An array of droplet-shaped structures was printed onto a flat substrate. These droplet structures were on the size scale of a few hundred micrometres, but the process of melting and extruding the polymer in the printing process also gave the surface some degree of smaller scale roughness. This roughness was then increased further, by functionalising the surface with silver nanoparticles. This functionalisation was achieved *in-situ* and also rendered the surface antimicrobial. Due to the inherent chemical hydrophilicity of silver, the surfaces also required a subsequent treatment with a fluoroalkyl silane (FAS) to render them chemically hydrophobic. While these surfaces did not achieve the typically defined conditions of superhydrophobicity, they were found to be highly hydrophobic and were also antimicrobial. Hence, these surfaces were deemed to be potentially useful for commercial applications in healthcare industries.

FDM 3D printing was also used to create a surface with anisotropic wetting behaviour. This was achieved through printing a surface with 1-dimensional roughness in the form of protruding lines extending in one direction across the surface plane. These surfaces were printed using ABS or polylactic acid (PLA). Different shapes, sizes and spacings of these lines were investigated and these parameters were optimised. The resulting surface displayed significant anisotropy in its wetting behaviour with highly hydrophobic behaviour observed in the direction parallel to the protruding lines, but significantly more hydrophilic behaviour in the perpendicular direction. Hence, this surface allowed the movement of water in one direction across the surface but hindered movement in the perpendicular direction. This surface was then treated with a FAS, and subsequently treated with ion implantation in selected areas, using varied fluence of Ar^+ or C^+ ions. The FAS treatment served to change the surface chemistry from that of the printed polymer to a generic hydrophobic chemistry, using a surface treatment that is applicable to many different substrate materials. The ion implantation treatment significantly decreased the hydrophobicity of the treated areas of the FAS functionalised surface; in fact the ion implantation treatment was found to render the selected areas formally hydrophilic. This allowed for the design of a surface with both hydrophilic and hydrophobic areas, that allowed for movement of water in only one direction across the surface. Such a surface has potential applications in water harvesting, utilising the hydrophilic areas for condensation of water from the air, and the hydrophobic areas for movement of this water across the surface toward a collection tank.

The research carried out herein led to the successful increase in hydrophobicity of wool fabrics using both physical and chemical processes. 3D printing was also successfully utilised to create two different surfaces with controlled wetting behaviours. Firstly, a surface with high hydrophobicity and antimicrobial activity was produced. And secondly, a surface with anisotropic wetting behaviour and areas of hydrophilicity and areas of hydrophobicity was achieved. Possible applications of these surfaces were considered.

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List of Abbreviations

θ	Contact angle
γ	Surface tension
18-MEA	18-methyl eicosanoic acid
2D	2-dimensional
3D	3-dimensional
ABS	Acrylonitrile butadiene styrene
Ag/AgCl	Silver/silver chloride
ATR	Attenuated total reflectance
CA	(Static water) contact angle
CA _{Para}	Contact angle viewed from parallel perspective
CA _{Perp}	Contact angle viewed from perpendicular perspective
CAD	Computer aided design
CAH	Contact angle hysteresis
C-B	Cassie-Baxter
CI	Confidence interval
CLIP	Continuous liquid interface production
CTVA	Constant thickness varied angle
DLP	Digital light projection
EDS	Energy dispersive X-ray spectroscopy
FAS	Fluoroalkane silane/siloxane
FCC	Face-centred cubic
FDM	Fused deposition modelling
FT-IR	Fourier transform infrared spectroscopy
II	Ion implantation
IP	Intellectual property
IR	Infrared
NP	Nanoparticle
NPA	Nanopore array
NTA	Nanotube array
NVS	Nanovesuvianite structure
PDMS	Polydimethylsiloxane
PET	Polyethylene terephthalate

PIII	Plasma immersion ion implantation
PLA	Polylactic acid
PVP	Polyvinyl pyrrolidone
RoA	Roll-off angle
SEI	Secondary electron imaging
SEM	Scanning electron microscopy
SLA	Stereolithography
SLS	Selective laser sintering
SoD	School of Design
SPR	Surface plasmon resonance
SRIM	Stopping range of ions in matter
Std Dev	Standard deviation
TCL	Triple-phase contact line
TPU	Thermoplastic polyurethane
UV	Ultra-violet
VUW	Victoria University of Wellington
XRD	X-ray diffraction

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Chapter 1

Introduction

1.1 Context

The purpose of this research was to develop new technologies to produce novel surfaces with useful wetting behaviours. This was done using two individual substrates, wool fabrics and 3D printed polymer surfaces. Firstly, this research aimed to produce highly hydrophobic wool fabrics in a commercially viable manner in order to create stain and water repellent natural fibre fabrics. Secondly, this research aimed to produce superhydrophobic surfaces and surfaces with anisotropic wetting behaviour using 3D printing for rapid prototyping. These areas of research concern the same theory and methods but they were utilised in different ways to achieve different outcomes. As such, the background and theory will be explained in the introduction chapter with relevant points being introduced and reiterated in each results chapter.

1.2 Wetting: Hydrophobicity and Hydrophilicity

Wetting has been widely studied for many decades, dating back to the derivation of Young's Equation in 1805 (1.1).¹ In more recent times, the focus of these studies has been cases of extreme wetting behaviours, specifically superhydrophilicity and superhydrophobicity in particular. Superhydrophobic surfaces exist in nature, commonly among plants and insects. A well-known example of this is the 'lotus leaf' (*Nelumbo nucifera*). The lotus leaf exhibits very high water repellency as water droplets are observed to bead up on the surface and roll off at low angles.² This

phenomenon has been observed in many other organisms, including flower petals, butterfly wings and beetles.³ A major benefit of superhydrophobic surfaces to living organisms is the associated ‘self-cleaning’ property, also known as the ‘lotus-effect’, whereby a water droplet rolling along the surface will collect any small particles of dust or debris and remove them.⁴ Superhydrophobicity can also be useful when used in non-uniform surfaces, whereby the resulting surfaces enable water capture and flow as seen in some beetles (*Stenocara gracilipes*), found in the arid Namib Desert.⁵ The back of the beetle is covered with small hydrophilic bumps surrounded by hydrophobic channels. As water condenses from fog, onto the hydrophilic bumps, droplets grow until they are big enough to fall into the hydrophobic channels that direct the water into the beetle’s mouth, allowing it to survive. Researchers have been attempting to mimic these natural surfaces for many years, to achieve synthetic surfaces with similar, desirable wetting properties.^{6–9}

1.2.1 Measurements and Definitions

There are many ways to characterise how water interacts with a surface, and although the field of study is large and dates back centuries, there is a significant lack of standardisation within the literature with regard to how the wetting behaviour of a surface is measured and reported.¹⁰ That being said, typically, researchers will report the static contact angle of a surface, usually with the contact angle hysteresis, advancing/receding contact angle or the roll-off angle also being reported. The static contact angle (generally referred to as simply contact angle) is the primary indicator used to determine and define the wettability of a surface. The contact angle is defined as the angle between the surface and the tangent to the curve of the droplet at the triple phase contact line (TCL), where vapour, liquid and solid meet at the edge of the droplet, as shown in Figure 1.1. If a surface is completely wetted by a water droplet, it has a contact angle (CA) of 0° , conversely if a surface completely repels a water droplet, it has a CA of 180° . It is widely accepted that a surface with a static water CA of less than 10° is deemed superhydrophilic, less than 90° is hydrophilic, greater than 90° is hydrophobic and greater than 150° is superhydrophobic. The boundary between hydrophilic and hydrophobic behaviour is considered to be 90° due to the early development of models such as the Young Equation (Equation 1.1) and their included cosine terms. These terms give a clear mathematical boundary at 90° as the cosine of 90° is zero. However, as these models are only approximations, scientifically it has been argued that 65° may be a more appropriate boundary between hydrophilic and hydrophobic behaviour after Vogler¹¹ analysed the differences in the structure of interfacial water.^{12,13}

Figure 1.1 Diagram showing static water contact angle of a hydrophilic surface (left) and hydrophobic surface (right). The surface tensions between solid liquid, liquid vapour, and solid vapour interfaces (γ_{SL} , γ_{LV} and γ_{SV} , respectively) are also shown.

When a droplet is applied to a surface it comes to rest at a local energy minimum.¹⁴ This induces energy barriers for advancing and receding movements which can cause hysteresis; how this hysteresis can be controlled is discussed later in this section. This contact angle hysteresis (CAH) is another commonly used measurement that indicates the wetting behaviour of a surface, as it gives a representation of how easily a droplet moves across the surface. This is measured as the difference between the advancing (θ_{adv}) and receding (θ_{rec}) contact angles of a droplet immediately prior to movement of the TCL (see Figure 1.2). This movement of the TCL can be induced either by tilting the surface and causing the droplet to roll where θ_{adv} is the angle at the front of the droplet and θ_{rec} is the angle at the rear of the droplet, or by increasing and decreasing the volume of the droplet (to measure θ_{adv} and θ_{rec} , respectively). The roll-off angle (RoA) is the angle at which the TCL advances when the surface is tilted, starting from horizontal (0°). However, one must be aware that the measured RoA of a surface is dependent on droplet mass¹⁵ and so it is important that this is taken into consideration when comparing measurements from different studies. It has been suggested that $10.3 \mu\text{L}$ is a suitable standard volume for RoA measurements.¹⁰ CAH and RoA are related¹⁰ and both are a measure of how easily a droplet moves across a surface; some researchers favour one measurement over the other, while some report both or neither measurements. Together, static CA with either CAH or RoA give a general summary of the wetting properties of a surface.

In the literature there are many instances of researchers giving different definitions of superhydrophobicity.^{3,16,17} These definitions usually follow the same general guidelines with slight differences to satisfy the conditions of the surfaces prepared by the respective researchers. Most agree that a static water CA of greater than 150° is required but there is disagreement regarding additional requirements, such as low CAH and low RoA. It can be argued that having a high static water CA alone is insufficient as some surfaces may achieve this, while water droplets still become pinned on the surface due to high adhesion and consequently have a high CAH and high

Figure 1.2 Diagram showing contact angle hysteresis measurement. $CAH = \theta_{adv} - \theta_{rec}$ where θ_{adv} is the advancing contact angle and θ_{rec} is the receding contact angle and RoA is the angle at which the droplet begins to move across the surface. All three measurements are taken at the moment immediately before movement of the TCL.

RoA. Whether this surface should truly be called superhydrophobic, as it does not completely repel water, is debatable. For some applications, the high static water CA is sufficient, but for many, it is the low CAH or low RoA that gives the most benefit. Hence, a superhydrophobic surface is most commonly defined as having a static water CA of greater than 150° and a RoA of less than 10° with a $10 \mu\text{L}$ droplet. This definition was used for this research. However, it is important to note that the values for these cut-offs are determined somewhat arbitrarily, and a surface with a high CA and a low RoA, but that does not meet these particular values, may be found to be just as useful in some applications as one that truly satisfies the defined conditions of superhydrophobicity. In fact, in real world applications, the degree of wettability is often compromised in order to enhance the performance of the material in other aspects, such as improved mechanical or optical properties.¹⁰

1.2.2 Early Theory and Models

Young was the first to propose an equation to predict the contact angle of a droplet on a perfectly smooth surface.¹ This is presented as Equation 1.1 where θ is the contact angle of a smooth surface, and γ_{SV} , γ_{SL} , and γ_{LV} are the surface tensions between the solid vapour, solid liquid and liquid vapour interfaces, respectively. This equation was modelled on an ideal surface, but no surface is perfectly flat even at the atomic scale, and it has been determined that the roughness of a surface has an important influence on the contact angle.^{18,19} This was first realised by Wenzel¹⁸ who expanded on Young's equation by including a roughness factor. This is presented as Equation 1.2, where θ' is the contact angle of a rough surface and r is the ratio of the actual area of a rough surface to the geometric projected area.

The Wenzel equation assumes that the interface between the solid and liquid phases

is homogeneous, now known as the Wenzel state. Cassie and Baxter¹⁹ proposed another equation involving a roughness factor which assumes a heterogeneous interface where pockets of air are trapped between the droplet and the solid surface (see Figure 1.3), now known as the Cassie-Baxter (C-B) state. This is presented as Equation 1.3, where θ' is the contact angle of the rough surface, f_1 and f_2 are the area fractions of the two types of interface (liquid solid, and liquid air) and θ_1 and θ_2 are contact angles of each interface.

Figure 1.3 Diagram showing an interface on a smooth surface as described by Young (left), a homogeneous interface on a rough surface as described by Wenzel (centre) and a heterogeneous interface on a rough surface as described by Cassie and Baxter (right).

$$\cos\theta = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}} \quad (1.1)$$

$$\cos\theta' = \frac{r(\gamma_{SV} - \gamma_{SL})}{\gamma_{LV}} = r\cos\theta \quad (1.2)$$

$$\cos\theta' = f_1\cos\theta_1 + f_2\cos\theta_2 \quad (1.3)$$

The Wenzel and Cassie–Baxter equations led to the notion that surface roughness will enhance the inherent chemical hydrophobicity or hydrophilicity of a surface. That is to say, if a flat surface is hydrophobic, increased surface roughness will increase the hydrophobicity, leading to a higher CA; and if the flat surface is hydrophilic, increased surface roughness will increase the hydrophilicity, leading to a lower CA (see Figure 1.4).²⁰ These equations are also the basis for defining the boundary between hydrophilic and hydrophobic behaviour as CA of 90°. However, it has been shown that increasing the surface roughness of a relatively flat surface with CA < 90° can lead to an increase in CA, further supporting the idea that 65° is a more appropriate boundary for hydrophilic/hydrophobic behaviour.²¹

Figure 1.4 Graph showing general relationship between roughness (r) and CA (θ_w) based on theoretical models, indicating effect of roughness to enhance inherent chemical hydrophobicity or hydrophilicity (θ_0 indicates CA of flat surface).²⁰ With permission of Springer.

1.2.3 Recent Views

The Wenzel and C-B models were widely accepted by the scientific community as they were seen to generally fit the trends observed. However, other models were also proposed^{22,23} and have gained traction in recent years²⁴ as researchers have discovered inadequacies in the Wenzel and C-B models, where they do not accurately describe the CA of a surface.^{25,26}

The Wenzel and C-B models consider the junction between the three phases (solid, liquid, gas) as a two-dimensional area. In contrast, in 1944, Pease²³ suggested considering the junction as a one-dimensional system of the three-phase contact line. This work was followed by Bartell and Shepard,²² who examined the effect of physically heterogeneous islands on CAs. This work involved a smooth surface with a CA of 98° which was then roughened to increase the CA to 148° . Additionally, a separate sample was prepared with a small rough island added to the smooth surface. The rough island was completely encompassed by a water droplet, and the CA was measured as 97° , similar to that measured of the smooth surface. The conclusion of this work was “that Wenzel’s modification of the Young equation is not justified for roughness of a microscopic or macroscopic magnitude”.²² This suggests that the properties of the surface at the one-dimensional TCL are the determining factors with respect to the apparent contact angle, not the properties across the whole surface area in contact with the droplet.

These works went largely unnoticed as the majority of researchers utilised the Wenzel and C-B models (see Figure 1.5),²⁴ but are now the subject of great debate among researchers in the field.^{24,26,27} In 2003, Extrand²⁵ produced similar results to those of Bartell and Shepard’s physically heterogeneous islands, but instead investigated the effects of chemically heterogeneous islands (see Figure 1.6) and again found that the interactions at the TCL were the determining factor of contact angle. In 2007, the failings of the Wenzel and C-B models were highlighted by Gao and McCarthy²⁴ in an article titled “How Wenzel and Cassie Were Wrong”. In this article, the authors highlighted those who have previously questioned the Wenzel and C-B models and succinctly reproduced the results of Bartell and Shepard,²² and Extrand.²⁵ The conclusion of this work was “that contact angle behavior (advancing, receding and hysteresis) is determined by interactions of the liquid and the solid at the three-phase contact line alone and the interfacial area within the contact perimeter is irrelevant.” The authors also make note of saying “We do not advocate never using Wenzel’s or Cassie’s equations, but they should be used with the knowledge of their faults. They support the incorrect concepts that contact area is important and that interfacial free energies dictate wettability.” This indicates that although the Wenzel and C-B equations may not be fully representative of the true wetting behaviour of surfaces, in acknowledging the limitations of the models and applying them to only the area fractions surrounding the TCL, they are still of some use.

1.2.4 Surface Chemistry

As discussed above, it has been shown that in order to obtain a superhydrophobic surface, the surface must be chemically hydrophobic (low surface free energy) with some degree of roughness.^{18,19,23} This chemical hydrophobicity of the surface can be achieved in two ways. Firstly, the surface can be composed of inherently chemically hydrophobic materials, such as some hydrocarbon-based polymers²⁹ or fluoropolymers.⁷ Alternatively, a surface can be produced with desired surface roughness composed of a hydrophilic material, followed by a post-treatment where the surface is functionalised to render it chemically hydrophobic.

Many surface treatments have been used previously. Badyal and co-workers use CF_4 plasma treatments to lower the surface free energy of their rough surfaces.^{7,30} This is a very effective method and the plasma treatment can also impart some surface roughness, further increasing the hydrophobicity of the surface. However, this method is very technical and costly. Many other researchers use liquid-phase treatment with fluoroalkyl silanes (FAS) to lower the surface free energy of their

Figure 1.5 Graph of citations per year for Wenzel,¹⁸ Cassie and Baxter,¹⁹ and Pease²³ articles.²⁴ Information gathered from Web of Science, core collection data.²⁸

Figure 1.6 Diagram indicating difference between measuring the CA of a droplet on a homogeneous surface (left), of a droplet on a surface with a physically heterogeneous island (centre) and of a droplet on a surface with a chemically heterogeneous island (right).²⁴ Reprinted with permission from Ref.²⁴ Copyright 2007 American Chemical Society.

surfaces. Those which have been shown to work well include heptadecafluorodecyltrimethoxysilane,^{31,32} (tridecafluorooctyl)-triethoxysilane (Dynasylan F8261),³³ and another commercially-available FAS sold as Dynasylan F8815.³⁴ This method is widely used as it is much simpler and cost-effective, however it does rely on the substrate being reactive with the FAS. If the substrate does not react with the FAS, it is possible to cross link the FAS molecules to form a layer on top of the surface without diminishing the scale of any already established surface roughness, however the layer is less durable. The last example given of FAS, Dynasylan F8815, is especially useful as it is stable in aqueous solution for up to 24 hours, further simplifying the process and eliminating the need for costly and environmentally damaging organic solvents. This surface treatment was investigated in this research.

1.2.5 Surface Roughness

It has been widely established that in order to create a highly hydrophobic surface, the surface requires a low free energy (low surface tension) and a high degree of roughness. However, the particular ways roughness patterns affect the CA and other measures of wettability have not been conclusively established.

Work by Gao and McCarthy demonstrates the importance of the TCL in the CAH.^{35,36} This work describes the need for a convoluted TCL. This convolution can be achieved by roughening the surface, which decreases the CAH and promotes a low RoA, as a more tortuous TCL is more highly energetic and hence has lower kinetic barriers to TCL movement. Work by Öner and McCarthy emphasises this point, by investigating the differences in wetting behaviour of surfaces containing posts of different shapes and spacings.³⁷ It was concluded that the shape of the pillars was important in determining the CAH of water droplets, as the receding contact angle was increased by up to 15° depending on the shape of the pillar. The pillars in this study were prepared by photolithography and etching, hence they

were in a highly ordered array with consistent heights. The authors proposed that the TCL needs to be more contorted in the plane by forming an irregular array and must also be contorted in three dimensions, not only in the X-Y plane, in order to further destabilise the TCL. The results of this work also showed that the spacing of these posts is critical. The posts must be close enough together so that the droplet sits in a C-B state and does not fall between them into a more Wenzel-like state. In a Wenzel state, pinning of the droplet tends to occur due to greater solid-liquid contact and the presence of capillary forces. However, the spacing between the posts must also be great enough to maintain an air pocket beneath the droplet and minimise solid-liquid contact. In a controlled laboratory investigation, one can easily optimise the size of the features and breadth of spacing to achieve minimal solid-liquid contact and maximum air-liquid contact to optimise the hydrophobic behaviour of a surface. However, the optimised parameters are heavily dependent on the size of the droplet, as the roughness must be of an appropriate size relative to the droplet and must support the droplet in a C-B state. Hence, depending on the application outside of the lab, where droplet size may vary significantly, the optimisation becomes more complex. One must consider keeping the spacing narrow enough and keeping the features big enough to preclude any small droplets falling into a Wenzel-like state, while not inducing so much solid-liquid contact that larger droplets experience a relatively flat surface with little relative roughness.

The trapping of air-pockets is another important factor to consider in wettability. This was demonstrated by Lai et al.¹⁶ This study involved analysing the differences in wetting behaviour of surface with area-contact, line-contact and point-contact with a water droplet. This was done by using three different surface roughness patterns, the first a nanopore array (NPA), the second a nanotube array (NTA) and the third a “nanovesuvianite structure” (NVS), see Figure 1.7. The NPA served as a surface with area-contact between the liquid and solid; this surface was found to have the highest CAH. The NTA served as a surface with line-contact; this surface was found to have lower CAH than the NPA surface. The NVS served as a surface with point-contact; this surface was found to have the lowest CAH of the three surfaces. This trend can be explained by considering two factors. Firstly, as Gao and McCarthy had shown, the convolution of the TCL leads to lower CAH.^{36,38} Secondly, Lai et al. discussed the effects of capillary adhesive forces caused by the trapping of closed air pockets. It was found that to achieve a low CAH, a surface required point-contact (convoluted TCL and minimal solid liquid interaction) as well as the trapping of air in open pockets. Trapping air is required for superhydrophobicity as it keeps the water droplet in a C-B state and decreases the area of solid-liquid contact. However, if the air is trapped in a closed air pocket, such as a pore or tube, the capillary adhesive forces cause pinning of the water droplet and hence a much

higher CAH.

Figure 1.7 Schematic of surfaces used in the study by Lai et al.¹⁶ a) Capillary adhesion is induced when a water droplet on a closed air pocket is drawn upwards because the convex air-liquid interface causes an inward pressure ΔP . b) NPA surface with area-contact. c) NTA surface with line-contact. d) NVS surface with point-contact. Nanopores were approximately 30 nm in diameter, nanotubes varied from 40 to 100 nm in diameter and 0.2-1.2 μm in height. With permission, copyright 2009 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

Hierarchical Surface Roughness

In order to establish the optimal roughness, researchers have examined many superhydrophobic surfaces found in nature. The most extensively researched example is the lotus leaf, with a static water CA of 162° .³⁹ The lotus leaf surface has been observed to have a hierarchical micro- and nano-structure (see Figure 1.8) composed of micro-scale bumps due to the epidermal cells and the entire surface is also covered with nano-scale epicuticular wax crystals.^{39,40} This wax also imparts the chemical hydrophobicity (low surface free energy) to the surface. This hierarchical surface roughness has been found in many other examples of superhydrophobic surfaces in nature,^{9,39–41} and has been shown to be very important in creating superhydrophobic surfaces.^{20,41–43} This follows from previous discussion, as hierarchical roughness serves to further convolute the TCL.

Figure 1.8 SEM images at different magnifications (left to right: lowest magnification to highest magnification) showing the hierarchical surface roughness present on the lotus leaf.⁴¹ Reproduced from Ref⁴¹ with permission of The Royal Society of Chemistry.

In 2012, Bhushan and Lee investigated the effect of different levels of hierarchy on the wetting behaviour of a surface.⁴² This study involved chemically etching one, two or three levels of roughness onto a surface (see Figure 1.9) and comparing the CA with that of a smooth surface. It was determined that all roughened surfaces showed greater hydrophobicity than a comparable smooth surface with CA increases of $60 - 70^\circ$. The surface with one level of roughness was found to be the least hydrophobic of the rough surfaces. The surface with two levels of roughness was more hydrophobic with higher CA and lower CAH, and the surface with three levels of roughness was found to be the most hydrophobic but only slightly more so than the surface with two levels of roughness (see Figure 1.9). This demonstrates that added hierarchy in a surface can cause a less stable TCL, and hence increase the hydrophobicity of the surface, but two levels are generally sufficient to induce superhydrophobicity.

A number of studies have been conducted into how these different levels of roughness affect the wetting behaviours of surfaces. Shi and colleagues created FAS-functionalised Al-Mg alloy surfaces with microstructures, nanostructures or both

Figure 1.9 Schematic of surfaces used by Bhushan and Lee⁴² with one, two and three levels of hierarchical roughness and a graph of their respective CA and CAH compared to relatively flat surface. The levels of roughness were 0.6, 5 and 12 μm in diameter, respectively. Reproduced from Ref⁴² with permission of The Royal Society of Chemistry.

micro- and nano-structures (hierarchical structures) and compared their contact angles.⁴⁴ They found that the surface with just nanostructures had the lowest CA, the surface with just microstructures had a higher CA and the surface with hierarchical structures had the highest CA (129.5° , 149.6° , and 160.5° respectively). However, the difference between the contact angles of the nano- and microstructured surfaces was quite large, whereas the microstructured and hierarchical structured surfaces had more similar contact angles. This suggests that the microstructure has the greatest effect on the static water contact angle of a surface and the nanostructure only slightly increases this measure of hydrophobicity. This theory is supported by work presented by Peng and Bhushan, who created superhydrophobic FAS-functionalised aluminium surfaces and investigated the effect of nanostructure, microstructure and hierarchical structure on the wettability of the surface.⁴⁵ Their results agreed with those of Shi *et al.* suggesting microstructure induces a greater CA on a surface (158°), than nanostructure (152°), but the hierarchical combination of micro- and nano-structure induces a slightly greater CA (160°). Peng and Bhushan also investigated the effect of these structures on the RoA of a surface. These results were similar to those for the CA values, whereby the nanostructured surface had the highest RoA, followed by the microstructured surface, with the hierarchical surface having the lowest RoA. However, the relative difference between the RoA values was more significant between the microstructured and hierarchical surfaces, indicating that the nanostructure has a greater influence on the RoA than it does on the CA of a surface.

Following from the given examples of synthetic and natural superhydrophobic surfaces, it has been determined that to be superhydrophobic a surface needs to have low surface tension and a hierarchical surface roughness with both micro- and nano-structures that effectively convolutes the TCL of water droplets in three dimensions. It has also been seen that reporting two measures of the wettability, both the CA and either CAH or RoA is important as the effect of the nanostructure on the CA is small, but CAH/RoA measurements show that added nanoroughness has a significant impact on increasing the water repellency. As discussed, many examples of superhydrophobic surfaces have been produced in the laboratory. However, most of these surfaces are produced using methods such as plasmachemical modification,^{7,21} chemical etching,⁴⁶ or photolithography,^{37,47} which are costly and difficult to replicate on a larger scale for commercial production.

1.2.6 Anisotropy

It has been established that both the chemistry and the roughness of a surface affect its wetting behaviour, and so it follows that anisotropy in the surface chemistry or surface roughness can cause anisotropy in the wettability of a surface. Morita *et al.* investigated the effect of anisotropic surface chemistry by creating surfaces with alternating stripes of hydrophilic and hydrophobic areas.⁴⁸ Significant elongation of the test droplets was observed in the direction parallel to the surface stripes, and the apparent CA of the surface varied when measured from a perspective parallel to the stripes compared to a perspective perpendicular to the stripes (see Figure 1.10), in fact the parallel CA was measured to be $10 - 30^\circ$ greater than the perpendicular CA. It was proposed that this variation was due to the energy barrier to wetting. That is to say, in the perpendicular direction the droplet is limited by the periodic hydrophobic stripes, but in the parallel direction there is no periodic energy barrier to wetting and the droplet is allowed to advance continuously, causing elongation of the droplet in this direction and a lower CA when viewed from the perpendicular perspective.⁴⁹

The same trends are observed with anisotropic surface roughness. Chen *et al.* investigated CA anisotropy in parallel grooved surfaces using both experimental and theoretical data.⁵⁰ Similarly to Morita *et al.* it was found that the droplets were elongated in the direction parallel to the grooves and the measured CA was higher when viewed from an angle parallel to the grooves than from a perpendicular angle. Chen *et al.* also observed multiple equilibrium shapes of the droplet on the surface, depending on how many grooves the droplet spanned. This is shown in Figure 1.11, and it can be seen that when the droplet spans fewer grooves it is forced to 'balloon' out in the perpendicular direction. It was reported that with fewer channels spanned, the measured parallel CA increased and the free energy of the droplet decreased. This suggests that the edges of the grooved structure presents a physical barrier to movement of the TCL, hindering spreading in the perpendicular direction but allowing spreading in the parallel direction.

Controlling the spreading of a liquid meeting a sharp edge was investigated by Liimatainen, Sariola and Zhou.⁵¹ Gibbs gave a relation that describes the range of possible CA at a mathematically sharp edge, called the Gibbs inequality condition, given as Equation 1.4, where θ_0 is the natural contact angle of the liquid on the surface, θ is the equilibrium contact angle, and ϕ is the edge angle.⁵² Liimatatinen *et al.* demonstrated that by creating surface roughness with sharply undercut edges ($\phi \rightarrow 0$) the upper bound of the Gibbs inequality is dramatically increased and

Figure 1.10 Schematic of an elongated water droplet on a physically anisotropic surface, showing parallel and perpendicular CA measurement perspectives.

Figure 1.11 Theoretical model showing different equilibrium shapes of droplets on a surface spanning four (left and centre left) or three (centre right and right) grooves, calculated by Chen *et al.*⁵⁰ Reprinted from Journal of Colloid and Interface Science, 281, Chen, Y.; He, B.; Lee, J.; Patankar, N. A., Anisotropy in the wetting of rough surfaces, 458-464, Copyright 2005, with permission from Elsevier.

liquids are ultimately pinned, even in cases where the liquid would naturally wet the surface.

$$\theta_0 \leq \theta \leq (180^\circ - \phi) + \theta_0 \quad (1.4)$$

The phenomenon of severe pinning at edges also has an effect on the RoA, which is clearly seen in anisotropic surfaces. Yoshimitsu *et al.* investigated the effect of anisotropic surface roughness on the RoA of a surface.³² In their work, the RoA of a surface with anisotropic groove structures (2-dimensional roughness) was compared to that of a surface with pillar structures (3-dimensional roughness). It was found that the groove structure had a much lower RoA in the direction parallel to the grooves than in the perpendicular direction, and the RoA of the pillar surface was between these two values. This is to be expected, when considering movement of the TCL in the case of the droplet moving on the grooved surface in the parallel direction, although there is greater adhesive force due to greater solid-liquid contact compared to the pillar surface, the barrier to movement is low as the droplet does not approach an edge. The barrier to movement for a droplet on the pillar surface is higher as it approaches the edges of pillars in both directions, hence its RoA is higher. Finally, when we consider the droplet movement on the grooved surface in the perpendicular direction, there is a much greater barrier to movement with a large continuous edge, in addition to greater adhesive forces to overcome due to increased solid-liquid contact compared to the pillar surface. Importantly, the results from this study again demonstrate the need of reporting at least two measures of wettability. It was found that the pillar surface had the highest measured CA (139°), higher than the grooved surface measured from both perpendicular and parallel directions (117° , 135° respectively). This shows that even though the CA indicates a more

water repellent surface, the pillar structure is not the most efficient water shedding surface.

Figure 1.12 Channel (left) and pillar (right) structured surfaces investigated by Yoshimitsu *et al.*³² Reprinted with permission from Ref.³² Copyright 2002 American Chemical Society.

Although anisotropy in the surface roughness has been shown to cause dramatic anisotropy in the wetting behaviour of a surface, it is possible to make a surface with such extreme wetting behaviours that this surface anisotropy is overcome and the surface is super water repellent in both parallel and perpendicular directions, as demonstrated by Gao, Yao and Jiang.³¹ In this work, surfaces with microgrooves were prepared by laser etching. It was found that this method of preparation caused nanoprotusions on the surface which became increasingly rough with decreasing width of the microgrooves. As was expected, the surfaces with less rugged nanoprotusions showed significantly anisotropic wetting behaviour. However, on surfaces with increased nanoroughness, this anisotropy was almost completely lost, with the surface showing superhydrophobic behaviour in every direction. Results showed that surfaces with more rugged nanostructures displayed much higher hydrophobicity with CA approaching 180°, very low CAH and RoA approaching 0°.

It has been shown that anisotropy in the structure and chemistry of the surface can cause anisotropy in the wetting behaviour of a surface. This can be utilised in applications that require directional flow or water-shedding. Alternatively, if anisotropy is not desirable in an application it can be overcome by increasing the hydrophobicity of the surface so that the TCL is sufficiently convoluted in every direction so as to induce effective water repellency in every direction.

1.3 Wool

Wool is produced by many animals such as sheep, rabbits, goats and alpacas. The majority of commercial wool products are made from sheep wool. This research involves only sheep wool and henceforth only this wool will be discussed. Wool is a natural fibre and is used in the production of many textiles, including clothing, upholstery and carpets. Wool is a desirable material for these products due to its natural soft texture, low flammability, low thermal conductivity and high durability.⁵³ Wool is also generally desired over synthetics due to the associated environmentally friendly connotations as a natural product. As wool is a natural fibre, its structure is complex, containing many components. This multi-level structure is shown in Figure 1.13.⁵³ The most important property of wool fibres for industry classification is the fibre diameter. Wool with finer fibre diameter is softer and hence more desirable for clothing and luxury items, whereas wool with coarser fibre diameter is stronger and more suited to upholstery and carpets. These categories are presented in Table 1.1.⁵³

Figure 1.13 Schematic of the structure of a wool fibre of approximately 20 μm diameter.⁵³ Republished with permission of Elsevier Science & Technology Books, from *Wool: Science and Technology*, Simpson, W. S.; Crawshaw, G. H., Woodhead Publishing Ltd, 2002; permission conveyed through Copyright Clearance Center, Inc.

Wool is a protein fibre and hence most of its chemical functionality comes from the

Table 1.1 Wool types classified by fibre diameter.⁵³

Wool Type	Fibre Diameter / μm
Superfine merino	< 20
Merino	20-24
Fine crossbred	25-28
Medium crossbred	29-32
Strong wool	> 32

amino acid residues found within. Amino acid residues are distinguished by their side chains, which determine their acidity/basicity and hydrophilicity/hydrophobicity. Wool will react with a wide range of chemical functionalities. The main types of reactive groups from the amino acid residues in wool are amide bonds, side chains of amino acid residues and disulphide crosslinks.⁵⁴ The major amino acids found in wool, and their side chain chemistry, are summarised in Table 1.2. This chemical reactivity allows for a range of effective chemical treatments being developed and employed in the commercial processing of wool.⁵⁵ Wool also contains 0.8-1% lipids.⁵⁵ However, many lipids are almost completely removed in commercial processing. The external lipids are made up of oils such as lanolin and the internal lipids consist mainly of cholesterol, fatty acids and polar lipids.⁵³ One of these internal lipids, the fatty acid 18-methyl eicosanoic acid (18-MEA), is covalently bound to the surface of the fibre via a thioester bond.^{56,57} This monolayer of 18-MEA is enough to impart a natural hydrophobicity to the surface of the wool, whereas the internal area of the wool is hydrophilic due to the high concentration of amino acids.⁵⁸ It is important to note that although the 18-MEA causes the surface of the wool fibres to be hydrophobic, the CAH for natural wool fibres is generally quite high due to the hydrophilicity of the internal area of wool fibres. This hydrophilicity causes pinning of the TCL when water comes in contact with the end of a wool fibre (where the hydrophilic internal area is exposed) and hence a high CAH, so although the wool fabrics have a relatively high CA, they are not functionally very hydrophobic as they do not effectively repel water.

1.3.1 Processing

Raw wool is contaminated with impurities from farming and collection and the fibres are very disordered after being removed from the sheep by shearing, hence the raw material must undergo several processing steps to transform it into a usable material, these steps are summarised in Figure 1.14.⁶⁰ First the wool is sorted, by colour and fibre diameter. Then the first processing step is scouring to remove impurities and clean the wool. Impurities removed in the scouring step include dirt

Table 1.2 Amount of major amino acids found in wool.^{55,59}

Amino Acid	Amount (mol%)
Glycine	8.6
Alanine	5.3
Valine	5.5
Leucine	7.7
Isoleucine	3.1
Phenylalanine	2.9
Tyrosine	4.0
Serine	10.3
Threonine	6.5
Aspartic acid	6.4
Glutamic acid	11.9
Histidine	0.9
Arginine	6.8
Lysine	3.1
Methionine	0.5
Cystine	10.5
Tryptophan	0.5
Proline	5.9

and pesticides picked up on the farm and also naturally occurring contaminants from the sheep such as dead skin, sweat residues and the naturally occurring wool oil lanolin. At this stage the wool is mostly clean but the fibres are messy and tangled. These tangled wool fibres are then carded. Carding is a process that involves several rollers with teeth to mix and tease out the fibres, to make them easier to manipulate in further steps. At this point in the process the resulting wool bundles are called tops. The next step is gilling, which aligns these fibres parallel to each other using a wide comb. At this point the wool fibres are cleaned and ordered but often still contain some larger contaminants such as pieces of grass and other vegetable matter. These contaminants are removed in the combing step. The combing step separates and recombines the wool fibres, while removing contaminants and short fibres. Short fibres tend to weaken a yarn and give a rougher texture, so it is desirable to remove them before the spinning process. Before the spinning process the bundle of clean, long, parallel wool fibres must be drawn into a fine strand, this step is called drafting and produces what is called a roving which is the material used in spinning. The roving is then spun and drawn into single yarn. These single yarns are very fine and quite weak so they are often spun into double or triple yarns for fabric making. During these processes the wool is subjected to a number of chemicals, such as solvents, detergents or lubricants, as well as heat and physical agitation, so it is important to ensure the processing steps are as gentle as possible and do not compromise any of the wool's desirable natural properties, in particular the soft texture.⁵³

Figure 1.14 Flow chart showing the steps in commercial wool processing from fleece to fabric, for both the woollen process (red arrows) and the worsted process (blue arrows).⁶⁰

Wool can be made into two kinds of product, woollen or worsted, depending on the processing steps.⁶⁰ Woollen processing is a shorter system and produces rougher products. Woollen processing skips the steps of gilling, combing and drafting, and goes straight from tops, after carding, to yarn spinning (see Figure 1.14). This produces a less uniform yarn. Woollen processing is commonly used to produce carpets but can also be used in garments although the fabric appears more textured and feels more rough. The worsted process is a lengthier route but produces a much more even and softer wool. The worsted process involves all the steps outlined above and produces uniform, well-ordered, soft yarns for fabric making.

Wool carpets can be made from yarn by weaving, knotting or tufting, and wool fabrics can be made from top wool by felting, or can be made from yarn by weaving or knitting. This research investigated woven and knitted textile fabrics. In weaving, the yarn is woven into a fabric by passing a weft yarn under or over a number of warp threads. Different patterns can be achieved by altering the number of warp threads each weft yarn passes over or under (see Figure 1.15). In a woven fabric the yarns are aligned horizontally or vertically, allowing little elasticity in the fabric and when cut, the fabric tends to fray. In knitting, yarn is pulled into interlocking loops (see Figure 1.15), this can be done using a single yarn or with an individual yarn for each loop, with the latter being less prone to unravelling, but most wool fabrics are knitted using a single yarn. As with weaving, different patterns can be achieved by manipulating how these loops interlock. This looped structure allows for greater elasticity of the fabric.

Figure 1.15 Schematic diagram showing wide and close up views of how yarns interlock in woven (A/B) and knitted (C) fabrics. Reprinted from Tran, P.; Ngo, T.; Yang, E.; Mendis, P.; Humphries, W., *International Journal of Damage Mechanics*, 23, 359-376, copyright 2014 by SAGE Publications, Ltd. Journals, with permission of SAGE Publications, Ltd.⁶¹

Wool fabrics then go through a number of finishing processes to enhance the properties of the fabrics, these properties include the appearance (especially colour), and chemical and physical properties of the fabric depending on the intended use of the final product. The finishing processes can be divided into three groups, pre-treatment, colouring and functional finishing.⁶² Finishing processes can be done at any stage of wool processing, whether on tops, yarns or fabrics, but fabric finishing is most common.⁶²

Pre-treatment finishing processes on wool commonly include washing and scouring of woollen fabrics, and bleaching for both woollen and worsted fabrics. Washing and scouring in these finishing steps is done in a similar fashion as the washing and scouring of raw wool in the initial processing, using similar detergents and conditions, in order to produce a clean wool product. Most wool fabrics are bleached in order to give a uniform white colour and to increase the absorption of dyes and other treatment solutions.⁶² Fabrics to be used without dyeing or to be dyed light or pastel colours are always bleached with hydrogen peroxide, this achieves a very bright white result, but does compromise the mechanical properties of the wool and decreases the photo-stability.^{63,64} In other cases, reducing agents are used for bleaching wool, commonly thiourea dioxide, and sodium formaldehyde sulfoxylate.⁶⁴ These reducing agents are more gentle than hydrogen peroxide so do not achieve such high levels of brightness but cause less damage to the wool.⁵³ Wool has relatively low photo-stability compared to other textiles and upon exposure to light or heat, wool is known to undergo discolouration. As wool contains many photo-active compounds, the colour can change over time, particularly upon exposure to sunlight. This causes a noticeable yellowish hue in wool. These discolourations have been attributed to the degradation of the amino acids present in the wool. This degradation is known to occur more readily after bleaching and it is through this process that the photo-stability is reduced.⁵³ Along with decreased photo-stability, bleaching can also cause the strength of the fibres to be decreased as they become more dry and brittle.⁶⁴

After pre-treatment wool is often coloured in a dyeing process. Dyeing processes can be discontinuous, continuous or semi-continuous. Discontinuous or ‘batch-dyeing’ involves the wool fabric being added to a vat or bath of dye-stuff solution, where the dye-stuff is absorbed and fixed to the wool fibres. Subsequent washing and post-dyeing processes are often used to then remove any unfixed dye-stuff from the fabric.⁶² Continuous and semi-continuous dyeing processes both involve applying the dye-stuffs in a padding mangle, followed by fixing of the dye-stuff either immediately with heat, steam or chemicals (continuous process) or by batch processes (semi-continuous). Both continuous and semi-continuous processes also require washing to remove unfixed dye-stuff and fixing agents.⁶² Brightening agents, such as fluorescent

whitening agents, are often applied to fabrics to counter the yellowish hue in wool, these can be applied in similar processes to dyestuffs.

After pre-treatment and/or dyeing, the wool is finished for use as commercial fabric to enhance or introduce desired properties, depending on the end-use of the fabric. These processes can be physical or chemical and are used in different combinations for different end uses. A common physical finishing process is felting, also called milling or fulling. Felting the fabrics requires heat, moisture and agitation; this opens the cuticles on the individual wool fibres and allows them to interlock, leaving a thicker fabric with smaller area and a closer, but less defined weave. This process is practically irreversible as the fibres will not disentangle. This is beneficial as it gives the material a more uniform appearance and serves to consolidate the fabric into a more dense material that is more abrasion-resistant. After felting, fabrics tend to have many fibres protruding from the surface, causing the fabric to feel rougher to the touch. To smooth the surface, fabrics are often ‘trimmed’ and pressed to cut or flatten protruding fibres. A common chemical finishing process is often subsequently applied to prevent further felting, especially upon laundering. The material is often chemically treated with an ‘anti-shrink’ treatment, this allows the fabric to maintain its size, shape and texture upon use. Anti-shrink treatments are sometimes applied to yarn, but more commonly the anti-shrink treatment is applied to the finished fabric. These treatments often involve polymers. The most common treatment is the chlorine-Hercosett process.^{65,66} This process first involves a chlorine pretreatment to allow for uniform spread of the following polymer across the wool fibre. This pretreatment is then followed by treatment with the polyamide-epichlorohydrin-based Hercosett polymer, which is then cured to form a film on the surface of the wool fibres.⁶⁶ This Hercosett film swells in water to prevent the movement of the wool fibres that leads to felting.⁶⁵ Wool is sometimes also chemically treated to enhance other properties, including increasing their flame retardant properties, usually involving a zirconium or titanium-based compound, or decreasing the static electrical charging of wool, often with quaternary ammonium salts.⁵³

As discussed raw wool must undergo a number of chemical and physical processes to become a commercial textile. All of these processes change the physical and chemical properties of wool and need to be implemented in series in many combinations; so when developing new physical and chemical treatments, it is important to understand these changes and to develop new treatments that work successfully in conjunction with other existing treatments.

Research recently completed in our group demonstrated the effect of felting on the wetting behaviour of non-woven wool textiles.⁶⁷ This research showed that felting

wool can increase its natural hydrophobicity to near superhydrophobicity. Upon treatment with a FAS, Dynasylan F8815, samples of felted 16 μm wool were rendered nearly superhydrophobic with measured CA of up to 155° , CAH of 2° and RoA of 28° with a 10 μL droplet; compared to contact angles of approximately 130° for commercial merino wool fabrics. It is proposed that by felting woven and knitted wool textiles, similar increases in hydrophobicity may be achieved.

1.4 3D Printing

The process of building a structure layer by layer, called additive manufacturing, freeform fabrication, or colloquially referred to as 3D printing, is a relatively new technology and as such is surrounded by a very active field of research. New developments in 3D printing are regularly appearing in both the literature and commercially in the marketplace. 3D printing was initially a small and restricted technology, with few methods established and limited materials available for printing in these ways. However, it is now becoming a very useful fabrication tool for rapid prototyping with many methods existing and many different materials being used, including polymers, ceramics, and metals. With such variation in technologies, each method of 3D printing has its particular benefits and drawbacks and it is important to select the right method to allow for the use of particular materials and the desired resulting physical and mechanical properties.

Metal 3D printing has been developed and is done using one of three general methods, powder bed, powder fed or wire fed. However, each method uses either a laser or electron beam energy source and is hence very expensive and technical.⁶⁸ Ceramics are also used for 3D printing but require further processing such as drying and firing, as per usual ceramic production.⁶⁹ This research concerned polymer based 3D printing technologies. Some of the very first 3D printing technologies were developed using polymer printing, and these methods have evolved over the years to become very robust and reliable. While some polymer 3D printing technologies are highly technical, others are cheap and straightforward, allowing for easy, rapid prototyping even for new users. The most common and well-established methods of printing polymers are stereolithography (SLA), digital light projection (DLP), selective laser sintering (SLS), continuous liquid interface production (CLIP), and fused deposition modelling (FDM), which was used in this research.^{70,71}

The 3D printing method used in this research was FDM, which was commercialised in 1991 and is now one of the most important rapid prototyping technologies.^{70,72}

FDM involves melting and extruding a thermoplastic filament through a die into a 2-dimensional shape on a print bed, the print head is then raised and another 2-dimensional shape extruded, to build a 3-dimensional structure (see Figure 1.16). Many thermoplastics can be used in FDM, commonly acrylonitrile butadiene styrene (ABS), polylactic acid (PLA) and nylon. FDM is a very low cost and straightforward method of 3D printing but has lower print resolution than other printing methods. Many models of FDM printers are available in the marketplace and they are very popular with domestic users and small scale businesses due largely to the accessibility and simplicity of the technology. The FDM printers available for purchase are all different but all employ the same basic printing technology and are generally either open source, build your own, ‘reprint’ printers or prebuilt printers that come under warranty with specific user guidelines. For most domestic and beginner 3D printing users the prebuilt machines are preferable as they require less expertise and the software they come with offers a lot of support for simple printing using standard polymer filaments. Commercially available prebuilt FDM printers include the UP series of printers, and Makerbot printers. However, for more experimental printing the reprint machines are often preferred. As reprint printers come in parts and require a lot of assembly, they are highly customisable by simply assembling with different parts or in slightly different configurations. It is even possible to print reprint printer parts using other 3D printers. These printers come with open-source software and also work using the software available with other commercially available printers. The open-source software allows for control over every setting in the print and so allows very particular control over how the print runs and hence fine tuning of the final product properties. The open source software also allows printing from code which allows even greater control of the design and running of the print. Commonly used reprint printers include the Prusa and Mendelmax ranges of printers.

SLA was one of the first methods of polymer 3D printing to be developed.⁷³ It employs a bath of resin that is cured in particular areas by a laser, usually UV radiation; the bath is then lowered and another layer of resin is spread on top of the existing layer before the curing process is repeated.⁷⁰ This allows for the layer by layer production of 3-dimensional structures. SLA is a fast and accurate method of 3D printing, but is mostly used with photosensitive resins with poor mechanical properties and the printing process is highly technical; hence SLA is mostly used for the production of prototypes with reduced functionality.⁷⁰ DLP is a newer technology that works using the same principles as SLA. In DLP, instead of curing the resin with a single laser, it is cured with a light projection so the whole layer is cured at once, decreasing the print time compared to SLA. SLS is another process similar to SLA, but involving semi-crystalline polymer powder in place of the resin used in SLA, with a bed of powder being sintered by a laser before another

Figure 1.16 Schematic of FDM printing showing thermoplastic filament being fed from spool through heated print head to produce a 3D printed object.⁷¹

layer of powder is deposited on top and the process repeated.⁷⁴

CLIP is one of the newest and most advanced 3D printing technologies, again using light to cure photo-active polymer resins.⁷⁵ In contrast to previous methods, CLIP uses a bottom-up approach and the part is built in a continuous fashion as opposed to layer-by-layer.⁷⁶ This is achieved by continual curing of the resin at the bottom of a pool and elevating the cured polymer from above in a continuous fashion. This serves to improve the mechanical strength of builds that is usually compromised by the inherent layers in other prints and also allows a much faster print.⁷⁷ This technology offers great advancements in the area of 3D printing but is still being further developed and at present is very advanced and highly technical. While these and other methods of 3D printing polymers offer higher resolution than FDM printing (1-10 μm z-axis resolution compared to approximately 100 μm for FDM), due to their highly technical nature the apparatus cost hundreds of thousands of dollars, whereas, commercial FDM printers can be purchased for less than a thousand dollars. This saving in cost was determined to outweigh the loss in resolution for this work.

Many other technologies of 3D printing exist and some have been used to print highly hydrophobic surfaces. One method investigated was multijet printing, developed by Objet Geometries Ltd.⁷⁸ This method involves printing liquid photopolymer resins through a number of jetting heads that are then cured by UV light before subsequent layers are printed.⁷⁹ This technology has been used to print highly hydrophobic surfaces in the past ($\text{CA} \geq 150^\circ$, but $\text{RoA} > 10^\circ$), as it offers high printing resolution (16 μm) which allows for the creation of the small scale roughness needed for very hydrophobic surfaces.⁶⁷ However, this printing method is highly technical and expensive, also in order to print the small scale of roughness required, the printer is operating at the limit of its resolution which diminishes the precision of any designed surface features, introducing variation between prints.

Another, more basic, 3D printing method previously used to print highly hydrophobic structures is one which involves delivery of a silicone material through a syringe attached to a robotic dispenser, in a process similar to FDM.²⁹ This method allows for printing of very fine structures as the needle on the syringe can have a very small diameter, as well as allowing for fine control over the shapes of the structures printed. Barahman and Lyons used this syringe printing technology to print very fine “Hershey kiss” shaped structures of poly(dimethylsiloxane) (PDMS) onto a glass substrate (see Figure 1.17).²⁹ The tips of these Hershey kiss structures were uniformly angled ($\pm 5^\circ$) and produced anisotropic highly hydrophobic surfaces. The advancing and receding contact angles of the surface were increased in all directions

by at least 30° compared to the contact angles of a flat PDMS surface which were reported as $115^\circ/85^\circ$ ($\theta_{\text{adv}}/\theta_{\text{rec}}$).

Figure 1.17 Hershey kiss shaped PDMS structures printed by Barahman and Lyons with angled tips, producing anisotropic superhydrophobic surfaces.²⁹ Structures are $750\ \mu\text{m}$ high and the post pitch is $500\ \mu\text{m}$ in both x and y directions. Reprinted with permission from Ref.²⁹ Copyright 2011 American Chemical Society.

This research aimed to produce highly hydrophobic surfaces using FDM printing. This method of printing is fast, cheap, and easily accessible, accommodating the rapid prototyping required to produce numerous varied structures in materials that are easy to work with. Reprap FDM printers were used in order to fine tune the prints, print from code and increase the print resolution, allowing for novel experimental surfaces to be printed.

1.4.1 Polymer Filaments for FDM

For FDM printing, the polymer material to be printed is used in the form of a filament. There are many commercial suppliers of FDM filament, and most have varieties of the same polymers. The most common polymers available as FDM filament include nylon, PLA, ABS, thermoplastic polyurethane (TPU) and ultra-high molecular-weight polyethylene terephthalate (PET). Although these filaments are composed mostly of the named polymer they also contain a number of other chemicals, such as copolymers, plasticisers, fillers and pigments. These additional chemicals are used to make the filaments easier to print and to give different aesthetic and mechanical properties to the final printed product. As these filaments are commercial products, and often protected or patented intellectual property, it is difficult to ascertain the exact chemical composition of purchased filaments, although the

major component is always the named polymer. In the process of drawing the polymers into filaments they are melted and extruded, this can potentially cause some carbonisation in the filament material, again altering the final chemical composition of the filament from the usual polymer chemistry. Different polymers offer different mechanical properties to the final printed product but also require different printing specifications. Obviously the different polymer filaments have different optimal extrusion temperatures due to different melting points/glass transition temperatures. Other important factors are the viscosity and heat capacity of the filament as it is extruded, and the cooling behaviour and layer adhesion of the print. For these reasons, filaments of the same polymer from different suppliers can be formulated to have different properties and there are also varied formulations of some polymers available from the same supplier, such as “soft PLA”, “PET+” and “PET-T”, which are essentially blends of different copolymers or different plasticisers in conjunction with the named polymer to give formulations with different printing properties or different mechanical properties in the printed product.

It is important to consider these different chemical compositions of filaments when investigating the surface chemistry of prints. Although we know there is the chemical functionality of the named polymer present in the filament there may be other functionality present too, introduced with the addition of plasticisers, copolymers and pigments. For example, in nylon filament the amine functionality from the nylon itself is expected to be the major chemical functionality but the filament may also contain inorganic compounds, such as TiO_2 from pigments, or other organic functionality, such as esters or carboxylic acids, from plasticisers and copolymers. Therefore, when considering the chemical hydrophobicity/hydrophilicity of the print surface it is difficult to anticipate the wetting behaviour based on the named chemical functionality alone, as the substrate will likely contain increased chemical functionality leading to increased hydrophilicity. It is also important to consider this unknown chemistry when planning chemical treatments of the surface. It is expected that any proposed chemical treatments will interact and bind with the substrate, which can be anticipated based on the expected polymer chemical functionality, but other mechanisms of interaction may be dominant due to the unknown functionality present.

In this work commercial FDM polymer filaments were used. The exact chemical composition of these filaments is proprietary to the manufacturers, and hence no mechanistic studies were performed. The chemical reactivity and wetting properties of the substrates were anticipated to be those of the named polymer, but were tested to determine the true nature of the polymers.

The three polymers used in this work were PET, ABS and PLA. The chemical structure of the named polymers in these filaments is given in Figure 1.18. The native CA of a virgin polymer surface can be found in the literature but rarely do two reported values agree. Due to the heavy dependence of CA on the physical nature of the surface, reported values tend to vary, sometimes up to $\pm 20^\circ$. Approximately median values for virgin polymer surfaces found in the literature are 73° for PET,⁸⁰ 90° for ABS,⁸¹ and 72° for PLA.⁸² While these values do vary somewhat, the notion that ABS will have a higher inherent CA than PET or PLA, and that PET and PLA will have similar CA values, can be understood when examining their respective chemical structures. It can be seen that ABS has the most hydrophobic chemical functionality in its structure, with a noticeable lack of oxygen and amine functionality, and so ABS is likely to have a higher CA than PET or PLA. Furthermore, PET and PLA have similar functional groups, and so it is likely they will have similar CA values. While examining the literature and the chemical structures of the named polymers can give insight into which polymer filaments are likely to be hydrophobic, but as it is impossible to know the chemical structure and hydrophilicity/hydrophobicity of other filament components, this information can only be used as a guide and the wettability must be investigated and confirmed for each filament. It is also important to note that the relative concentrations of acrylonitrile, butadiene and styrene components in ABS filaments can vary and these variations can have an effect on the physical and chemical properties of the final polymer.

1.4.2 3D Printing Software

Many different software programs are used for FDM printing. The first step in printing is creating a 3D computer aided design (CAD) model of the structure to be printed. This can be done using any of a number of available software programs, such as Solidworks, AutoCAD, SketchUp or Rhinoceros3D. These programs allow the user to design a 3D model of the structure which is saved as a .stl file. The printers themselves, especially reppap models, are often operated using a host program such as Repetier. Other printers have onboard, included software that can act as a host program. This software allows for control of the basic printer operations and acts as an interface between the printer and the computer, this software is also responsible for monitoring prints and will determine if a structure is manifold or otherwise unsuitable for printing (for example, if it includes large overhanging areas). Before a host software can send a print to the printer, the .stl file must be converted to G code, which is readable by the printer. This is done using a slicing program, such as Slic3r, which is included in the Repetier host program. Slic3r takes the 3D CAD

PET

Acrylonitrile

Butadiene

Styrene

PLA

Figure 1.18 Chemical structures of PET, ABS and PLA, showing expected functionality of each polymer.

model and ‘slices’ it into 2D layers, determining how the print will be executed. The slicing program is also responsible for specifying the settings for the print, including extruder temperature, layer height, print speeds, etc. After the CAD model has been converted to G code, this can be sent to the printer, and the print will proceed, while being monitored by the host software. In some 3D CAD modelling software, such as Rhinoceros3D with the Grasshopper plug-in, it is possible to convert a CAD model to G code and send this straight to the printer from the host program. This can be a useful work around if the desired settings are not programmable using a slicing software.

1.5 Ion Implantation

Ion implantation (II) is a surface modification method that is used on many different materials with applications primarily in the microelectronics industry. Ion implantation involves bombarding a surface with high velocity ions. The ions progressively lose energy upon entering the surface of the material through both distance interactions with the charges (electronic stopping) and collisions with nuclei in the material (nuclear stopping).⁸³ If the kinetic energy of the incident ion is greater than the ionisation energy of the target atom or the binding energy of the target molecule, electrons or atoms can be displaced from the target material. These recoiled particles can then transfer energy to other particles in the material and cause a cascade of collisions.⁸⁴ This leads to changes in the structure and chemistry of the material within the implantation range, due to displacement of atoms and the addition of foreign incident atoms. The collisions of ions in the target can be considered based on the theory of scattering particles, and models can be used to calculate the “ion track” of an ion penetrating a surface and the track of recoiled target atoms; an example of this is shown in Figure 1.19.⁸⁴ These models can also be used to calculate the distribution of incident ions in the surface and the distribution of target atom vacancies after II treatment, as shown in Figure 1.20.⁸⁴

Ion beam radiation has been found to be particularly effective at modifying polymer surfaces, compared to other types of radiation, such as UV-light, γ -ray, X-ray or electron beams.⁸⁵ The ion beam radiation causes surface modification through several mechanisms. Some knock-out of target atoms and some deposition of incident ions upon the target surface is known to occur, as well as damage caused by nuclear and electronic collisions between the ions and the target, which leads to carbonisation of the surface.⁸⁶ In polymers, nuclear stopping, where the ions are

Figure 1.19 Calculated ion track of ten nitrogen ions penetrating a polyethylene surface, showing path of penetrating ions and recoiled carbon and hydrogen atoms.⁸⁴ Reprinted from Ion Beam Treatment of Polymers, Kondyurin, A; Bilek, M., 1-10, Copyright 2008, with permission from Elsevier.

Figure 1.20 Left: Calculated distribution of nitrogen ions in polyethylene surface for 1000 penetrating ions at 20 keV. Right: Calculated distribution of target atom vacancies in polyethylene surface after penetration of 1000 nitrogen ions at 20 keV.⁸⁴ Reprinted from Ion Beam Treatment of Polymers, Kondyurin, A; Bilek, M., 1-10, Copyright 2008, with permission from Elsevier.

slowed down by momentum transfer to target atoms, causes chain scission, whereas electronic stopping, where the ions are slowed down by exciting the electronic system of the target, causes cross-linking, see Figure 1.21. Random chain scission occurs when an atom is displaced from a target molecule and causes permanent damage to the surface.⁸⁷ Scission is responsible for degradation of the polymer, and if this scission occurs in the polymer backbone this degradation leads to products with lower average molecular weight. Conversely, cross-linking occurs when a valence electron is excited or removed from a target molecule and results in the formation of reactive free radicals that readily cross-link polymer chains.⁸⁷ This has the effect of increasing the average molecular weight of the polymer. However, incomplete reactions of free radicals can increase the chemical reactivity and promote oxidation of the polymer. The effects of ion beam radiation on polymers have been shown to darken the polymer surface,⁸⁵ change the electrical and physical properties (such as conductivity and hardness or abrasion resistance) of the polymer,⁸³ and increase the wettability of the polymer surface.^{88,89}

Figure 1.21 Schematic of random chain scission (top) and cross-linking (bottom) which occurs in ion implantation processes.^{85,87}

The increased wettability of polymer surfaces after ion beam treatment is predominantly due to the carbonisation of the surface which increases with fluence, and can be affected by other polarity changes such as free radicals and oxygen containing groups at the surface, depending on the chemistry of the polymer. Carbon atoms that are knocked from the polymer backbone during the II process (recoiled carbon atoms) remain in the system and can react with undamaged polymer molecules, again leading to cross-linking of the polymer, where the recoiled carbon atom is inserted into a C-H bond (see Figure 1.22).⁹⁰ These reactions are common at low fluence where the concentration of recoiled carbon atoms is low and the concentration of undamaged polymer molecules is high. However, as fluence is increased, the

concentration of recoiled carbon atoms is increased and the concentration of undamaged polymer molecules is decreased. Hence, at higher fluence a recoiled carbon atom has a greater chance of reacting with a free radical. These reactions lead to carbonisation of the surface through the production of carbon clusters with irregular structure, potentially including a range of unsaturated double and triple bonds as well as five and six membered rings and conjugated structures (see Figure 1.22).⁹⁰

Figure 1.22 Schematic of reactions with recoiled carbon atoms, demonstrating cross-linking at low fluence and generation of carbon clusters at high fluence.⁹⁰

The effect of this surface modification on the CA of the surface is very dramatic, for example, the CA of polyethylene changes from 90° before treatment, to $15 - 20^\circ$ after ion beam treatment, even at relatively low fluence of 10^{12} to 10^{13} atoms cm^{-2} .⁸⁶ However, this extreme increase in wettability is not stable and the wettability decreases over time.⁸⁹ This phenomenon is known as hydrophobic recovery and has been the subject of much research, but the mechanism of how the polymer regains its hydrophobicity is not fully understood. The hydrophobic recovery is related to the instability of the chemical structure of the polymer after treatment, with increased concentration of free radicals and unstable chemical groups with high polarity. Overtime, these unstable groups undergo chemical reactions to produce a stable structure with a low concentration of free radicals and higher concentrations of oxygen-containing groups stabilised by cross-linked carbonised structures.⁸⁹ The rate at which the hydrophobic recovery occurs after ion beam treatment has seen to be dependent on the type of ion beam treatment, and is a great deal slower after ion implantation than other methods, such as plasma immersion ion implantation (PIII). In plasma treatments, the treated surface is not carbonised and so after hydrophobic recovery the surface has the same CA as the untreated surface. However, in ion implantation, the surface is significantly carbonised and so even after hydrophobic recovery, the polymer surface has a lower CA than the untreated surface. Due to this layer of carbonisation, the chemistry of the surface is not dependent on the chemistry of the polymer and all polymers should recover to approximately the same

CA value.

Hydrophobic recovery has been observed by many researchers in many different polymers. However, some instances have been observed where the wettability of the II treated polymer surface is stable, and no hydrophobic recovery occurs. Hydrophobic recovery is halted when the II treatment is performed at sufficiently high fluence to cause irreversible damage to the chemical structure of the polymer surface. The exact magnitude of this required fluence is dependent on the nature of the polymer surface, but after this fluence is achieved, the wettability of the treated surface is stable and does not change over time. This is due to the chemical structure of the treated surface after treatment differing at low and high fluence, and the stability of these structures. At low fluence, the chemical structure of the surface is altered through mostly cross-linking and chain scission. When this surface is removed from the vacuum chamber and exposed to air, with some free radicals still present, the resulting structure can be reversed to the initial, stable polymer molecules, and hydrophobic recovery is observed. It is when there are many stable, conjugated groups on the surface after carbonisation during high fluence II treatment, that the new chemical structure of the surface is sufficiently stable to prevent hydrophobic recovery upon reaction with air and remaining free radicals.

In this work II was used to treat the surface of anisotropic 3D printed polymer samples. As II treatment is easily patternable using a mask, this allowed for further specific design and control of the wetting behaviour in different areas of the 3D printed surfaces. The samples were printed using ABS and PLA and functionalised with FAS. To the researcher's knowledge there is no existing literature on II treatment of anisotropic ABS or PLA 3D printed surfaces or any polymer surfaces functionalised with FAS. However, the surfaces investigated in this work were expected to follow established trends and be rendered hydrophilic after II treatment. The hydrophobic recovery of these samples was also investigated by using different fluence levels in the II treatment and repeat measurements of CA and RoA performed after ageing of the treated samples.

1.6 Applications

Surfaces with controlled wetting behaviour have many applications. Water repellent wool textiles have applications in water and stain repellent clothing and fabrics. Surfaces with areas of both hydrophobic and hydrophilic areas or surfaces that allow the flow of water droplets in one direction are also useful in water collection

and water shedding applications. Combining superhydrophobicity with other properties such as antimicrobial activity can open up even more applications, such as bacteriostatic/antimicrobial surfaces for hospitals and other public spaces.

1.6.1 Water and Stain Repellent Fabrics

Highly hydrophobic woven wool fabrics can be used as water repellent clothing, upholstery and carpets. Fabrics that are water repellent are also repellent to stains, especially water-based stains.⁹¹ This presents an application in high-performance fabrics, that require less laundering and less frequent replacement. In clothing, this offers a benefit of keeping the garment cleaner and stain-free for longer, reducing the need for laundering and lengthening the life-span of the garment, which is important for the consumer. In upholstery and carpets this offers benefits in public spaces such as public transport as well as in elderly care and hospitals, where upholstery is often soiled. In households, water repellent surfaces can prevent common stains on upholstery and carpets, such as those caused by spilled drinks.

As this relates to a commercial industry there are standardised tests and guidelines specified by the industry to determine the practical, functional water repellency of fabrics. These differ from the scientific test of CA and RoA measurements and place greater importance on the performance of the fabrics in conditions defined to simulate regular fabric use. These tests analyse other measures of fabric wettability, such as water absorption and water penetration.

1.6.2 Water Capture Devices

Surfaces with both hydrophobic areas and hydrophilic areas have been shown to have applications in water capture. Even in nature, the *Stenocara* beetle uses this concept to survive in the arid Namib desert.⁵ In some previously reported water capture devices, strictly superhydrophobic and superhydrophilic surfaces are utilised, with areas of high CA and low CAH or low CA and high CAH.⁹² However, it is also possible to create water capture devices with surfaces containing less extreme hydrophilic and hydrophobic areas.⁷ The critical factors in water capture applications are the ability to trap water on the surface and the ability to then collect this water efficiently. Firstly, the ability to trap water is granted by having small areas of hydrophilicity that allow for nucleation of droplets due to condensation. Secondly, the ability to collect the water efficiently is granted by areas of sufficiently

low adhesion to allow movement of the droplet. It is also useful to have this droplet movement controlled in only one direction to allow collection of all harvested water. This second factor allows some compromise in the hydrophilicity/hydrophobicity of the surface, it does not need to be strictly superhydrophobic/superhydrophilic, it only must have low enough adhesion that a droplet will roll down the surface at some achievable angle when the droplet reaches some achievable volume. Hence, by controlling the wetting behaviour of a surface, a water capture device could be produced with lower specifications than strictly superhydrophobic/superhydrophilic surfaces or surfaces with areas of both hydrophobicity and hydrophilicity. This was investigated in this research project using 3D printing. 3D printing is a useful tool for these investigations as the rapid prototyping allows for many different surface designs to be tested and optimised.

1.6.3 Water Shedding

Water shedding is an important property of surfaces in many application areas. As discussed above, water harvesting devices can benefit from unidirectional flow in order to efficiently collect the harvested water. Another area where this property is beneficial is heating and cooling. Heat exchangers in refrigerators are critical to the function of the appliance and the heat exchanger efficiency dramatically impacts the power usage of the appliance. While in use, the cold surface of the heat exchanger is exposed to humid air and so water condenses onto the surface. This water then freezes and creates a layer of ice, commonly in the form of frost, on the heat exchanger. While uniform ice is a good conductor of heat and does not dramatically reduce the efficiency of the heat exchanger, frost contains pockets of air which insulate the heat exchanger, causing a rapid decline in efficiency. Much of the energy used by a refrigerator is dedicated to the removal of frost on the heat exchanger surface, in the ‘anti-frost cycles’ whereby the heat exchanger is warmed to melt the ice and remove the detrimental frost from the surface. In order to increase the energy efficiency of refrigerators and minimise their power usage this issue must be addressed. To increase the efficiency of the appliance, the condensation and freezing of water onto the surface can be controlled so as to create a uniform layer of ice (without forming the insulating frost) to increase the heat conductivity of the encumbered surface and also control the melting and shedding of the ice layer so that shorter anti-frost cycles can be implemented, using less energy while achieving the same results. This can be done by creating and implementing a surface with specific hydrophilic areas for water to condense onto and promote the formation of uniform ice, while also having the large hydrophobic areas on the surface to shed the water and melting ice efficiently during the anti-frost cycles.

1.6.4 Bacteriostatic/Antimicrobial Surfaces

Superhydrophobic surfaces have been shown to have ‘passive’ antimicrobial activity, this is referred to as bacteriostaticity.^{17,93,94} This passive antimicrobial activity can be enhanced by adding other chemicals to the surface with ‘active’ antimicrobial activity, such as silver.^{33,34,95} Silver has been known to be an antimicrobial agent for many years, with high activity against Gram-negative bacteria such as *Escherichia coli* (*E. coli*) as well as Gram-positive bacteria such as *Staphylococcus aureus* (*S. aureus*) and even some fungi.^{17,96–98}

The bacteriostaticity of highly hydrophobic surfaces has been shown in several previously reported studies. For example, Vilčnik and colleagues treated cotton fabric with a FAS to achieve a static water CA of approximately 150° and observed a $99.3 \pm 0.1\%$ reduction in *E. coli* on the surface compared to an untreated cotton fabric.⁹³ Also, Yoon and co-workers created a superhydrophobic surface by applying a carbon nanotube-polytetrafluoroethylene coating to stainless steel plates and measured the antimicrobial activity against *E. coli* under both stagnant and flow conditions.⁹⁴ They reported that under stagnant conditions only a 25% reduction in *E. coli* was measured, whereas under flowing conditions there was a reduction of up to 80% of adhering *E. coli* cells. This difference can easily be attributed to the ‘self-cleaning’ behaviour of shedding debris observed with superhydrophobic surfaces.

The combination of this hydrophobic bacteriostaticity and active antimicrobial activity has been studied by Khalil-Abad and co-workers, who functionalised cotton fibres with silver nanoparticles (Ag NPs) and octyltriethoxy silane.⁹⁵ The Ag NPs were of many sizes and provided a multi-sized roughness to the surfaces, allowing for a static water CA of 151° but the surface was also found to have a high RoA and pinning of water droplets occurred. In these experiments, the surfaces were found to have great antimicrobial activity against both *E. coli* and *S. aureus* bacteria. Yin and colleagues also showed that surfaces functionalised with Ag NPs had prolonged antimicrobial effects on a superhydrophobic surface compared to a Ag NP functionalised surface that was hydrophilic (CA of 54°).

These previously reported experiments show the value of using superhydrophobicity as a way to create bacteriostatic/antimicrobial surfaces, especially when used in conjunction with additional antimicrobial agents such as Ag NPs.

1.7 Project Outline

The work presented in this thesis concerned the development of functional surfaces with controlled wetting behaviours on two substrates, woven and knitted wool fabrics, and 3D printed polymers, for potential industrial and commercial applications. Through this research novel surfaces were developed and novel treatments with interesting effects and applications were also investigated.

Research with woven and knitted wool fabrics concerned the development of water repellent wool fabrics for use in commercial carpets, upholstery, bedding and garments. These products benefit from water repellency as it renders them resistant to water-based stains, reducing the need for laundering and lengthening the lifetime of the product. In making these surfaces for commercial applications it was important to develop synthetic methods that are easy to scale-up, do not require specialist equipment not currently used by the industry, do not produce excessive hazardous chemical waste, and are cost-effective. In order to be fit for purpose these fabrics did not necessarily need to be technically superhydrophobic, they needed only to effectively repel water so spilled liquids were not absorbed into the fabrics, and allow for easy clean up, whether by shaking or blotting with a cloth or towel. Hence, while traditional measures of wettability such as CA and RoA were analysed for clarity, other measures of performance were also investigated including water absorption tests.

Firstly, physical modification of the wool fabrics was investigated. As physical modifications can be performed on large scales by existing commercial processing machinery with little additional chemical waste and few additional materials, if the necessary wetting behaviour could be achieved with physical modification alone this would be a process adopted very easily into commercial processing by manufacturers. However, while the hydrophobicity of the fabrics was often increased using these physical modification methods, the fabrics were deemed suitable for only a select few fabric applications. Chemical processes were then investigated in order to alter both the physical and chemical nature of the wool fabrics. Modification of the physical nature of the wool was achieved by increasing the surface roughness via functionalisation of the wool with nanoparticles and microparticles of gold, silver/silver chloride or calcium carbonate. These added particles also changed the chemistry of the wool surface, changing the hydrophobicity/hydrophilicity of the fibres, along with subsequent post-treatment with a FAS to increase the hydrophobicity. Functionalised fabrics were found to be highly water repellent and performed well in water absorption tests also. The developed functionalisation processes were deemed to be successful and commercially viable, and hence were determined to

have potential as commercial processes for use in industry.

3D printing was also investigated as a method for creating surfaces with controlled wetting behaviour. 3D printing was used as a method of rapid prototyping to produce surfaces with designed surface roughness patterns and then post-treated with FAS to control the surface chemistry. Two kinds of surfaces were investigated in this work. Firstly, work was carried out to create a superhydrophobic surface. Surface roughness was created by designing and printing a roughness pattern with a regrap FDM printer, which allowed for very fine patterning in precise shapes. These surfaces were then functionalised with silver nanoparticles using a facile, aqueous method to give the surface hierarchical roughness and added functionality due to the known antimicrobial activity of silver nanoparticles. These surfaces were found to be highly hydrophobic, but did not surpass the boundaries set for superhydrophobicity. Even so, these surfaces did show high water repellency in both CA and RoA measurements and were functionalised with an antimicrobial agent making them novel, highly functional surfaces.

3D printing was also used for rapid prototyping of surfaces with specific wetting behaviours for water harvesting and water shedding. Surfaces with anisotropic roughness were printed and ion implantation and FAS treatments were used to render the surfaces entirely hydrophilic or hydrophobic, using methods that could be patterned to produce surfaces with both areas of hydrophilicity and areas of hydrophobicity. In applications where water shedding is important, such as water collection and heat exchanger surfaces, the water only needs to move across the surface in one direction when tilted or vertical. As such, the required RoA is higher than a surface to be used only at low angles or horizontal and the water only needs to be free moving in the direction of the tilt, allowing the use of simple anisotropic surfaces with roughness in only two dimensions. Producing a functional surface with roughness in only two dimensions allows for easy scale up using other manufacturing processes in a continuous process and minimises production costs.

Chapter 2

Experimental Methods

2.1 Materials and Instruments

Our links to industry have provided us with samples of woven wool textiles; these were sourced from Camira Fabrics Ltd., UK. These samples were manufactured from New Zealand wool and are of different fabric types, at different stages of finishing. Merino wool fabrics were also manufactured and provided by Dr Peter Ingham at AgResearch in Lincoln, New Zealand. One of these fabrics was woven and the other knitted, both fabrics were manufactured using minimal amounts of lubricants and minimal processing, with no dyes or post-treatments.

Two 3D printers were used in this research. Firstly, the MendelMax 2 FDM printer. This printer is privately owned by a student at the School of Design (SoD) at Victoria University of Wellington (VUW). As this is an “open-source” printer it can be customised with different parts and used with any software and any available, printable polymer. This particular printer is highly customised to achieve higher resolution prints. Secondly, a MendelMax 3 FDM printer was purchased and is located at VUW School of Chemical and Physical Sciences. The MendelMax 3 printer is very similar to the MendelMax 2, but the former has a dual extruder, allowing for two materials to be printed in one object. The MendelMax 3 printer is similarly customised to allow higher resolution prints. The MendelMax printers were chosen for a number of reasons, in addition to the low cost of the printers themselves and facile operation, there were two key factors to consider. Firstly, as the printers are open-source we were able to use highly technical software of our choice. Secondly they use solid polymer filaments which can be purchased from a number of retailers, or produced in the lab, allowing for investigation of a number of polymer substrates.

Although the exact chemical composition of these commercially available filaments are often unknown and can contain numerous additives, the major polymers in the filament are known. Three polymer filaments were used in this research. Firstly, a filament called PET+ was purchased from MadeSolid in California, and ABS and PLA filaments were purchased from Makers Tool Works in Oklahoma. More detailed information about how the printers and polymers were used can be found in Sections 2.3.1 and 2.3.2.

2.1.1 Chemicals and Solutions

For surface functionalisation of both 3D printed and wool substrates, the FAS commercially available as Dynasylan F8815 was used. This FAS was chosen as it is stable in aqueous solution for up to 24 hours so is easy to use and lends itself well to commercial application. However, its exact chemical structure is unknown as it is a protected commercial surface treatment agent, hence measurements of uptake and leaching were not performed and no reaction mechanisms with the substrate surfaces are proposed. All dilutions and solutions of FAS used distilled water as the solvent. A commercial wool detergent was used to wash wool fabrics before treatments, this was “Kindness” brand wool wash, which can be purchased from a supermarket. An industrial wetting agent (anionic surfactant) was used to aid in uniform absorption of treatment solutions, this wetting agent was Huntsman’s albaflow ffa, kindly provided by Wool Yarns Ltd., Lower Hutt. This wetting agent was diluted to a stock solution containing 1 wt% wetting agent, and this 1 wt% solution was used in further experimental procedures.

Other stock solutions prepared and utilised in further experimental procedures were as follows. Tannic acid was purchased from Sigma Aldrich (ACS reagent grade) and a solution of 1 wt% tannic acid was prepared. Silver nitrate and concentrated hydrochloric acid were purchased from Fisher Scientific (both analytical reagent grade), and a 1000 ppm silver solution, 0.1 M HCl solution and a 1 M HCl solution were prepared. Calcium chloride (laboratory grade, $\geq 93\%$) was purchased from Biolab (Australia) Ltd., and a 1 M solution was prepared. Sodium carbonate ($\geq 99.5\%$ purity) was purchased from Prolabo (France) and a 1 M solution was prepared. Au^{3+} solution was prepared by colleagues within the research group. This solution was prepared via dissolution of gold metal in aqua regia (3:1 solution of hydrochloric and nitric acids). Excess nitric acid was then removed through the addition of urea. The resulting solution was then decanted and distilled to remove excess acid and the solution diluted to obtain approximately 4 wt% Au^{3+} . The precise concentration of this solution was found by atomic absorption spectroscopy to be 3.80 wt% Au^{3+} .

2.2 Wool Fabrics

Wool fabrics were subjected to both chemical and physical treatments in order to increase their surface roughness, as well as chemical treatment with the FAS to increase the chemical hydrophobicity. This investigation was focussed on chemical treatments that are minimally harmful to both end users and the environment. Some fabrics were treated both chemically and physically to determine how these treatments worked together to influence the wetting behaviour.

2.2.1 Chemical Treatments

FAS Functionalisation

Wool fabrics were treated with FAS Dynasylan F8815. For this treatment, an aqueous solution of the FAS was prepared and the wool was treated with 0.1 – 5 wt% FAS with a 1:10 ratio of wool to FAS solution for two hours. For example, for a 5 wt% treatment, a 1 g sample of wool was submerged and fully wetted in 10 mL of 0.5 wt% solution of FAS in distilled water. After two hours in the solution, the fabric was then gently squeezed dry and placed straight in an oven at 80 °C for a further two hours. This served to fully dry the fabric and form a coated layer of the FAS polymer.

Gold Nanofunctionalisation

The method used for gold nanofunctionalisation is a proprietary method developed by Prof. Jim Johnston, Dr Kerstin Lucas (née Burrridge), and Dr Thomas Nilsson and owned by Noble Bond Ltd.^{99,100} A gold colloid was prepared by adding 0.6 mL of a 1 wt% tannic acid solution to a solution of 45 μL of 4 wt% Au^{3+} solution in 60 mL of distilled water while stirring. The reduction of Au^{3+} to gold nanoparticles occurred within two minutes, observable by the distinct colour change of the solution from very pale yellow to deep burgundy red. However, the colloid was left stirring for two hours to ensure complete reduction. Following the gold colloid synthesis, 1.5 mL of a 1 wt% wetting agent solution was added to the colloid, and the pH of the colloid was adjusted to pH 2.0 with 1 M HCl.

A sample of each fabric (woven and knitted merino) was then taken and weighed, each sample weighed 0.7 g. These samples were washed in a solution of 60 mL of hot

tap water and 0.5 mL of “Kindness” wool wash detergent. The samples were then rinsed in hot tap water and squeezed to remove excess water. The washed samples were then submerged in a solution of 1 mL of 1 wt% wetting agent solution in 20 mL of hot tap water to fully wet the samples. Each sample was then removed from the wetting agent solution, squeezed to remove excess water, and submerged in 30 mL of gold colloid, as prepared above. The samples were left submerged overnight on a shaker table to ensure full uptake of the gold nanoparticles. The samples were then removed from solutions, rinsed with cold tap water and dried at room temperature.

Ag/AgCl Functionalisation

The method used for Ag/AgCl functionalisation was based on that developed by Dr Eldon Tate and Prof. Jim Johnston.¹⁰¹ Samples of both merino fabrics were cut and weighed. The samples were of similar areas but as the woven fabric is more dense, the sample weights differed. Woven fabric samples were 0.7 g and knitted fabric samples were 0.5 g. First, samples were fully wetted and washed in a solution of 60 mL of hot tap water and 0.5 mL of “Kindness” wool wash detergent. The samples were then rinsed in distilled water to displace contaminant chloride ions, and then squeezed to remove excess water but kept wet to promote full wetting in subsequent steps. Samples were soaked in solutions of appropriate volumes of 1000 ppm Ag^+ solution to provide 5 wt% silver (50 mL of 1000 ppm Ag^+ solution per 1.0 g of wool) with added distilled water to make the total volume up to 40 mL to fully submerge the samples. The samples were left submerged in solution, on a shaker table at room temperature for two hours. Solutions were then decanted and samples rinsed with distilled water. Rinsed samples were briefly patted dry between paper towels and put immediately into 40 mL of aqueous solutions containing a ten times excess of Cl^- ions (50 mL of 0.1 M HCl per 1.0 g of wool) and 2 mL of 1 wt% wetting agent solution. Samples were left in these solutions for 24 hours on a shaker table at room temperature in ambient light conditions. Solutions were again decanted and samples finally rinsed with distilled water and dried at room temperature.

Unsuccessful variations of the above successful method were also investigated to optimise the process and successfully functionalise the surfaces. These are summarised in Table 2.1. After the first iteration, involving only rinsing with distilled water before treatment, not using a wetting agent, and rinsing but leaving the samples fully wet between samples, the surface was left very light and unevenly coloured. This indicated that the ions were not absorbed efficiently or evenly across the surface, producing the light, uneven colouration. In the second iteration, the samples were washed with soap before treatment (“Kindness” wool wash) to remove contaminants

and provide a uniform surface for treatment. A wetting agent was also introduced. As the wetting agent contains chloride ions, it could not be added to the Ag^+ solution (or the silver would precipitate out as AgCl before the wool was added), so had to be used with the chloride solution. The sample was also patted dry with paper towels between solutions. The wetting agent promoted the absorption of chloride ions into the wool fibres and the partial drying prevented the AgCl immediately precipitating into the solution and not throughout the fabric on individual fibres. This led to a darker colouration, indicating increased absorption of the chloride and silver ions. However, the colour was still patchy on the surface. It was determined that this patchiness was due to non-uniform absorption of the silver ions, because the samples were not fully wetted when placed into the second soak solution, and could not be squeezed or manipulated in this solution to promote wetting as this would have released the absorbed chloride ions into solution and led to AgCl precipitation in solution. Hence, it was determined that the silver solution had to be used first, followed by the chloride solution with added wetting agent.

Table 2.1 Variations of the Ag/AgCl functionalisation method attempted in finding optimal successful method.

Pre-wash	Order	Wetting agent	Between solutions	Colour
d. H_2O	Cl^- , Ag^+	None	Rinsed	Light, uneven
Soap, d. H_2O	Cl^- , Ag^+	In Cl^- solution	Rinsed and patted	Darker, patchy
Soap, d. H_2O	Ag^+ , Cl^-	In Cl^- solution	Rinsed and patted	Dark, even

One drawback of the final method used in this synthesis is the determination of the concentration. In the past, this synthesis was performed by adding chloride ions in excess, followed by a known amount of silver ions as the limiting reagent. Due to concentration gradients, it is unlikely for a sample to absorb all chloride ions in the first solution, so chloride was added in excess. In the following solution the silver ions are attracted to the negatively charged chloride ions, overcoming the concentration gradient and allowing almost complete absorption of the silver ions from solution. Therefore the concentration of AgCl could be determined by controlling the amount of silver added. However, in the method used in this research, for reasons outlined above, the silver was added first, followed by the chloride. As silver is a relatively expensive material it is not economically viable to add silver in large excess, but it is necessary to add enough silver to induce significant uptake of silver ions from the solution by the sample. It was not possible to add the chloride ions in a limiting manner as the concentration of chloride in the wetting agent (added to the chloride solution) was unknown, so the chloride ions were still added in excess. It is assumed that most silver ions were absorbed but only an approximate concentration can be determined in this way. It would be possible to analyse the residual silver solution after removing the wool sample to determine the remaining amount of silver and hence the uptake of silver ions by the wool. However, the wool is rinsed and patted

dry after soaking in the silver solution and upon soaking in the chloride solution, some AgCl is precipitated out into solution. As such, determination of the final concentration of silver in the sample is not trivial and was not considered in this work. Samples were soaked in silver solutions with approximately 5 wt% silver (equating to approximately 6.64 wt% AgCl), and assumed to uptake the majority of the silver ions.

Calcium Carbonate Functionalisation

The method used for the CaCO_3 functionalisation was based on the method developed for the Ag/AgCl functionalisation above. Samples of each merino fabric were cut and weighed. The following synthesis method includes volumes of solutions used for 1 g of wool, but was be scaled for 0.5-3 g samples. First, samples were fully wetted and washed in a solution of 100 mL of hot tap water and 1.0 mL of “Kindness” wool wash detergent. The samples were then rinsed in distilled water and squeezed to remove excess water but kept wet to promote full wetting in subsequent soaking steps. Samples were soaked in 50 mL aqueous solutions containing 500 μL of calcium chloride solution (1 M), to give approximately 5 wt% CaCO_3 in the final samples. The samples were left submerged in solution, on a shaker table at room temperature for two hours. Solutions were then decanted and samples rinsed with distilled water. Rinsed samples were then briefly patted dry between paper towels and immediately put into 50 mL aqueous solutions containing 1.5 mL of sodium carbonate solution (1 M) and 2.5 mL of 1 wt% wetting agent solution. Samples were left submerged in these solutions for 24 hours on a shaker table at room temperature. Solutions were then again decanted and samples finally rinsed with distilled water and dried at room temperature.

2.2.2 Physical Modifications

Hand Felting

Woven wool fabrics from Camira Fabrics, Ltd. were hand-felted. This involved placing a sample of fabric on a bamboo mat, fully wetting it with hot soapy solution, and rolling the mat up with the sample inside. The solution used to wet the fabric was a solution of hot tap water and a small amount of commercial “Kindness” wool wash, approximately 0.2 mL per 100 mL of water. The wet sample was then rolled up in the mat and rocked back and forth 50 times, rolled up a bit more and rocked

back and forth another 50 times. The mat was then unrolled, the sample rotated 90° and the process repeated. After this process had been completed in each of the four directions on one side of the sample, it was then flipped over and the process repeated in each of the four directions on the reverse side of the sample. This was deemed to constitute one hand-felting process and is summarised in Figure 2.1. Each sample was subjected to zero to five total successive hand-felting processes, to investigate the effect of further degrees of felting, before being air-dried.

Figure 2.1 Schematic showing the process of hand-felting used. Step 1: Place fabric sample on bamboo mat, fully wet with soapy water. Step 2: A. Roll sample up in bamboo mat and rock back and forth 50 times, B. Roll up further and rock back and forth another 50 times, C. Unroll and rotate sample 90 degrees. Repeat Step 2 four times. Step 3: Flip sample over. Repeat Steps 1 and 2 on other side of sample.

Trimming

Samples of woven wool fabrics were trimmed to remove protruding fibres. This simply involved one pass of a razor blade across each surface (each side of the sample) in four directions (top to bottom, bottom to top, left to right, and right to left). This was performed on samples that had previously been hand-felted.

2.3 3D Printed Surfaces

2.3.1 MendelMax 2 Printing

All samples printed on the MendelMax 2 printer were modelled and printed by Liam Gilberston from the SoD at VUW. The MendelMax 2 printer itself was owned by Liam and was slightly modified from the standard model, including the addition of a finer diameter print nozzle. Initial samples were printed on the MendelMax 2 printer using PET+ and ABS filaments, using conditions outlined in Table 2.2. These are commercially available polymer filaments, the exact chemical composition is unknown. However, they are primarily composed of PET and ABS respectively, along with comparatively small amounts of additives such as plasticisers and whiteners. The primary programs used for generating 3D computer aided design (CAD) digital models for 3D printing on this printer were Rhinoceros 5.0 and the Grasshopper parametric modelling add-on. For direct G-code generation the Silkworm plugin for Grasshopper was used supplemented by Slic3r, an open source slicing program for tool path generation. For data tree operations within Grasshopper the Tree Sloth plugin was used, and Repetier Host was implemented as a 3D printing host, again supplemented by Slic3r.¹⁰² The details of printed structures will be discussed in Chapters 5 and 6.

Table 2.2 Standard printing conditions used for PET+ and ABS filament with MendelMax 2 printer.¹⁰²

Filament	Extruder Temperature	Bed Temperature
PET+	270 °C	60 °C
ABS	230 °C	100 °C

2.3.2 MendelMax 3 Printing

Further samples were printed on the MendelMax 3 printer using ABS and PLA filaments, using conditions outlined in Table 2.3. This printer was owned and operated by the research group, but was assembled and modified with help from Liam Gilbertson. As with the MendelMax 2 printer, the MendelMax 3 printer was fitted with a finer diameter print nozzle (0.25 mm) than the standard printer (0.4 mm). Again, the filaments used were commercially available polymer filaments as above, and so the exact chemical composition is unknown. The program used for generating 3D CAD models for 3D printing on this printer was Rhinoceros 5.0. Repetier Host was again implemented as a 3D printing host, again supplemented by Slic3r. The details of printed structures will be discussed in Chapter 6.

Table 2.3 Standard printing conditions used for ABS and PLA filament with MendelMax 3 printer.

Filament	Extruder Temperature	Bed Temperature
ABS	230 °C	100 °C
PLA	200 °C	70 °C

2.3.3 FAS Functionalisation

Some 3D printed polymer surfaces were treated with FAS Dynasylan F8815. An aqueous solution of the FAS was prepared and the polymer structure was treated with a solution of 0.1 – 5 wt% FAS for 2 hours. Subsequently, the structure was placed in an oven at 80 °C for a further 2 hours, to dry the structure and form a coated layer of the FAS polymer.

2.3.4 Silver Nanofunctionalisation

Some 3D printed polymer surfaces were functionalised with silver nanoparticles to add a nanoscale roughness. As the samples were quite hydrophobic to begin with, they were wetted with distilled water using a clean sponge to force the water into the surface structure. These wetted samples were then added to 5 mL of 1000 ppm Ag^+ solution. As the samples floated, it was important to place them in the solution with the structured surface down. The samples in Ag^+ solution were then placed in a water bath at 70 °C. The reduction of Ag^+ to Ag nanoparticles can be observed in the colour change of the surface, due to the well-known strong colour of silver nanoparticles. Over time an orange colour developed and deepened on the surface

of the 3D printed samples. However, if the samples were left in solution for too long, too much reduction occurred and the surfaces were plated with bulk silver, with the characteristic grey metallic appearance. This process was optimised to allow sufficient time for nanoparticle formation while avoiding silver plating of the samples. Successful samples were left in solution at 70 °C for 8 hours before being removed from solution and dried at room temperature. These samples were finally rendered a light orange colour on the surface.

Filament Surrogate

A small amount of ABS filament was also functionalised with silver nanoparticles, to be used as a surrogate for high resolution SEM and EDS analysis in place of actual samples (see Section 5.2.2). To produce this surrogate, a small section of ABS filament was used, approximately 2 cm long. This piece of filament was cut into several smaller segments and melted onto a glass slide, using a hot plate set to 250 °C. Once melted the polymer was removed from the heat, pressed slightly using another glass slide to flatten the surface, then allowed to cool at room temperature. Once cool the polymer was lifted off the glass slide, added to 5 mL of 1000 ppm Ag⁺ solution, and placed in a water bath at 70 °C for 8 hours. The polymer was then removed from solution and dried at room temperature. This functionalised polymer was a similar light orange colour as the functionalised 3D printed samples produced above.

2.3.5 Ion Implantation Treatments

Ion implantation (II) was carried out at GNS Science under the supervision of Dr Jérôme Leveneur. The first II samples were prepared using Ar⁺ ions at 9.6 keV with a fluence of 10¹⁴, 10¹⁵, or 10¹⁶ atoms cm⁻² on each of the three kinds of sample (ABS, ABS-FAS, and PLA), totalling 9 samples. The second II samples were prepared using 5 keV C⁺ ions extracted from a CO gas source. Implantation with fluence of 10¹⁴ or 10¹⁵ atoms cm⁻² was performed on each of the three kinds of sample, totalling 6 samples. Fluence of 10¹⁶ atoms cm⁻² of carbon was also achieved on a PLA sample, but not ABS or ABS-FAS samples due to time restrictions and limited ion beam availability. The two energies were chosen in order to lead to a similar implantation and ion beam damage profile for all implantations. Implantation ranges of 19.9 ± 0.2 nm were calculated using the Stopping Range of Ions in Matter (SRIM) software.¹⁰³ The beam current density was kept low (< 3 μA) for both sets of implantation to prevent significant heating of the samples.

2.4 Characterisation Techniques

2.4.1 Goniometer: CA and RoA Measurements

A goniometer that was constructed by a former member of Prof. Johnston's research group and engineers from the VUW mechanical workshop was used in this research to determine static CA and RoA. The goniometer is comprised of a back lit sample stage, a display that reads the angle of the stage and a high definition camera, mounted on a smoothly rotating steel bar attached to a stepping motor, see Figure 2.2. Static water CA measurements were taken by capturing a photo of a 10 μL droplet of distilled water on the surface with the sample stage levelled. The volume of the droplet was measured in a gas-tight syringe and the droplet placed gently onto the surface from above, without the droplet free-falling at any point to minimise impact on the surface. The image was then analysed using the computer program ImageJ with a plug-in called Dropsnake to calculate the left and right CA values.^{104,105} Three droplets were analysed per sample and three calculations were performed on each droplet, with the left and right CA averaged for each calculation. These nine values were then averaged and the mean taken to represent the final value, with the standard deviation considered as the uncertainty (or 95% confidence interval, where specified). To analyse RoA, the stage was slowly and smoothly tilted. As soon as there was advancement of the TCL the tilting was stopped and the angle on the display was taken as the RoA. This measurement was taken three times and the lowest RoA measured was recorded. This RoA measurement was assigned an uncertainty of $\pm 5^\circ$ for all measurements. RoA can only be measured up to 70° , as the instrument can only rotate to this angle. Samples which showed droplet movement at less than 70° were measured and their RoA values reported. If samples did not have a measurable RoA the samples were manually tilted to approximately 90° . Samples which did not show droplet movement at less than 70° but showed droplet movement when held at 90° were assigned a RoA of 90° . Samples on which the test droplets remained pinned when tilted to greater than 90° are determined to be pinned and given no RoA value.

Uncertainties

It is important to note that there are large uncertainties associated with all CA and RoA values measured in this research. This is due to several factors. Firstly, the uncertainties associated with measurements of wool substrates are generally

Figure 2.2 Set up of goniometer: 1) Angle display. 2) Back light. 3) Sample stage. 4) High definition camera. 5) Steel bar attached to motor.

larger than those of 3D printed substrates. This is due to the inherent variation in wool as a natural product. When testing different areas of a fabric, the physical and chemical properties of the individual wool fibres can vary causing noticeable changes in measurements. As the value given for CA is an average of nine measurements, from three different areas, these variations can cause large variances and hence give a large standard deviation, which is given as the uncertainty. Secondly, in measuring the CA of a surface, the software must determine the TCL point and the line of the edge of the droplet. If either of these lines are obscured in anyway or difficult to determine, this can change the CA calculation, giving a greater or lesser value than should be calculated, which in turn alters the average CA reported and can increase the standard deviation/uncertainty. See Figure 2.3 for examples of obscured lines. In the literature, most reported CA values are measured for a droplet on a flat planar surface with only very fine surface roughness, that cannot be clearly seen without a microscope. However, in this work the surfaces produced were highly structured with variable morphologies and roughness on a scale that was clearly visible. In wool, it is common for protruding fibres to be found between the camera and the droplet, across the TCL or the outline of the droplet. This obscures the TCL or the line of the droplet and can affect the calculated value. When a fibre is obviously obscuring these lines, the image was disregarded, but often it was difficult to determine if the protruding fibre was in front of, behind or in line with, the droplet. If the fibre was behind the droplet it should not affect the CA, if it was in line with the droplet then it will affect the CA but this is a real effect and should be included in the calculations. Also, when measuring both wool and 3D printed surfaces, the TCL

or the edge of the droplet can sometimes be hard to determine due to the surface roughness. This was a major challenge in this research and a systematic approach was taken to provide meaningful data and results. The identification of trends was a very important part of data analysis, for an example of such trends, see Figure 3.3.

Figure 2.3 Left: Example of how software defines TCL and line of droplet to calculate CA. Centre: Example of protruding fibre obscuring the line of the droplet (red arrow). Right: Example of obscured TCL.

As the uncertainties on these values were sometimes large, it can be difficult to observe trends as the values differ but error bars overlap. Hence looking at one treatment on one substrate and determining its effect was difficult. It is more useful to look for trends where the same treatment is applied to different substrates or slightly different treatments are applied to the same substrate to establish trends. This approach was used and obtained data and results were evaluated and discussed accordingly.

2.4.2 Scanning Electron Microscopy

Scanning electron microscopy (SEM) was used to analyse the structure of surfaces. This analysis was performed on a high resolution JEOL-6500F field emission scanning electron microscope or a low resolution, low vacuum JEOL-JSM-6610LA scanning electron microscope. SEM imaging allowed the analysis of the arrangement of wool fibres and the measurement of fibre diameters and spacing of wool fabrics. SEM imaging also allowed for the analysis of 3D-printed surfaces, including measurement of the dimensions of 3D-printed surface structures.

For SEM analysis, non-conductive samples, such as those produced in this work, are generally coated with a layer of conductive material, commonly carbon, in order to eliminate charging on the surface under the electron beam and allow for clear imaging of the sample. However, as the surface of the samples was the focus of this research, coating of the surfaces was sometimes not viable as this would have significantly altered the surface and prevented further testing of the sample.

However, the JEOL-JSM-6610LA SEM can be operated at low vacuum. This allows more particles into the atmosphere of the examination chamber, allowing for charges to dissipate away from the sample. The pressure required to sufficiently dissipate charges depends on the conductivity of the sample, with higher conductivity requiring less pressure, hence the pressure used in low vacuum analysis was dependent on the composition of the sample being analysed, and is recorded with each image obtained. Low vacuum analysis allowed for the imaging to be completed without coating the surfaces with a conductive layer of carbon, so the surfaces were not always altered by SEM preparation. However, this low-vacuum capable instrument could not achieve magnifications necessary to analyse the micro-/nanoparticles present in some samples. These samples were analysed using the higher resolution instrument, the JEOL-6500F, after being carbon coated. The samples analysed with the JEOL-JSM-6610LA SEM were prepared simply by fixing the samples to an aluminium stub with carbon tape. The samples analysed with the JEOL-6500F SEM were prepared by fixing them onto an aluminium or brass stub with carbon tape and subsequently coating the stubs with a layer of carbon. The thickness of this carbon layer was dependent on the number of coats used, which was decided based on the substrate and its behaviour under the electron beam. As standard, samples were coated twice, resulting in a 16 nm layer of carbon, but some samples that were especially susceptible to electron beam damage were coated three times, resulting in a 24 nm layer of carbon. Both wool fibres and 3D printed polymers were found to be severely damaged by the electron beam and so a thick layer of carbon, large aperture, and low probe current were required to successfully analyse the samples. Even so, some beam damage was present in images and some samples could not be analysed at high magnification.

2.4.3 Energy Dispersive X-ray Spectroscopy

Energy dispersive X-ray spectroscopy (EDS) is commonly used to determine the elemental composition of surfaces. In this research EDS was used to analyse chemically treated surfaces. This analysis was carried out on a JEOL-6500F field emission scanning electron microscope or a JEOL-JSM-6610LA SEM, which are each fitted with EDS probes. EDS can also be performed at low vacuum on the JEOL-JSM-6610LA instrument. This provided information about the elemental composition of the surfaces, confirming the presence of certain elements after chemical treatments, such as silicon and fluorine after FAS treatment or metals after Au, Ag, Ag/AgCl, or CaCO₃ functionalisation. Samples were prepared and analysed under the same conditions as SEM imaging, detailed above. As the samples were susceptible to severe beam damage, some samples could only be analysed for short time periods before

the samples became so damaged that the software was unable to complete probe tracking and analysis was terminated. This limited the resolution and magnification possible for some EDS maps.

2.4.4 X-ray Diffraction

X-ray diffraction (XRD) measurements were used to determine the presence of crystalline silver and silver chloride in wool fabrics after Ag/AgCl treatment, to confirm the success of these treatments. XRD measurements were performed on a PANalytical X'Pert Pro MPD diffractometer with a copper X-ray source, a voltage of 45 kV and a current of 40 mA. Samples were prepared simply by attaching the fabrics to a glass slide with adhesive tape, pulled taut to keep the test surface as flat as possible. This glass slide could then be loaded onto the flat stage for analysis. Scans were performed from 20-60 °2 θ , using a step size of 0.01313° for 119.6 seconds, and a scan speed of 0.027937 °s⁻¹. Diffraction patterns obtained were compared with those in the ICDD database with either star or indexed quality, to determine the composition of crystalline components detected.

2.4.5 Infrared Spectroscopy

Infrared (IR) spectroscopy was used to analyse the chemical bonding present in polymer samples before and after functionalisation with silver. The bonding modes present in the polymer before and after functionalisation were compared to determine what changes may have occurred in the polymer chemistry to facilitate the reduction of Ag⁺ to Ag⁰. Attenuated total reflectance (ATR) Fourier-transformed IR (FTIR) spectroscopy was performed on a Bruker Tensor 27 ATR-FTIR instrument. Samples were prepared for ATR-FTIR analysis by melting some ABS polymer filament onto a glass slide using a hot plate. This melted polymer was then cooled and solidified before being analysed as the untreated ABS polymer filament sample. This sample was approximately 2 mm thick. This sample was then functionalised with silver nanoparticles as described in Section 2.3.4 above. This functionalised sample was then analysed as the silver functionalised ABS filament (ABS-Ag) sample. The window on the instrument was cleaned with acetone before and after each measurement was taken to eliminate sources of contamination. Obtained ATR spectra were then processed using the Bruker OPUS software and converted to absorbance FTIR spectra.

2.4.6 Fabric Tests

Fabrics intended for use in commercial industries are subject to industrial tests and standards, and scientific measurements such as CA and RoA values are not commonly used. As such, further testing of the wetting behaviour was conducted on some treated fabric samples to determine the performance of the treated fabrics in more commercial settings. Samples were only subjected to these further tests if their hydrophobicity was significantly increased compared to the blank samples, with respect to the CA and RoA values.

Water Absorption Testing

The propensity of wool fabrics to absorb water was tested using a water absorption test. These tests involved a wool sample on a holder on an analytical balance. The balance was tared with the sample and holder, and then a 100 μL water droplet was gently deposited on to the surface. The accurate weight of the droplet was noted and the droplet was left to sit on the surface for 5 minutes. After that time had elapsed, the sample and holder were lifted (keeping the sample flat), removed from the balance, and tilted 90° and gently shaken in order to remove residual surface water. The sample was then placed back on the balance and the weight of the water left on the sample was noted. This testing process is summarised in Figure 2.4. The weight of the water left on the sample was expressed as a percentage of the initial water weight, to represent the amount of water retained by the wool sample. Each sample was measured three times and an average of these results was reported as the measured value. The balance used had an associated error of ± 0.0005 g, and this uncertainty was propagated through calculations accordingly. The samples tested were dried at slightly elevated temperatures (approximately 50 °C) and then cooled to room temperature before each measurement. The tests were performed at room temperature using an analytical balance with an enclosed weighing platform, minimising the likelihood of any water evaporating from the surface.

Figure 2.4 Steps involved in the water absorption test method.

Chapter 3

Wool Fabrics - Increasing Macro-/micro-scale Roughness

In this chapter the research discussed concerns attempts to increase the hydrophobicity of wool fabrics by increasing the surface roughness alone, through physical modification, as opposed to chemical treatments. This was to be done using physical modifications that could be easily implemented in industry using existing machinery, so as to be introduced into commercial plants without large investments or significant changes to the plant. The 18-MEA found on the surface of the wool fibres is sufficient to induce generally hydrophobic wetting behaviour in existing commercial wool fabrics. However, when water is left on the wool surface it is sometimes absorbed into the wool and when the hydrophilic internal area of the fibres is exposed, for example at a fibre end, this can cause hydrophilic behaviour to be observed, especially with regard to pinning. If a water droplet comes in contact with an exposed hydrophilic end of a fibre then the droplet will be strongly adhered to the surface even at angles of 180° . As chemical modification was not to be implemented in this chapter, the issue of pinning was expected to prevail. In fact, as the physical modifications proposed were anticipated to break and expose more protruding fibre ends, this issue could likely be worsened. However, as the aim of this chapter was to increase the micro- and macro-scale roughness it was expected that any water droplets would effectively be held further from the true surface of the fabric, atop protruding fibres, those broken and exposed by physical modifications. Therefore, although the additional protruding fibres were likely to increase the problem of pinning, the pinned droplets should be held away from the surface preventing absorption and allowing for quick and easy removal of the water droplets from the surface by a more absorbent material, for example a towel. This would in effect create a surface that is fit for purpose as a fabric that is stain and water repellent, even though it is

potentially less hydrophobic by standard scientific measures (CA or RoA values).

Existing commercial methods of producing more stain-/water-repellent fabrics involve costly additional machinery (plasma coating) or chemical treatments. In the commercial processing of wool, there are several chemicals involved, ranging from low grade detergents to more sophisticated anti-shrink and fire retardant chemical treatments. The use of so-called “harsh” chemicals is unavoidable but it is important to minimise their use as it can diminish the marketability of the product as many consumers are attracted to natural fibres over synthetic fibres, due to the generally negative connotations of chemically produced synthetics. Therefore if the natural fibre is subjected to numerous chemicals in processing, the same negative connotations could be applied to the natural fibre product. Hence, the use of chemical treatments was avoided, and physical treatments using only water and detergents were investigated.

This chapter discusses both preliminary work to design and establish the general effects of physical treatments, followed by more thorough investigations into the specific effects of each treatment on different fabrics. The latter part of this work was completed in collaboration with an intern student working in the research group, Yannick Ramser. The initial investigations were performed and the majority of the results were gathered before Yannick carried out some further investigations to provide additional data on the effects of the physical treatments, designed in preliminary investigations, with the supervision and guidance of the author. Yannick’s data are also presented here, with independent analysis and discussion by the author.

3.1 Preparation

For the preliminary work, five wool fabrics supplied by Camira Ltd., UK, were used. These fabrics varied in stage of manufacture and fibre type, as detailed in Table 3.1. All fabrics had been subjected to some degree of felting in the finishing process. These fabrics were used for the preliminary investigations as it was important to include fabrics at different stages of manufacture. As the aim was to design a treatment to be applied in commercial finishing processes, it was important to determine if the physical treatments had different effects before and after commercial finishing, to establish if the treatments needed to be used at a certain point in the finishing process.

Table 3.1 Specifications of fabrics supplied by Camira Ltd., UK.

Fabric Name	Manufacturing Stage		Fibre Class
	<i>Dyed</i>	<i>Finished</i>	
Brown	Brown	Yes	Fine
Orange	Orange	Yes	Coarse
Chequered	Multi	Yes	Coarse
Blue	Blue	No	Coarse
Grey	Grey	No	Coarse

3.1.1 Physical Modifications

All samples were subjected to physical treatments in order to increase their surface roughness without the use of additional chemicals, not already used in commercial processing. These physical treatments included hand-felting and trimming. The only chemicals used in these processes were water and a mild detergent (see Chapter 2).

Hand Felting

Felting was investigated as a way to increase the surface roughness by increasing the amount of protruding fibres on the surface, as demonstrated in Figure 3.1. It was anticipated that this could potentially cause the suspension of water droplets to be positioned away from the true fabric surface and prevent absorption of the water into the fabric. The hand-felting procedure was carried out as described in Section 2.2.2. Two samples of each fabric were produced, by applying one or two successive hand-felting processes to each fabric. In total, ten samples were produced. It was noted that the felting often resulted in shrinkage of the fabric, this is a known effect of felting and was expected, but the degree of shrinkage varied between samples. The variation in degree of shrinkage is likely due to a number of factors including, nature of the fibres, degree of machine felting during processing, and nature of treatments used in commercial finishing. It has been shown that the fibre diameter and crimp has an effect on shrinkage due to felting; resistance to felting shrinkage has been shown to increase as fibre diameter and crimp increase.¹⁰⁶ In the manufacturing process the samples had all been previously machine felted but not necessarily to the same degree, as the degree of felting is determined by the application and desired texture of the final fabric; as felting strengthens the fabric by making it more dense and resistant to abrasive wear but roughens the surface producing a less desirable texture to the touch. In the final finishing stages of manufacturing, some fabrics also undergo an anti-shrink treatment, helping to prevent further felting in laundering processes. A summary of shrinkages can be found in Table 3.2, below.

Figure 3.1 Schematic of surface fibres before and after felting, showing more protruding fibres and increased height after felting.

Table 3.2 Amount of shrinkage measured in each sample after one hand-felting process.

Sample	Initial Width/Length	Final Width/Length	Area Loss
Brown	70/72 mm	68/71 mm	4%
Orange	40/55 mm	40/52 mm	5%
Chequered	70/70 mm	65/66 mm	12%
Blue	55/55 mm	53/54 mm	5%
Grey	70/52 mm	70/50 mm	4%

It was observed that the chequered fabric was the most affected by the felting process in terms of shrinkage, and the brown and grey fabrics were the least affected. This is likely due to a combination of factors, including fibre diameter, degree of previous commercial felting, and presence of anti-shrink treatment.

Trimming

Trimming was investigated as a subsequent step after hand-felting. Hand-felting tends to roughen the surface not only on the micro-scale but on the macro-scale. This makes the fabric rougher to the touch. The soft texture of wool fibres is one of its many desirable properties and so fabrics with increased roughness and a rougher feel cannot be used in some applications, particularly those where the fabric is in contact with the skin. Hence, trimming was used to remove some of the protruding fibres after hand-felting. A schematic of the effects on surface fibres is given in Figure 3.2. It was anticipated that cutting the fibres would increase the chemical

hydrophilicity of the surface due to the increase in exposed internal area of the fibres. However, the process was used to investigate if the breakage of fibres and smaller scale roughening of the surface due to the hand-felting would leave a surface that was less rough than the felted surface but more rough than the blank surface. While this would achieve a less hydrophobic sample than just hand-felting, it would represent a process that could be applied to a wider range of commercial fabrics for a range of applications. Smaller samples were cut from the felted samples that had been subjected to two processes of hand-felting for each fabric type. These samples were then further modified with one trimming process. As expected, the trimming process removed a number of short fluffy fibre sections from the wool fabric surface, which collected on the razor. The resulting surface was softer to the touch and thinner than the surface before trimming, due to the loss of protruding fibres.

Figure 3.2 Schematic of surface fibres before physical treatments and after felting or felting and trimming, showing exposed hydrophilic ends in red. Felted fabric shows more roughness with more protruding fibres and more exposed ends than the blank fabric, the felted and trimmed fabric shows less large scale roughness and more exposed ends than either blank or felted fabrics.

Chemical Treatment

In order to determine how useful the physical modifications could be in place of chemical treatments, blank fabric samples were also treated with Dynasylan FAS, for comparison purposes. This treatment was performed using the standard procedure as outlined in Section 2.2.1 to produce a functionalised fabric of 2 wt% FAS.

3.2 Imaging

Each fabric was imaged on the goniometer before treatments (blank), after two hand-felting processes and after two hand-felting processes and trimming. These images are shown in Figure 3.3. It can be clearly seen that the felting increased the macro-scale roughness of the surface by increasing the amount of protruding fibres; the samples that had been subjected to two hand-felting processes were found to appear the most “fluffy” of the imaged samples for every fabric type. It was also seen that the trimming significantly reduced this macro-scale roughness compared to the felted samples with significantly less protruding fibres seen on the surface of these samples. This is especially clear in the Chequered sample (C in Figure 3.3). The blank chequered sample is somewhat rough before treatment, but the roughness is significantly increased after felting with the protruding fibres obscuring the droplet on the surface. This is in contrast to the trimmed chequered sample which has less protruding fibres and less roughness than the felted sample, but also less than the blank sample. For other fabrics that are less rough before treatment, the difference between the blank and trimmed samples is less obvious, but the increase in roughness of the felted samples is clear for each fabric. However, the amount of protruding fibres in the felted samples were generally not enough to support the droplet away from the fabric surface. The exception to this was the blue fabric. In the sample of blue fabric that had been subjected to two hand-felting processes, test droplets were sometimes suspended atop protruding fibres and away from the true surface of the fabric. An occurrence of this was photographed and shown in Figure 3.4. The protruding fibres form a support structure for the droplet and can be seen holding the droplet up, away from the surface of the fabric. This would prevent the absorption of the droplet into the wool fabric and was an encouraging result. However this behaviour was only seen to occur in one of three test droplets applied to the surface, likely due to the non-uniformity of the surface, and was not seen in any other fabric samples.

Figure 3.3 Goniometer images showing height and amount of protruding fibres on blank fabrics, fabrics after two hand-felting processes, and fabrics after two hand-felting processes and trimming. A: Brown, B: Orange, C: Chequered, D: Blue, E: Grey, fabrics respectively. All droplets 10 μ L.

Figure 3.4 Goniometer image showing a test droplet suspended atop protruding fibres on a sample of blue fabric after two hand-felting processes.

3.3 CA and RoA

The CA and RoA values for these samples were measured along with values for blank samples. A summary of all values can be found in Figure 3.5. RoA values were attempted to be measured for all samples, but in all cases it was found that the test droplets were pinned to the surfaces both before and after treatments.

Figure 3.5 Graph showing CA of all fabrics before and after physical modifications and after chemical treatment for comparison.

It can be seen in Figure 3.5 that hand-felting generally increased the CA of the fabrics compared to the blanks, but there was no consistent significant difference

between performing one or two felting processes. Conversely, the trimming process was found to significantly lower this CA to about the same CA as the blank fabrics. This was expected as the surface roughness was decreased, while the chemical hydrophobicity was also decreased, in exposing more internal area of the cut fibres. The average felted CA of each fabric sample was found to be approximately the same as the CA for FAS functionalised fabrics. This is a positive result, as it shows the felting process had an effect on the fabric in making it more hydrophobic, without the use of any new chemicals. Fabrics that had been commercially finished did not consistently perform differently to those which had not been finished and hence finishing was not found to be a significant influence on the effects of the treatments, and so these treatments could be implemented at any step of the finishing process.

The effects of felting and trimming on the fabrics were quite varied between fabrics and no strict trends were observed for every sample tested. This is due to several factors, including the natural variation in the wool, the differences between the wool fabrics through different processing, and variation in potential for felting. The felting process was seen to increase the CA of fabrics, but was also found to affect the fabrics differently, as demonstrated with different rates of shrinkage, and this indicates that although the same felting process was used for each fabric, the process caused different changes in the different fabrics.

3.4 Further Investigations

As the results of the initial investigations indicated that felting generally increased the CA of wool fabrics, but were generally inconclusive with respect to a consistent and uniform increase across different fabrics, several more thorough investigations were performed. These investigations were designed and supervised by the author, and samples were prepared and data were collected by Yannick Ramser. In these investigations the fabrics used were different to those used in the initial investigations. These fabrics were chosen and supplied by Camira Ltd., UK. These fabrics were all popular, finished, commercial fabrics, that are commonly used in upholstery of seating and panelling (for acoustic applications). As the preliminary investigations found no significant difference between finished and unfinished fabrics with respect to the effect of the physical treatments, only finished fabrics were investigated in these further experiments, to eliminate some variation between the fabrics. Here, three fabrics were investigated to determine if the physical treatments had uniform effects on different fabrics, as would be necessary for a commercial treatment. The fabrics are summarised in Table 3.3. Two of the fabrics used were wool

blends, containing 5% nylon, while the other was 100% wool. Wool blends are very commonly used in commercial fabrics and so these fabrics were included to determine the effect of the treatments on both wool and wool blend fabrics, to represent commonly used wool fabrics in industry.

Table 3.3 Finished commercial fabrics supplied by Camira Ltd., UK, used in further investigations by Yannick Ramser.

Fabric Name	Composition	Weight	Application
Synergy	95% wool 5% nylon	400 g m ⁻²	Seating
Blazer Lite	100% wool Non-metallic dyestuffs	355 g m ⁻²	Panelling
Landscape	95% wool 5% nylon Non-metallic dyestuffs	400 g m ⁻²	Seating

3.4.1 Preparation

These samples were subjected to the same physical and chemical treatments that were used in the preliminary investigations: hand-felting, trimming and FAS functionalisation, as described in Section 2.2. Where the initial samples investigated were felted only one or two times, in these investigations, each fabric was felted up to five times, and the subsequent trimming and FAS treatments were performed on samples of each fabric after each stage of felting, to determine the effect of further felting, to find the optimal number of felting processes and to determine the effect of the trimming. In total this produced 18 samples per fabric, as summarised in Table 3.4.

Table 3.4 Samples produced by Yannick Ramser for each of three fabrics used.

Felted x0	Felted x0 + Trim	Felted x0 + Trim + FAS
Felted x1	Felted x1 + Trim	Felted x1 + Trim + FAS
Felted x2	Felted x2 + Trim	Felted x2 + Trim + FAS
Felted x3	Felted x3 + Trim	Felted x3 + Trim + FAS
Felted x4	Felted x4 + Trim	Felted x4 + Trim + FAS
Felted x5	Felted x5 + Trim	Felted x5 + Trim + FAS

3.4.2 CA Measurements

The CA of each sample was measured, and these values are summarised in Figure 3.6. The data point for the Synergy fabric sample that was felted three times, trimmed

and treated with FAS is missing from this graph as the sample was lost. The CA values of fabrics treated with FAS with no physical modifications (felting or trimming) were also measured for comparison, and are presented in Table 3.5. RoA values were not measured for these samples. Although when researching hydrophobicity and superhydrophobicity it is very important to report at least two measures of hydrophobicity (as discussed in Section 1.2.1), as these samples were being tested for a specific aspect of hydrophobicity and not their general behaviour, it was determined that the CA values would be sufficient. As initial investigations showed significant pinning in all samples, it was determined that the RoA values did not offer any insight into the wetting behaviour of the surfaces and the CA values were sufficient to compare the behaviour of different samples, as this measurement was seen to adequately describe the behaviour of previously investigated surfaces (Section 3.3).

Table 3.5 CA values of blank fabric samples and those samples treated with FAS with no physical modifications.

Fabric	Blank CA	FAS CA
Synergy	135°	147°
Blazer Lite	130°	158°
Landscape	135°	155°

Firstly, we can consider the effect of additional felting processes. It was found that the untreated fabrics that had not been felted had the lowest CA, when compared to fabrics that had been felted. This supports the earlier conclusion that felting increases the CA of wool fabrics. However, with increased number of felting processes, there is no consistent trend, and CA values can increase or decrease between successive felting processes, but remain higher than the CA value of the fabric before felting. When a fabric is manufactured it undergoes some degree of felting, and this is followed by some smoothing that occurs in the finishing processes, through physical modifications such as pressing or chemical modifications such as application of lubricants or resins in finishing treatments. These results indicate that one hand-felting process is sufficient to roughen the smooth finished fabric to increase the CA, and further felting of the rough fabric does not serve to significantly or uniformly increase the roughness or CA further.

Analysis of this data shows there is no evidence to suggest a higher degree of felting results in a higher CA. As sufficient roughness can be achieved through only minimal felting, this shortens the time and mechanical input required of a potential commercial treatment developed, and so is a positive result.

As felting increases the roughness of the surface on a macro-scale and diminishes the softness of the fabrics to the touch, trimming was investigated as a method

Figure 3.6 Graphs showing CA values of all samples produced of each fabric, with black dashed lines representing the CA measured for each untreated fabric.

to improve the hand-feel of felted fabrics. It is clear to see the effect of trimming on the CA values of the fabrics. In each individual graph in Figure 3.6, it can be seen that the columns representing samples that have been felted and trimmed are consistently lower than the lines representing the CA of the untreated fabrics. This shows that the trimming had a negative effect on the CA of the wool fabrics, increasing the wetting of each fabric at every stage of felting. The FAS treatment of fabrics after trimming served to show the effect of the trimming, independent of the increased chemical hydrophilicity due to the increased number of exposed fibre ends, by rendering the surface chemically hydrophobic. The trimmed and FAS treated samples had higher CA values than the untreated fabrics before felting, and generally had lower CA values than comparable felted samples before trimming and FAS treatment. This indicates that the roughness of the felted samples before trimming was very high and the trimming had significantly reduced this roughness. While the samples that were felted, trimmed and treated with FAS were found to have higher CA values than the untreated blank samples of the same fabric, the CA values of the treated samples were lower than the blank fabric samples treated with FAS (Table 3.5). As the FAS is highly chemically hydrophobic, this treatment significantly increases the CA of surfaces, as seen when comparing the felted and trimmed samples to those which were felted, trimmed and treated with FAS. Hence, although the felted, trimmed and FAS treated samples have higher CA values than the comparable blank untreated fabrics, this is due to the effect of the FAS, not due to the physical modifications. In comparing samples that have been felted, trimmed and treated with FAS to comparable fabric samples that have been treated with FAS but not subjected to any physical modifications we can see the effect of the physical modifications on the surface roughness. Hence, while it was proposed that the trimming could have potentially only eliminated the overtly protruding fibres and retained a surface with some increase in roughness from the felting, this was not observed. The CA values of the physically modified samples, compared to those without the physical modifications, show that the physically modified samples were much less hydrophobic. As all samples were treated with FAS and hence had comparable surface chemistry, this difference in CA and hydrophobicity is attributed to the difference in surface roughness.

3.5 Conclusions

Trimming was found to decrease the CA of felted samples, and analysis of FAS treated samples showed that the trimming process served to reduce the surface roughness to below the level of the blank untreated samples. Hence it was con-

cluded that trimming was not a useful step to include in a process to increase the hydrophobicity of wool fabrics. Commercial treatments need to be reliable and consistent, producing the same desired results on every fabric, every time. Although felting was found to increase the hydrophobicity of the fabrics, the effects were inconsistent between different fabrics and increased the hydrophobicity of some fabrics more than others. The process of felting also shrinks fabrics to different degrees, and diminishes the desired soft texture of wool fabrics. While in most applications the texture of the wool fabric is important, it is less important in other applications where the fabric does not come in contact with skin, such as panel upholstery for acoustic applications. Hence, while the use of felting to increase the hydrophobicity of wool fabrics may be useful in some fabrics for some applications, it is not viable as a universal commercial treatment for all wool fabrics.

Chapter 4

Wool Fabrics - Increasing Nanoscale Roughness

The research discussed in this chapter concerns the development of a chemical treatment to be applied to commercial fabrics during processing to render the fabrics hydrophobic and water-repellent. This was investigated through the functionalisation of wool fabrics with nanoparticles and microparticles in order to increase the surface roughness, to increase the overall hydrophobicity. These experiments were performed on two wool fabrics in order to determine if the devised treatments were suitable for general wool processing. The wool fabrics used in this chapter were undyed merino fabrics that were each produced from different merino fibres. The fabrics were both worsted, but one was knitted, while the other was woven. The knitted and woven fabrics had different wetting behaviours before treatment, with the untreated woven fabric being more hydrophobic than the untreated knitted fabric. This was easily demonstrated, as the untreated knitted fabric was found to absorb test water droplets after a few minutes, whereas the woven fabric did not (see Section 4.3.3). Measurements of CA and RoA were taken for droplets before this absorption occurred, hence these measurements of the untreated knitted sample overstate the hydrophobicity of the fabric as they do not account for this absorption, which is generally deemed to be highly hydrophilic behaviour. These differences in wettability could be due to any number of differences between the fabric, potentially including the different wool fibre arrangements, arising from the different fabric production methods (knitting or weaving).

As discussed in Section 1.2.5, hierarchical surface roughness is of great benefit in creating highly hydrophobic surfaces and hence nanoparticles were desirable for these experiments as this would introduce nano-scale roughness to the micro-scale

roughness already present in the fabric due to the arrangement of the wool fibres themselves which were $\leq 25 \mu\text{m}$ in diameter. However, strictly nano-sized particles were not necessarily required, small micro-sized particles could suffice. The added particles simply need to be of a smaller size than the fibre dimensions to induce hierarchical roughness.

These treatments were being investigated for the application of producing water and stain-repellent fabrics. The final treated surfaces did not need to be strictly super-hydrophobic to be fit for purpose as commercial stain-repellent fabrics, but needed to effectively repel water and use synthetic methods that are easily implemented into commercial processing plants. CA and RoA values were measured as indicators of the wetting behaviour of treated fabrics, but other industry related tests were also performed and used to determine whether or not the treatments were suitable for the intended commercial application.

4.1 Gold Nanofunctionalisation

The first treatment investigated involved functionalising the wool fibres with gold nanoparticles. Gold nanoparticles were chosen for the initial treatment as the researchers have prior experience in the functionalisation of wool fibres with gold nanoparticles, and as such the synthesis used in the treatment was relatively straightforward.¹⁰⁷ The functionalisation method used in this work was developed by Dr Kerstin Lucas (née Burrige), Dr Thomas Nilsson and Prof. Jim Johnston.^{99,100} The progress of gold nanoparticle uptake is easily observed due to the strongly coloured nature of gold nanoparticles. Gold nanoparticles are surface plasmon resonance (SPR) active.¹⁰⁸ SPR is the resonance oscillation of conduction band electrons caused by incident electromagnetic radiation. In gold nanoparticles, this causes a sharp absorption in the visible region of the spectrum, causing colloids to be intensely coloured.^{109,110} The prepared gold nanoparticle colloid was ruby red and over the course of the functionalisation the colour of the colloid faded and the fabrics in turn became coloured. Metallic gold surfaces have been reported as hydrophilic with CA values of $60 - 65^\circ$;¹¹¹ hence the gold nanoparticle functionalisation itself was expected to lead to a net decrease in the chemical hydrophobicity of the fabrics, with lower CA and higher RoA, and so a subsequent FAS treatment was also used in this investigation, to render the surface chemically hydrophobic.

Functionalisation of the fabrics with gold nanoparticles was achieved after the samples were left submerged in a gold colloid to allow uptake of the gold nanoparticles

by the wool fibres. It was observed that almost all of the colour from the gold colloid was taken up by the wool fabrics but the remaining solutions were not quite colourless. However, as seen in Figure 4.1, the samples were strongly coloured and so sufficient uptake was deemed to have taken place. After functionalisation with gold nanoparticles, a section of each of the treated samples was also functionalised with FAS, using the standard procedure described in Section 2.2.1, to achieve a functionalised fabric with 2 wt% FAS. Samples of untreated fabrics were also functionalised with 2 wt% FAS using the same method, for comparison.

Figure 4.1 Photographs of knitted and woven wool fabrics functionalised with gold nanoparticles showing pink-purple colouration, compared to white untreated fabrics (left side of each respective image).

4.1.1 SEM and EDS Characterisation

SEM and EDS analysis was carried out on fibres from both knitted and woven fabrics functionalised with gold nanoparticles, this analysis was performed using the higher resolution, high vacuum SEM. Due to the wool being prone to beam damage, the samples were coated with carbon three times and a low probe current was used. This reduced the beam damage significantly, but did not eliminate the problem entirely and so the analysis was still limited in achievable magnification. SEM imaging was used to characterise individual wool fibres from the fabrics functionalised with gold nanoparticles. Although the characteristic colouration was observed in the functionalised fabrics due to the SPR of gold nanoparticles, the nature of the uptake of gold nanoparticles and their presence on the surface was investigated. As gold has high atomic mass, backscatter mode was used to easily identify areas that may contain gold, and EDS mapping was then used to confirm the presence of gold in these areas.

SEM imaging showed gold nanoparticles distributed across the surface of the wool fibres in both knitted and woven samples. The distribution of gold nanoparticles was similar between the two samples, with fibres from the woven sample observed to have slightly more coverage than those of the knitted sample (see Figure 4.2). It was

Figure 4.2 Backscatter SEM images of knitted and woven wool fabrics (left and right, respectively) at lower (top) and higher (middle) magnification, with gold EDS maps of higher magnification view (bottom).

observed that the gold nanoparticles on the fibres of the knitted fabric were more associated with the cuticle edges, while the gold nanoparticles on the fibres of the woven fabric were distributed more evenly across the cuticle surface. This difference in distribution of the gold nanoparticles on fibres is likely due to inherent differences in the fabrics themselves. However, it cannot be said whether this variation is due to the difference in the fibre arrangements (knitted/woven) or other differing factors between the fabrics, such as different wool fibres. For example, fibres with different surface energies would have different affinity for the gold nanoparticles, this difference in surface energy could be due to more or less surface area, dependent on the diameter, cuticle size/roughness and porosity of the fibres used. It can also be seen that higher concentrations of these particles were found along the cuticle edges, in samples from both fabrics. This is a common occurrence in gold nanoparticle-wool composites, due to the higher surface energy at these edges.⁹⁹

4.1.2 CA and RoA Measurements

The CA and RoA values for samples functionalised with gold nanoparticles alone and with gold nanoparticles and FAS were measured along with values for untreated fabric samples and untreated samples functionalised with FAS. A summary of all values can be found in Figure 4.3.

Figure 4.3 Graph showing static water contact angles of knitted and woven wool fabrics functionalised with gold nanoparticles (Au NPs) and/or FAS compared to untreated fabric samples.

As expected, it was found that the FAS treatment increased the CA of the gold nanoparticle functionalised fabrics, due to the increased chemical hydrophobicity of the FAS treated surface. The highest CA measured for the knitted fabric was the sample treated with both gold nanoparticles and FAS, for the woven fabric the gold nanoparticle and FAS sample had the same measured CA as the sample treated with FAS alone. As the FAS treated samples with and without gold nanoparticles had the same chemical hydrophobicity due to the same surface chemistry, the difference in CA of the knitted samples must be due to a difference in surface roughness. Hence, the gold nanoparticles were found to have successfully increased the surface roughness of the knitted fabric. As the CA values measured for the two woven samples treated with FAS were the same, it was determined that the gold nanoparticles did not have a sufficiently great effect on the surface roughness of the fibres to cause a measurable difference on the CA value of the woven fabric. The gold nanoparticle functionalisation alone was found to have different effects on each of the fabrics. In the woven sample, it was seen that the CA of the gold nanoparticle functionalised fabric was lower than that of the untreated fabric. As explained above, this was the expected effect due to hydrophilicity of gold. However, in the knitted sample, the measured CA of the gold nanoparticle functionalised fabric was found to be higher than the untreated fabric sample. This indicates that the surface was not rendered significantly more hydrophilic by the gold nanoparticles. SEM analysis revealed a more universal coverage of gold nanoparticles across the surface of woven wool fibres, and a more scarce coverage over the knitted wool fibres. Hence, it is proposed that the chemical hydrophobicity of the woven fibre surface has been altered much more than in the knitted fibres, as more of the initial hydrophobic surface has been covered with the hydrophilic gold nanoparticles. Therefore, while the CA of the woven sample is decreased due to decreased chemical hydrophobicity, the chemical hydrophobicity of the knitted sample is not reduced to the same degree, and so the increase in surface roughness is sufficient to increase the CA of the sample, even though the surface is slightly less chemically hydrophobic.

The RoA measurements of these samples are summarised in Table 4.1. As seen in the CA measurement results, the fabrics that were functionalised with both gold nanoparticles and FAS were found to have the most hydrophobic behaviour for both fabric types. However, as with the CA measurements, it was found that the gold nanoparticle treatment alone had different effects on the different fabrics. In the woven fabric, the gold nanoparticle treatment was found to induce an increase in RoA compared to the untreated fabric, so much so that the water droplets were pinned on the treated fabric, even at angles $\geq 90^\circ$. This result reflects the same effect seen in the CA measurements. It is proposed that this is due to the exposed chemically hydrophilic internal areas of the wool fibres and added chemical hydrophilicity

of the extensive coverage of the hydrophobic fibre exterior with hydrophilic gold nanoparticles. Conversely, in the knitted fabric, the gold nanoparticle treatment induced a decrease in RoA measurement compared to the untreated fabric sample, again resulting in a similar effect seen in the CA measurements. It is proposed that in the case of the knitted fabric, the coverage of gold nanoparticles on the wool fibres is more scarce, inducing a less significant effect on the surface chemistry of the fibres, but dramatically increasing the surface roughness, causing a net increase in hydrophobicity and a lower RoA measurement. This difference in nanoparticle coverage is also reflected in the RoA measurements for the two fabric types functionalised with both gold nanoparticles and FAS. The knitted fabric treated with both gold nanoparticles and FAS was found to have a higher RoA than the similarly treated woven fabric; this is due to the difference in nanoparticle coverage of the fibres, where without the FAS treatment the knitted fabric showed more hydrophobic behaviour due to the higher chemical hydrophobicity with still greatly increased surface roughness. However, when the gold nanoparticle treatment is used with the FAS we can see that the increase in surface roughness is even greater in the woven fabric due to the more extensive coverage of nanoparticles, leading to a lower RoA when the surface is rendered chemically hydrophobic.

Table 4.1 RoA measurements of untreated knitted and woven wool fabrics and fabrics functionalised with gold nanoparticles (Au NPs) and/or FAS. (Pinned denotes that the droplet was pinned on the surface, even at angles $\geq 90^\circ$).

Fabric	Untreated	Au NPs	FAS	Au NPs + FAS
Knitted	70°	25°	50°	25°
Woven	60°	Pinned	50°	15°

The gold nanoparticle functionalisation was found to be successful in increasing the surface roughness of both fabric types investigated, and was found to successfully increase the hydrophobic nature of the fabrics with respect to CA and particularly RoA measurements when used in conjunction with the additional FAS treatment. The treatment was also found to successfully increase the hydrophobicity of the knitted fabric without the need for the additional FAS treatment. However, as the woven fabric was found to be less hydrophobic after treatment with the gold nanoparticles alone, in a treatment designed for commercial fabrics the additional FAS treatment would be required to ensure the desired result is achieved. The requirement of this secondary FAS treatment and the use of gold, making this a high cost treatment, meant it did not show promise for commercial use; and so no further application focussed tests were performed. This investigation showed the importance of investigating processes on different wool samples, as different results were achieved with the different fabrics, and also showed the benefit of adding nanoparticles to wool to increase surface roughness for increased hydrophobicity and this concept was built upon in further investigations.

4.2 Ag/AgCl Functionalisation

The functionalisation of wool fabrics with gold nanoparticles and FAS was successful in increasing the surface roughness and hence hydrophobicity of the fabrics. However, gold is an expensive material, which offers no additional functionality to the product, and rendered one test fabric more chemically hydrophilic requiring a subsequent FAS treatment. As such, other materials were investigated in order to develop a process that could increase the surface roughness and hydrophobicity of the wool fabrics, without the need for an additional FAS treatment.

The functionalisation of polymers with Ag/AgCl is another area of expertise within the research group. Ag/AgCl particles have been shown to be antimicrobial and hence Ag/AgCl functionalisation provides polymers with antimicrobial activity.¹⁰¹ A facile Ag/AgCl functionalisation method was previously developed by Dr Eldon Tate and Prof. Jim Johnston and was the basis for the development of the synthetic method used in this work.¹⁰¹ However, due to the complexity of the natural polymer, the method developed by Tate and Johnston was significantly, iteratively altered in order to produce a successful, uniform functionalisation method for the novel substrate of wool fabrics, as discussed in Section 2.2.1. Ag/AgCl particles produced using this method are not strictly nanoparticles, but rather microparticles of AgCl with nanodomains of silver. Due to the nature of the synthesis, whereby AgCl is formed in the pores of the polymer, followed by partial photo-reduction to silver, the size of the AgCl particles is controlled by the size of the pores. In wool, these pores can be quite large. Even so, the size of the resulting AgCl particles would be smaller than the size of the wool fibres and the nanodomains of Ag upon these particles add a degree of nanoroughness to the particles themselves. The Ag/AgCl particles were formed *in-situ*, inside the pores of the wool fibres whereas the gold nanoparticles were synthesised *ex-situ* and bound to the surface, hence it was expected that a greater concentration of Ag/AgCl would be needed to affect the surface roughness of the fibres.

Washed samples of each fabric were soaked in solutions of Ag⁺, equivalent to 5 wt% silver, followed by soaking in dilute solutions of HCl, in ambient light. Like gold, silver nanoparticles are SPR active, so although the wool fabrics and AgCl are white, silver nanoparticles (nanodomains) are strongly coloured and so progress of the functionalisation reaction was easily observed as the AgCl was partially photo-reduced to silver nanodomains. After 16 hours in the chloride solutions, the samples had changed colour from white to pale purple. After an additional 8 hours in the daylight, the samples had changed to a darker brownish purple, as seen in Figure 4.4. After functionalisation with Ag/AgCl, a section of each functionalised sample was

also treated with FAS, using the standard procedure described in Section 2.2.1, to achieve a functionalised fabric with 2 wt% FAS. Samples of untreated fabrics were also functionalised with 2 wt% FAS using the same method.

Figure 4.4 Photographs of knitted and woven wool fabrics functionalised with Ag/AgCl, showing brownish purple colouration compared to white untreated samples of the same fabrics (right side of each respective image).

4.2.1 SEM and EDS Characterisation

SEM and EDS analysis was carried out on both knitted and woven fabrics functionalised with Ag/AgCl, this analysis was performed using the higher resolution, high vacuum SEM. Due to the wool being prone to beam damage, the samples were coated three times and a low probe current was used. This reduced the beam damage significantly, but did not eliminate this problem entirely, and so the analysis was still limited in achievable magnification. Although the characteristic colour of Ag/AgCl was observed in the functionalised fabrics, the elemental composition of particles was investigated with EDS. As silver has high atomic mass, backscatter mode was used to easily identify areas that may contain silver.

Firstly, fibres from the knitted sample were examined. Representative images and maps are presented in Figure 4.5. It was found that the wool fibres were successfully functionalised with Ag/AgCl as confirmed by EDS analysis. The EDS map of silver showed high concentrations in areas that appeared bright in backscatter SEM and although the EDS map of chlorine showed the presence of chlorine (chloride ions) across the whole fibre, the concentration was found to be slightly higher (brighter areas on the map) where the silver was also present. The chloride was added to the sample in excess in conjunction with a wetting agent so it is not surprising that the EDS map showed that the chloride had been absorbed and retained throughout the

fibres. The Ag/AgCl particles themselves were seen to be evenly distributed across the surface of the wool fibres. However, no visible increase of the surface roughness was observed. The particles were found to be quite small ($< 0.5 \mu\text{m}$ diameter) and were not seen to protrude from the fibre surface. It may be that the particles were sitting just below the fibre surface, in the pores of the wool fibres and were not big enough to visibly protrude from the surface to observably increase the surface roughness at the magnification used.

Figure 4.5 SEM images (top left: SEI, top right: backscatter) and EDS maps of silver (bottom left) and chlorine (bottom right) of a knitted fabric sample functionalised with Ag/AgCl.

Fibres from the woven sample was also examined and representative images and maps are presented in Figure 4.6. It was again found that the fibres were successfully functionalised with Ag/AgCl as confirmed by EDS analysis. The EDS maps of the woven sample showed, even more clearly than in the knitted sample, the presence of silver in the same areas as higher concentrations of chloride, indicating not just silver particle formation, but Ag/AgCl formation. Again, the distribution of particles was found to differ between the two fabrics investigated. The Ag/AgCl particles in the woven sample were found to be bigger (some up to $1 \mu\text{m}$ diameter) and more numerous than those in the knitted sample, and observably increased the surface roughness. These larger particles were seen to be clearly sitting upon the surface of the fibres.

Figure 4.6 SEM images (top left: SEI, top right: backscatter) and EDS maps of silver (bottom left) and chlorine (bottom right) of a woven fabric sample functionalised with Ag/AgCl.

4.2.2 XRD Analysis

The presence of Ag/AgCl was indicated by the characteristic colour change observed in the samples, as well as EDS analysis suggesting that areas with high concentrations of silver were correlated to areas with high concentrations of chloride. However, the presence of crystalline silver chloride was not confirmed with either of these methods. While the characteristic colour change observed was indicative of Ag/AgCl, and hence indicative of silver nanodomains/nanoparticles, SEM and EDS analyses were unable to detect these silver particles. As such, XRD analysis was performed to confirm the presence of both silver chloride particles and silver nanoparticles in the treated samples. The XRD patterns obtained from these samples are shown in Figure 4.7.

The XRD patterns for both fabrics show a large peak at $25.6^{\circ}2\theta$. This is attributed to naturally occurring keratin in the wool fibres. The intensity of this peak varies between fabrics due to the different wool types used in the manufacture

Figure 4.7 XRD patterns of knitted and woven fabric samples functionalised with Ag/AgCl overlaid with characteristic peaks seen for Ag and AgCl.

of these fabrics, containing different concentrations of crystalline keratin. Hence, it was not appropriate to normalise the patterns to this peak and no information could be obtained based on the intensities of other peaks relative to the intensity of these keratin peaks. All five characteristic peaks for silver chloride, in the range measured, were found in the XRD patterns, confirming the presence of silver chloride in the samples. The crystalline silver in the sample was at relatively low concentrations and so it was unlikely to show a strong signal in XRD analysis. However, a small peak was found in both XRD patterns corresponding to the 111 peak of the characteristic silver pattern, indicating the presence of crystalline silver particles in the samples. As both silver and silver chloride were found in the XRD patterns of treated fabrics, in conjunction with SEM/EDS data and the observation of the characteristic colour of Ag/AgCl the presence and successful synthesis of Ag/AgCl particles was confirmed in both samples.

4.2.3 CA and RoA Measurements

The CA and RoA values for fabrics functionalised with Ag/AgCl and with Ag/AgCl and FAS were measured along with values for untreated fabrics and untreated fabrics functionalised with FAS. A summary of all values can be found in Figure 4.8.

Figure 4.8 Graph showing static water contact angles of knitted and woven wool fabrics functionalised with Ag/AgCl and/or FAS compared to untreated fabrics.

It can be seen that the Ag/AgCl treatment had different effects on the different fabrics. Again, this is likely due to inherent differences between the wool fibres

themselves, and also the differences in the fibre arrangements in the knitted and woven fabrics. In the knitted fabric, although there was no difference in CA measured between the untreated sample and those treated with either Ag/AgCl or FAS, the untreated sample was found to absorb test water droplets, and this absorption was not observed for either treated sample. This indicates that while the CA was unchanged after these treatments, the hydrophobicity was increased with respect to other wetting behaviours. This is supported by the increase in CA measured after treatment with both Ag/AgCl and FAS, suggesting that the surface of the sample has been altered by these treatments and the surface roughness and chemical hydrophobicity have been increased. The untreated woven fabric was more hydrophobic than the untreated knitted fabric, and showed slightly different results after treatment with Ag/AgCl and/or FAS. The Ag/AgCl treatment on the woven fabric without FAS caused a large increase in the CA compared to the untreated fabric (approximately 10°), and at 150° it was also found to be greater than the CA measured for either the FAS treated sample or the sample treated with both Ag/AgCl and FAS. SEM analysis showed that the wool fibres in the woven fabric treated with Ag/AgCl were functionalised with a great number of quite large particles that were clearly protruding from the surface. This appears to have greatly increased the surface roughness and so, while some additional chemical hydrophilicity was introduced to the surface, large areas of the chemically hydrophobic exterior area of the wool fibres remained exposed. Hence, it is proposed that while the surface chemistry was rendered slightly less hydrophobic, the large increase in surface roughness produced an overall more hydrophobic surface with respect to CA measurements. This is in contrast to the knitted fabric, where SEM showed fibres were functionalised with smaller particles that did not obviously protrude from the surface, and may have been within the pores of the fibres. Hence, in the knitted sample, the Ag/AgCl treatment did not have a significant effect on the CA measurement as any small increase in surface roughness was negated by an increase in chemical hydrophilicity in the surface. However, when the knitted fabric was treated with both Ag/AgCl and FAS, this small increase in surface roughness was seen as the CA was increased after the surface was rendered chemically hydrophobic by the FAS treatment.

Table 4.2 RoA measurements of untreated knitted and woven wool fabrics and fabrics functionalised with Ag/AgCl and/or FAS.

Fabric	Untreated	Ag/AgCl	FAS	Ag/AgCl + FAS
Knitted	70°	60°	50°	10°
Woven	60°	40°	50°	40°

The RoA measurements for these samples are presented in Table 4.2. It can be seen that the Ag/AgCl functionalisation has had different effects on the different fabrics. In the knitted fabric, the Ag/AgCl treatment alone has caused only a slight decrease in RoA but the Ag/AgCl treatment with the FAS has caused a significant decrease

in the RoA to 10° . As a large decrease in the RoA is characteristic of increased small scale roughness, this result suggests that the Ag/AgCl has successfully increased the small scale roughness of the surface, as the Ag/AgCl and FAS treatments together resulted in a much lower RoA than the FAS alone. This is supported by the SEM characterisation which showed small Ag/AgCl particles which did not protrude far from the surface. This suggests the particles caused a significant increase in the smaller scale surface roughness (which impacts RoA), but did not significantly increase the larger scale roughness (which has a greater effect on CA) and when the Ag/AgCl treatment was used alone the increase in small scale roughness was counteracted by the increase in chemical hydrophilicity of the Ag/AgCl coverage on the surface of the wool fibres.

In the woven fabric, the RoA measurements for the sample treated with Ag/AgCl and FAS and the sample treated with Ag/AgCl alone were found to be the same. The values for the samples treated with Ag/AgCl (with and without FAS) were found to be slightly lower than the sample treated with FAS alone, indicating some increase in small scale roughness of the surface of the wool fibres. However, the decrease in RoA achieved was less than that achieved in the knitted fabric, indicating that the increase in small scale surface roughness was not as significant as the increase achieved in the knitted fabric. SEM imaging indicated that the knitted fabric was functionalised with a greater coverage of smaller Ag/AgCl particles than the woven fabric. Hence, the knitted sample had an increased chemical hydrophilicity on the surface, but after functionalisation with FAS, the increase in small scale roughness caused a large decrease in RoA. Whereas in the woven fabric, the larger particles caused an increase in surface roughness, but on a larger size scale. This had a weaker effect on the RoA, the chemical hydrophobicity of the surface was also less altered in the woven sample due to more disperse coverage of Ag/AgCl particles, and so the effect of the FAS was less dramatic. When comparing the untreated fabric to the fabric treated with FAS alone, it can be seen that the FAS treatment has only a small effect on the RoA of the woven fabric, and so a similar small effect would be expected in a largely unaltered surface after treatment with Ag/AgCl.

While the Ag/AgCl treatment without the use of FAS was found to be more successful in the knitted fabric than the woven fabric, the treatment was able to increase the hydrophobicity of both fabrics to some measurable degree. Hence, the Ag/AgCl functionalisation was deemed successful in increasing the hydrophobic nature of the fabrics with respect to CA and/or RoA measurements, with or without an additional FAS treatment. As this was also a straightforward treatment that offers the additional benefit of antimicrobial activity, it showed promise in commercial use, and so further application focussed tests were performed. These additional tests were

performed on samples treated with Ag/AgCl alone, without the additional FAS. Although higher hydrophobicity was achieved using both treatments together, the Ag/AgCl treatment alone reached high levels of hydrophobicity and the treatment is more commercially viable without the additional FAS treatment.

4.2.4 Water Absorption Tests

Water absorption tests were performed on samples of knitted and woven fabrics with and without the Ag/AgCl treatment to compare the treated surfaces to the untreated surfaces in conditions closer to those encountered by commercial fabrics in real-world situations. As this was not a standardised test, samples treated with FAS were also tested for comparison purposes, to show the relative performance of the Ag/AgCl treatment. The results of these tests are shown in Figure 4.9.

Figure 4.9 Graph showing percentage of water retained after water absorption test by untreated samples of knitted and woven fabrics, and those treated with Ag/AgCl or FAS.

With respect to CA measurements, both fabric samples were deemed hydrophobic when untreated. However, as shown in these tests, when a droplet was left on the surface of the untreated knitted fabric, the droplet was absorbed by the fabric. This shows that, while the CA indicates that this untreated fabric is hydrophobic, it shows hydrophilic behaviour when tested in a situation more closely related to daily life, outside of the laboratory. This suggests that CA measurements do not always give an accurate description of how fabrics will behave outside of the laboratory. While the

untreated knitted fabric absorbed the 100 μL droplet within the 5 minute duration of the tests, after treatment with Ag/AgCl, this no longer occurred. As seen in these results, the treated sample retained significantly less water than the untreated knitted sample, showing a great increase in hydrophobic behaviour. Even when compared to the FAS treatment, the Ag/AgCl treated knitted sample was found to retain the least water after these tests. Conversely, the untreated woven fabric was found to be highly hydrophobic and did not retain a great deal of water after these tests. As this fabric was more hydrophobic before the Ag/AgCl treatment than the knitted fabric, the effect of the treatment is less dramatic. However, it can be seen that the Ag/AgCl treatment has increased the practical hydrophobic behaviour of the woven fabric and caused a decrease in water retained after these tests. While the woven fabric treated with Ag/AgCl was found to retain more water than the woven fabric treated with FAS, the Ag/AgCl treatment still had a great effect on increasing the hydrophobic behaviour of the woven fabric. Hence, the Ag/AgCl treatment was deemed to have successfully increased the hydrophobic behaviour of both knitted and woven fabrics and produced surfaces that are more water-repellent. This indicates that the Ag/AgCl treatment has potential to be a viable commercial treatment for increasing the water and stain repellency of wool fabrics.

4.3 Calcium Carbonate Functionalisation

Although the functionalisation of fabrics with Ag/AgCl was successful and provided the added benefit of an antimicrobial agent, the fabric was also rendered a purple colour which could limit the applicability of the treatment in commercial fabrics where specific colours are often desired, and the added cost of silver may not be outweighed by the added benefit in all applications. Hence, calcium carbonate was also investigated. CaCO_3 has very low solubility in water and so a similar precipitation method, as that used in the Ag/AgCl functionalisation, could be developed.

Washed fabric samples were functionalised with CaCO_3 by soaking in a solution of Ca^{2+} ions followed by a solution of CO_3^{2-} ions. Unlike gold nanoparticles and Ag/AgCl, CaCO_3 is white and so the progress of the reaction could not be followed by colour changes, and so SEM and EDS analysis was used to confirm the successful functionalisation of fibres with CaCO_3 particles. After functionalisation with CaCO_3 the samples were also functionalised with FAS, using the standard procedure described in Section 2.2.1, to achieve a functionalised fabric with 2 wt% FAS. Samples of untreated fabrics were also functionalised with 2 wt% FAS using the same method.

4.3.1 SEM and EDS Characterisation

SEM and EDS analysis was carried out on fibres of both knitted and woven fabrics functionalised with CaCO_3 . These samples were again analysed using the higher resolution, high vacuum SEM, with a low probe current and three coats of carbon. As there was no observable colour change after the CaCO_3 functionalisation treatment, SEM and EDS were used to determine if the functionalisations had been successful.

Fibres from a knitted fabric sample treated with CaCO_3 were analysed and representative images and maps are presented in Figure 4.10. Many particles were found on the wool fibre surface which were found to be CaCO_3 after EDS analysis. These particles were of a large size distribution, ranging from $< 0.5\mu\text{m}$ to $> 2\mu\text{m}$ in diameter. The particles themselves were found to be quite rough, and the large particles were seen to be clearly protruding from the surface, increasing the surface roughness.

Figure 4.10 SEM images (top left: SEI, top right: backscatter) and EDS maps of calcium (bottom left) and oxygen (bottom right) of a knitted fabric sample functionalised with CaCO_3 .

Fibres from a woven fabric sample treated with CaCO_3 were also analysed and representative images and maps are presented in Figure 4.11. The functionalisation of the woven sample appeared to have similar effects as it did on the knitted sample.

However, there appeared to be large clusters of small CaCO_3 particles and these clusters were strongly associated with the cuticle edges. The clusters were larger than the particles found in the knitted sample, but the individual particles comprising the clusters appeared to be smaller than the particles found in the knitted sample.

Figure 4.11 SEM images (top left: SEI, top right: backscatter) and EDS maps of calcium (bottom left) and oxygen (bottom right) of a woven fabric sample functionalised with CaCO_3 .

4.3.2 CA and RoA Measurements

The CA and RoA values for samples functionalised with CaCO_3 and with CaCO_3 and FAS were measured along with values for untreated fabric samples and untreated samples functionalised with FAS. A summary of all values can be found in Figure 4.12.

It was found that the CaCO_3 functionalisation of the knitted fabric successfully increased the CA of the fabric surface. The sample with the CaCO_3 treatment alone was found to have a higher CA than both the untreated fabric sample and the sample treated with FAS alone. This indicates that CaCO_3 has successfully increased

Figure 4.12 Graph showing static water contact angles of knitted and woven wool fabrics functionalised with CaCO_3 and/or FAS compared to untreated samples.

the hydrophobic behaviour of the sample through increased surface roughness. The sample treated with both CaCO_3 and FAS had a higher CA than all other samples for each fabric. This indicates that the increased surface roughness after the CaCO_3 treatment was able to increase the overall hydrophobic behaviour of the sample more than the increased chemical hydrophobicity after the FAS treatment, and the combination of the two treatments has the greatest effect on the wetting behaviour by increasing both the surface roughness and chemical hydrophobicity. The CA results on the woven fabric treated with CaCO_3 and/or FAS do not show much change ($< 5^\circ$) in hydrophobicity after treatment. There was a slight increase in CA measured after all treatments, with the combination of CaCO_3 and FAS resulting in the highest CA measured. However, these increases were much less significant than those measured for the treatments of the knitted fabric. This could be due to the difference in coverage of the wool fibres by the CaCO_3 particles after treatment. As seen in the SEM images, the knitted fabric fibres had CaCO_3 particles dispersed across the whole fibre surface, whereas the woven fabric fibres had CaCO_3 particles aggregated together and mostly associated with the cuticle edges. This suggests that the CaCO_3 treatment created less surface roughness in the woven fabric than the knitted fabric and hence the difference in CA measured was less significant.

RoA measurements were taken and are summarised in Table 4.3, and the effect of the increased surface roughness after the CaCO_3 treatment was clearly seen. This is indicated by the lower RoA measurements for samples treated with CaCO_3 with and without the additional FAS. Even the samples with just the CaCO_3 treatment

alone were measured to have lower RoA values than the samples with just the FAS treatment. This shows the significant effect in increasing the surface roughness, even with a slightly decreased chemical hydrophobicity. A slight decrease was seen in the RoA values for the samples treated with both CaCO_3 and FAS ($20 - 25^\circ$) compared to the those treated with CaCO_3 alone (30°). This is due to the previously seen effect that the FAS does not have such a significant effect on the RoA values as it does on the CA values, but the increased chemical hydrophobicity does serve to decrease the RoA to some degree.

Table 4.3 RoA measurements of untreated knitted and woven wool fabrics and fabrics functionalised with CaCO_3 and/or FAS.

Fabric	Untreated	CaCO_3	FAS	$\text{CaCO}_3 + \text{FAS}$
Knitted	70°	30°	50°	25°
Woven	60°	30°	50°	20°

The CaCO_3 functionalisation was deemed successful in increasing the hydrophobic nature of the fabrics with respect to CA and RoA measurements, with and without an additional FAS treatment. As this was also a straightforward and cost-effective treatment it showed promise in commercial use, and so further application focussed tests were performed. These additional tests were performed on samples treated with CaCO_3 alone, without the additional FAS. Although higher hydrophobicity was achieved using both treatments together, the CaCO_3 treatment alone reached high levels of hydrophobicity and the treatment is more commercially viable without the additional FAS treatment.

4.3.3 Water Absorption Tests

Water absorption tests were performed on samples of knitted and woven fabrics with and without the CaCO_3 treatment to compare the treated fabrics to the untreated fabrics in conditions closer to those encountered by commercial fabrics in real-world situations. As this was not a standardised test, samples treated with FAS were also tested for comparison purposes, to show the relative performance of the CaCO_3 treatment. The results of these tests are shown in Figure 4.13.

Firstly if we consider the knitted fabric, we can see that the untreated sample retained close to 100% of water droplet volume in these tests, indicating that the droplet was absorbed by the material. However, after treatment with CaCO_3 , this water retention was dramatically decreased to less than 3% retention. While the CaCO_3 treatment did not reduce the water retention to the same degree as the FAS treatment on the knitted fabric, the CaCO_3 treatment had a strong impact on the

Figure 4.13 Graph showing percentage of water retained after water absorption test by untreated samples of knitted and woven fabrics, and those treated with CaCO₃ or FAS.

knitted fabric and significantly increased the hydrophobic behaviour of the fabric. However, this effect was not seen in the woven fabric. The untreated woven fabric was highly hydrophobic and was found to retain less water in these tests before treatment, than after treatment with CaCO₃.

In the knitted fabric, the CaCO₃ treatment had a dramatic effect on increasing the hydrophobic behaviour as the fabric displayed hydrophilic behaviour before the treatment. The absorption of water droplets seen in the untreated knitted fabric was not seen in the fabric after treatment. This is likely due to the increased surface roughness due to general coverage of small CaCO₃ particles and also due to some degree of felting occurring during the treatment process. As seen in Chapter 3, felting generally increases the hydrophobicity of wool fabrics. As the CaCO₃ treatment involves soaking and shaking in an aqueous solution, a small amount of felting is expected to have occurred and this is likely to have contributed to the elimination of the absorption behaviour of the untreated knitted fabric. Although the knitted fabric showed a great increase in hydrophobic behaviour, the treated fabric still retained some amount of water. This retention was also seen in the treated woven fabric, but to a larger extent. The retention can be attributed to the increased chemical hydrophilicity of the CaCO₃ particles causing an increase in adhesion of the water droplets. Where the knitted sample was seen to have increased the surface roughness with general coverage across the entire surface of the fibres, the woven fabric was found to have CaCO₃ particles more concentrated

around the cuticle edges. Therefore, the treated knitted fabric likely had increased felting and had greatly increased surface roughness and the effects of this outweighed the increase in chemical hydrophilicity; whereas the treated woven fabric likely had slightly increased felting and had somewhat increased surface roughness, but these effects were not seen to overcome the increased chemical hydrophilicity of the CaCO_3 particles. Here we see the competing effects of increased surface roughness and increased chemical hydrophilicity and have demonstrated the balance needed in order to overcome one another. Here, the surface roughness achieved in the knitted sample was sufficient to overcome the chemical hydrophilicity of the CaCO_3 particles, but the woven fabric achieved less increase in surface roughness and hence this was not sufficient to overcome the increase in hydrophilicity. Due to the increased chemical hydrophilicity of the treated woven fabrics due to the CaCO_3 present, the water was more strongly adhered to the surface and so in these tests, the majority of the droplet volume is lost due to the effect of gravity, but some volume of the droplet is held strongly to the surface. Hence, the woven fabric performed better in these tests without the added hydrophilic CaCO_3 particles.

As the CaCO_3 treatment was found to have different effects on the different fabrics, it was deemed unsuitable as a commercial treatment for wool fabrics. However, it is proposed that the different effects were due to the difference in distribution of particles across the surface of the different fabrics; and so, if the treatment was altered to achieve greater surface roughness across the surface of fibres of different fabrics, this treatment could potentially be commercially viable in the future.

4.4 Conclusions

Three chemical modifications were investigated on two types of wool fabric to develop a process of rendering commercial wool fabrics highly hydrophobic and water-repellent. Firstly, modification with gold nanoparticles was investigated. The gold nanoparticles successfully increased the surface roughness of the wool fabrics, but decreased the chemical hydrophobicity. Hence, in order to use this treatment to increase the hydrophobicity of fabrics, an additional FAS treatment was required. This was deemed successful but the commercial viability of the gold nanoparticle treatment was deemed to be low, due to the high cost of gold and the additional FAS treatment required.

An *in-situ* precipitation synthesis of Ag/AgCl was developed and investigated as another possible treatment. Samples of each fabric were successfully functionalised

with Ag/AgCl using this method and the success of the reaction was determined using colour observation, XRD and SEM/EDS analysis. The surface roughness was successfully increased after the Ag/AgCl treatment, but on a larger size scale than the gold nanoparticle treatment and the Ag/AgCl treatment increased the surface roughness to a greater degree, whereby the hydrophobicity of the surface was successfully increased, without the need for an additional FAS treatment. The wetting behaviour and water-repellency of the Ag/AgCl treated fabrics was tested and both fabric types were found to have increased hydrophobic behaviour with respect to water absorption tests. However, due to the differences between the two fabrics, the degree of change induced by the treatment was not consistent between fabric types. Even so, as both fabrics were successfully rendered more hydrophobic with the Ag/AgCl treatment, it was deemed to be a potentially viable treatment for application on commercial fabrics. While silver has a relatively high-cost, it contributes an additional benefit to the treated fabrics, as silver is antimicrobial, so this Ag/AgCl treatment can impart two desirable properties to treated fabrics.

Lastly, a treatment with CaCO_3 was investigated. Although Ag/AgCl adds a secondary benefit of antimicrobial activity, the cost of silver could be prohibitive in the commercialisation of the Ag/AgCl treatment, and the colour of Ag/AgCl limits the areas of application. Hence, a cheaper, white material was investigated, CaCO_3 . The CaCO_3 synthesis was similar to that of the Ag/AgCl treatment, with *in-situ* precipitation of CaCO_3 onto the wool. SEM/EDS was used to determine the treatment had successfully functionalised the wool fibres with CaCO_3 . The CaCO_3 functionalisation greatly increased the hydrophobicity of the knitted fabric, but this effect was not seen in the woven fabric, which remained unchanged with respect to CA and water absorption measurements, but did show a decrease in RoA value after treatment. However, as the CaCO_3 treatment did not successfully increase the hydrophobicity of both fabrics, it was deemed to be unsuitable as a treatment for application to commercial fabrics in this work. With optimisation of the treatment process, the CaCO_3 functionalisation could be commercially viable in the future.

While the gold nanoparticle and CaCO_3 treatments were not found to be commercially viable, the Ag/AgCl treatment was found to produce promising results. Due to the facile synthesis, success in increasing the hydrophobicity of two different wool fabrics, and the added benefit of antimicrobial activity, the Ag/AgCl treatment was determined to have potential as a treatment for commercial wool fabrics.

The results of this chapter also highlight the importance of testing novel processes on a range of fabric types, as the results varied significantly between the two fabrics used here. This variation is due to a number of known and unknown differences

between the fabrics. Although both fabrics were manufactured from merino wool and have undergone minimal processing, the small variations in wool type and greater variations in fibre arrangement allow for quite different behaviour in regard to the way the treatments were able to affect each fabric. Of the two fabrics used here, the knitted sample was much more hydrophilic and had a much more open yarn structure than the tight woven fabric. This potentially allowed for greater absorption of treatment solutions by the knitted fabric, contributing to the differences seen between the two fabrics.

Chapter 5

Towards Superhydrophobic 3D Printed Surfaces

The research discussed in this chapter concerns the development of a superhydrophobic surface using FDM printing as a rapid-prototyping tool in the design of surface roughness patterns. As discussed in Section 1.4, superhydrophobic surfaces have been created previously using 3D printing,^{29,112} but these investigations used more technical and less cost-effective methods. These previously used 3D printing technologies also had limited capabilities with respect to the surface chemistry of prints and resolution of designed surface roughness geometries. FDM is a cost-effective, easily accessible 3D printing technology, that allows the use of several polymers that can be subsequently post-treated to give chemical hydrophobicity and allow for analysis of the surface roughness independent of the surface chemistry. This work aimed to produce a superhydrophobic surface using this technology, and investigated increasing the application potential of the surface by increasing the surface roughness and introducing extra functionality by incorporating an antimicrobial agent in the form of silver nanoparticles.

The geometry of the designed surface roughness in this work was inspired by investigations reported by Barahman and Lyons.²⁹ In their work, a syringe was used to deposit “Hershey kiss” shaped structures on a PDMS surface, achieving highly hydrophobic surfaces. In this work, similar droplet shaped structures were modelled and printed. These droplet shaped structures are useful as they allow for printing of features with finer detail than the printer should usually be able to produce. As the stepping motors in FDM printers are generally capable of finer steps than the diameter of the nozzle on the print head, and so the resolution of a FDM printer is usually limited by this diameter of the nozzle. But, by printing structures in motion

and dragging the print head away as the flow of filament is slowly stopped, this allows for the filament to be drawn to a tip that is finer than the print nozzle diameter. Hence, this can allow for the production of detail finer than the usual resolution of the printer. And so, as it has been seen that finer microscale roughness can cause more highly hydrophobic wetting behaviour on a surface (see Section 1.2.5), finer printed detail was desirable for this work. This kind of printing is quite technical and requires some degree of expertise in coding and printing. For this reason, this work was done in collaboration with a student from the School of Design (SoD) at Victoria University of Wellington (VUW), Liam Gilbertson.

Silver nanoparticles were incorporated to add nanoscale roughness to these printed surfaces. Silver nanoparticles were chosen as they are easily synthesised and have been widely shown to be antimicrobial. It has also been shown that the combination of antimicrobial activity and hydrophobicity has a synergistic effect whereby the antimicrobial activity is prolonged and the hydrophobicity increased (see Section 1.6.4). Hence, it was proposed that the integration of silver nanoparticles into these surfaces would serve to increase the functionality of the surface by adding antimicrobial activity, in addition to increasing the surface roughness, and hence increasing the hydrophobicity. Silver nanoparticles are SPR active and are usually observed to appear a straw-like yellow colour, although the colour depends on the size and shape of the particles as well as the dielectric constant of surrounding media.¹⁰⁸ Silver nanoparticles are often synthesised using an aqueous solution of AgNO_3 as the silver precursor, in conjunction with a reducing agent and/or a stabilising agent, commonly polyvinyl pyrrolidone (PVP). The *in-situ* synthesis of silver nanoparticles within a polymer matrix (nylon or polyurethane) has been developed previously within the research group by Prof. J. Johnston and Dr Maria Parry.¹¹³ This synthesis relies on amide functionality within the polymer to reduce the Ag^+ to Ag^0 *in-situ*, and depending on the concentration of silver nanoparticles present, the resulting functionalised polymers appear varying shades of yellow or orange.

Samples were first printed and their wetting behaviours examined. It was found that the samples were quite hydrophobic, even before functionalisation with FAS. Samples were then functionalised with FAS and the optimal microstructure surface roughness design was determined with maximum hydrophobicity. A number of replicates of these optimal samples were then printed for silver nanofunctionalisation. Samples were also printed without the designed surface roughness. These ‘flat’ samples were used to determine the effect of the designed surface roughness and determine if the inherent roughness from the printing was sufficient to cause similar wetting behaviour to the designed roughness. Samples of the optimal structure and flat surface were functionalised with silver nanoparticles and/or FAS and their

wetting behaviours determined and compared.

As stated above, the samples investigated in this chapter were produced in collaboration with Liam Gilbertson, a summer research scholar from VUW SoD. Surface geometries were discussed and planned in collaboration, and Mr Gilbertson was responsible for the computer aided design, modelling and printing of all samples.

5.1 Developing the Microstructure

5.1.1 Printing

Drop shaped geometries were modelled as shown in Figure 5.1. This involved creating a model of a face centred cubic (FCC) array of spheres on a surface and assigning a retraction vector to each sphere. During the retraction the deposited filament is stretched to create the angled tip. This action is not possible using the standard 3D printing software, so these models were converted to G code and printed directly from this code, without additional slicing software normally used in 3D printing (Section 1.4.2). All samples were printed with the modified MendelMax 2 printer. The samples were initially printed with PET+ filament. PET+ was a desirable filament as PET is hydrophobic (native CA of flat PET surface is $73^{\circ 80}$) and is relatively soft which could lend itself well to the printing of the desired dragged droplet structures. However, the models printed using PET+ were unsuccessful as the material was of too low viscosity to be dragged up and away as desired, as the material continually flowed from the nozzle, creating a much different structure than modelled. The samples were then printed using ABS. ABS filament was chosen as it is also hydrophobic (native CA of flat ABS surface is $90^{\circ 81}$) and has well defined printing parameters and conditions.

After optimisation of the printing conditions for these structures, the variables manipulated between samples were the relative layer width and the feature spacing. The layer width indicates the amount of polymer extruded through the print head, a lower number indicates less polymer, which should produce finer features. Hence, altering this setting allows for tuning of feature size. The spacing indicates the distance between printed spheres in the same row and between every two rows of spheres (as each row is offset from its neighbours, this is the distance between aligned rows), as the spheres are arranged in a FCC pattern, this is the spacing of the unit cell. The specifications of each sample are described in Table 5.1.

Figure 5.1 CAD model of the droplet structures printed with ABS on a 10x10mm substrate using the MendelMax 2. Top: long distance view, bottom: close up plan view. Green=extruder nozzle, purple=printed substrate, yellow=spheres, blue=retraction vectors. Inset on bottom image shows a schematic of the model showing the spacing parameter in red.

Table 5.1 Specifications of each variable in printing the droplet structure samples in ABS filament with the MendelMax 2 printer.

Sample name	Relative layer width setting (Relative feature size)	Spacing
2-3	10/0	450 μm
2-4	10/0	500 μm
2-5	50/0	500 μm
2-7	60/0	500 μm
2-8	100/0	500 μm
2-9	10/0	600 μm
2-11	30/0	600 μm
2-14	70/0	600 μm
2-16	90/0	600 μm

FAS Functionalisation

All samples were functionalised with FAS after being soaked in a 1 wt% FAS solution for two hours, followed by drying in an oven at 80 °C for a further two hours. During the treatment it was difficult to fully wet the samples as they already displayed hydrophobic behaviour; the samples were wetted as much as possible but some still had very small bubbles on the surface when submerged in the solution, leading to potentially non-uniform coating across the surface.

5.1.2 SEM

SEM imaging was used to determine the shape of the structures achieved through printing of the droplet structure models. The SEM was operated in low-vacuum mode so the samples did not require carbon coating before analysis. This allowed for subsequent further testing and treatment of the surface but limited the achievable magnification for imaging. It was found that the shapes of the structures were similar between samples, with size and spacing varying slightly as per the change in printing variables. The shape of the structures was found to be close to the designed structure shape with some variation due to the printing process. The aim was to print small spheres and slowly drag the filament to a clean peak, but the actual printed structures appear to have the filament broken and torn from the structures. This is likely due to the speed of the print, the cooling of the filament during printing and the viscosity, cohesion and elastic properties of the filament. This achieves the same result of creating structures with features and roughness of a smaller scale than the usual resolution of the printer, limited by the nozzle diameter of the print head. The individual structures themselves are vaguely spherical in shape, a few hundreds of micrometres in diameter (depending on printing variables) with smaller rugged protrusions on the scale of just tens of micrometres (see Figure 5.2).

5.1.3 CA and RoA

The CAs of these samples were measured before and after treatment with FAS, the results are summarised in Figure 5.3. All samples were found to be hydrophobic before FAS treatment with CA measurements of at least 110°. An increase in CA was observed for all samples after FAS treatment. Sample 2-7 was found to have the highest CA before treatment of 128° and Sample 2-5 was found to have the highest

Figure 5.2 SEM images of perspective and front views of sample 2-9, showing size and shape of structures achieved.

CA after treatment of 143° , while 2-3, 2-4 and 2-16 were all $\geq 138^\circ$ after treatment. The uncertainty of these measurements vary from sample to sample, both before and after treatment. This is indicative of variation across the surface, due to both variation in the printing process before treatment and variation in the uptake of the FAS treatment itself.

Figure 5.3 CA of all 3D printed droplet structure samples before and after treatment with 1 wt% FAS solution. Dotted line denotes approximate CA of flat untreated ABS polymer, 90° .

No RoA values were measured for the untreated samples as the water droplets were found to be pinned to the surfaces at angles $> 90^\circ$. However, after treatment, all of the samples except for 2-3 had decreased RoAs; these were measured and are summarised in Figure 5.4. Treated samples 2-5 and 2-8 had the lowest RoA

measured of approximately 25°.

Figure 5.4 Measured RoA values for 3D printed droplet structure samples treated with 1 wt% FAS solution. RoA represented as 90° if water droplet was pinned (Sample 2-3).

There does not seem to be a clear trend in CA with respect to either layer width or spacing alone but these results do indicate that these properties play a complex role in the wetting behaviour of the surface and can be tuned to alter the CA and RoA of the surface. Sample 2-5 had one of the lowest RoA measurements, and also had the highest CA value after FAS treatment. Hence, as 2-5 displayed the most hydrophobic behaviour after treatment with regard to both CA and RoA measurements, this sample was selected as having the optimal microstructure surface roughness design parameters and was used in further investigations.

5.2 Developing the Nanostructure

5.2.1 Preparation

Several replicate samples of 2-5 were printed to be used in optimising a silver nanofunctionalisation synthesis. Several samples were also printed without the droplet shaped microstructures, to investigate the wetting behaviour of the silver nanofunctionalised and FAS treated flat samples compared to the microstructured samples.

Silver Nanofunctionalisation

Samples were functionalised with silver nanoparticles *in-situ*. The nanoparticle synthesis involved soaking a 3D printed sample in an aqueous solution of AgNO_3 at $70\text{ }^\circ\text{C}$ for 8 hours. The Ag^+ was reduced to Ag^0 nanoparticles on the surface and the progress of this reaction could be monitored by the colour change on the 3D printed surface. The printed samples were initially white and as the silver reduction reaction proceeded an orange layer could be seen forming on the surface, which subsequently turned a dark metallic grey colour when left for longer than eight hours (see Figure 5.5). These colour changes indicate the reduction of colourless Ag^+ to orange, SPR active Ag^0 nanoparticles and then to bulk metallic silver Ag^0 .

Figure 5.5 Photograph of an untreated 3D printed structured sample (left), a 3D printed structured sample functionalised with silver nanoparticles (centre), and a 3D printed flat sample plated with bulk silver (right), showing colour change from white to orange to grey over the course of the silver reduction reaction.

The reaction of reducing Ag^+ to Ag^0 is facile and will occur readily with even a weak reducing agent. Previously, many reactants and polymers have been shown to reduce silver, commonly including polyvinyl pyrrolidone, trisodium citrate, nylon and polyurethane.^{101,113} In the reduction reactions with polymers, it was the amine functionality in the polymer chemistry which was found to act as the reductant. As ABS contains few reactive functional groups (nitrile, alkyl, alkene and aromatic functionality only), it was not guaranteed that the ABS alone would have sufficient reductive power to reduce the silver ions to silver nanoparticles. However, reduction was seen to occur in solutions containing only aqueous solutions of AgNO_3 and 3D printed ABS polymer, detected by the characteristic colour change, this reaction was investigated using IR spectroscopy (see Section 5.2.3). As previously discussed in Section 1.4.1, 3D printing polymer filaments commonly contain additional undisclosed chemicals, in addition to the named polymer. These chemical additives are usually plasticisers, copolymers or pigments. Any of these additives could have been contributing additional chemical functionality responsible for the reduction of silver by the ABS filament. It was therefore concluded at this stage that the reduction of

Ag^+ to Ag^0 was likely caused by an additive in the ABS filament. However, later IR studies suggest the reduction is facilitated by the oxidation of $\text{C}=\text{C}$ double bonds to $\text{C}\equiv\text{C}$ triple bonds in the styrene monomer entities, this is discussed in Section 5.2.3.

FAS Functionalisation

Both blank and silver nanofunctionalised samples were treated with FAS. For samples that were treated with both silver nanoparticles and FAS, it was important to functionalise the samples with silver nanoparticles first, followed by the FAS, as the silver nanoparticles were hydrophilic and so the surface had to be subsequently treated with the hydrophobic FAS. This allows for the silver nanoparticles to increase the surface roughness while maintaining a chemically hydrophobic surface. Samples were functionalised with FAS after being soaked in a 1 wt% FAS solution for two hours, followed by drying in an oven at 80 °C for a further two hours. During the treatment it was again difficult to fully wet the samples as they already displayed hydrophobic behaviour; the samples were wetted as much as possible but some still had very small bubbles on the surface when submerged in the solution.

5.2.2 SEM and EDS

SEM and EDS were used to analyse the composition and morphology of the samples and confirm the presence of silver nanoparticles. As the ABS was very susceptible to beam damage, examination of the structured samples under the SEM was difficult. Carbon coating the samples was avoided in order to preserve the samples for further tests and modifications if necessary, the height of the printed samples also made them too large to fit in the chamber of the high resolution JEOL-6500F SEM. Hence, the structured samples were analysed without being coated with carbon, using the JEOL-JSM-6610LA SEM in low vacuum mode. This again limited the achievable magnification and scan count in EDS mapping. As the samples themselves were too large to be examined using the JEOL-6500F SEM, and destruction of the samples was to be avoided, a filament surrogate was prepared for higher resolution examination. This filament surrogate was a piece of ABS filament that had been functionalised with silver nanoparticles, using the same method used to functionalise the samples (see Section 2.3.4). This functionalised filament was used as a surrogate for high resolution SEM and EDS analysis, in place of the actual samples. This filament surrogate was coated with carbon several times and examined using a low probe current in order to minimise beam damage and to allow for

higher magnifications and nanoscale imaging as well as longer EDS mapping times. However, even under such conditions, the sample remained difficult to examine, and magnifications and mapping times were compromised.

Structured Samples

Due to the added silver in the functionalised structured samples, there was less charging observed during SEM examination which allowed for higher magnifications to be achieved compared to the non-functionalised surfaces. Upon examination at higher magnification it was found that there was additional smaller scale roughness in the polymer substrate than seen previously, as seen in Figure 5.6. This smaller scale roughness on the polymer is less than ten micrometres; still larger than silver nanoparticles but smaller than the large spherical microstructures (hundreds of micrometres) and protruding broken filament (tens of micrometres) that were previously seen. It is unknown whether this roughness in the polymer substrate was caused during the silver functionalisation process or if it was present in all samples from the printing process.

Figure 5.6 Low vacuum SEM images of droplet structure surface functionalised with silver nanoparticles and FAS, showing smaller microscale roughness.

SEM imaging in low vacuum was performed using back-scatter mode. This showed small bright areas where high density elements could be present within the sample. Many small bright areas were observed in the samples, which were potentially the added silver nanoparticles but could also be due to pigments and fillers in the filament such as TiO_2 . The larger bright areas are likely due to charging of the sample under the electron beam. In SEI mode, bright areas do not correlate to the composition of the material, but to a greater amount of electrons. Hence, if the sample is not sufficiently conductive to move the electrons away, the electrons can accumulate in some areas, usually peaks or corners of the sample, and appear as bright areas. When there is significant charging, this can also lead to bright areas

in backscatter mode which can complicate the analysis of images when examining for bright areas to indicate the presence of high density elements. Charging commonly occurs in non-conductive samples, such as these polymers when they are not coated with a conductive layer of carbon; and significant charging was observed in these samples. Hence, insight into the elemental composition of the surface was not obtained through SEM analysis alone, and it was important to use EDS analysis to describe the elemental composition of the surface, and in particular these small bright areas, to confirm the presence of high-density elements and distinguish these areas from areas of charging. Due to the limited mapping times possible, EDS could not provide definitive evidence as to the composition of these bright areas, but gave some information about their possible elemental composition. As seen in Figure 5.7, it appeared that some of the areas may contain titanium, as bright spots in the titanium map correlated with some of the bright spots in the SEM image, and the EDS map of silver showed a distribution of silver across the surface with some small spots of higher concentrations, also correlating to bright areas in the SEM image. However, the EDS spectrum, shown in Figure 5.8, showed the concentration of titanium was lower than that of silver. Overall, this indicated some nanoparticles had been formed, but the size of these particles was too small to be clearly detected at these magnifications.

Filament Surrogate

A piece of ABS filament was melted flat and then treated with silver using the same process as for treating the 3D printed samples. This filament was then coated several times with carbon and analysed using high resolution, high vacuum SEM and EDS. The analysis was performed using a low probe current in order to minimise beam damage, but the ABS was found to be severely damaged under the electron beam so this could only be minimised and not avoided entirely. Representative images and EDS maps are shown in Figure 5.9, where beam damage is seen as the darker areas in the SEM images (more clearly seen in the backscatter image).

In SEM imaging, many areas of high density were seen in backscatter mode, but many of these areas were found to be TiO_2 after EDS analysis showing a high concentration of titanium in these areas. This is not unexpected, as the filament is white in colour and TiO_2 particles, of 250 nm particle size, are commonly used as a white pigment. Aside from these larger particles of TiO_2 , there were indistinct areas of bright white seen in the backscatter images also. These areas likely represent the silver in the sample, as EDS analysis showed a high concentration of silver across

Figure 5.7 Annotated SEM image with corresponding silver (green) and titanium (yellow) EDS maps of silver functionalised droplet structures, showing possible areas of silver nanoparticles and TiO_2 particles.

Figure 5.8 The EDS spectrum of silver functionalised droplet structures, showing low concentration of titanium (yellow) compared to silver (green).

Figure 5.9 SEM images (top left: SEI, top right: backscatter) with corresponding silver (green) and titanium (yellow) EDS maps of filament surrogate, showing possible areas of silver and TiO_2 particles.

the whole surface (see Figure 5.9). These bright areas appear to have some small brighter points that could be silver nanoparticles. Higher resolution images and EDS maps of this area would be of great value in determining if there were discrete silver nanoparticles within these bright areas, but the amount of electron damage at higher magnifications and longer mapping times was prohibitive in achieving this. However, due to the colour of the sample, it was highly likely that silver nanoparticles were present in the surface. The distinct orange colour is typical of silver nanoparticles of approximately 20 nm diameter. Particles of this size are unlikely to be detected at the magnifications achieved here, further supporting the notion that the limited magnification was why these particles were not observed.

5.2.3 Infrared Spectroscopy

Infrared (IR) spectroscopy was performed on samples of ABS filament before and after functionalisation with silver. ATR FT-IR spectroscopy was used, and so a flat sample of filament was required, as accurate reflectance measurements cannot be performed if there is air between the sample and the detector. To achieve the required flatness, ABS filament was melted on to a glass slide, on a hot-plate at approximately 300 °C. The melted polymer was then cooled and chipped off the glass slide to reveal a flat surface. Some of this flat ABS was then functionalised with silver, using the same method as the 3D printed samples. IR analysis was performed as outlined in Section 2.4.5, and obtained spectra are presented in Figure 5.10 and Figure 5.11. As the exact composition of the ABS filament is unknown, the IR spectrum offers some insight into the chemical functionality present in the material. These types of materials often contain plasticisers, the majority of which are based on phthalates, with ester functionality. However, when assessing the spectrum of the untreated ABS filament, a noticeable feature is the lack of peaks associated with oxygen functionality, indicating that there is no significant concentration of -OH, C-O, or C=O functionality. In fact, the spectrum contained few strong peaks above the fingerprint region, and all major peaks could be attributed to expected functionality from ABS itself; $C\equiv N$ from the acrylonitrile, $C=C$ from the butadiene and $C=C-H$ from the styrene were all detected. This indicates that any additive compounds in the filament material are present in small concentrations, not significantly detected by IR analysis. A summary of major peaks and their assigned functional groups is given in Table 5.2.

As the relative concentration of silver used in the functionalisation treatment was low, the concentration of reacted ABS is also relatively low, and so when comparing

Figure 5.10 Overlay of ATR-FTIR spectra of ABS filament before and after silver functionalisation (ABS and ABS-Ag, respectively).

Figure 5.11 Overlays of detailed ATR-FTIR spectra of ABS filament before and after silver functionalisation (ABS and ABS-Ag, respectively), showing important areas of change, around 3500-3000 cm^{-1} , 2500-2000 cm^{-1} and 1800-1400 cm^{-1} .

Table 5.2 Major peaks and their assigned functional groups, found in the ATR-FTIR spectrum of untreated ABS filament, shown in Figure 5.10.

Wavenumber	Intensity	Functional group
3027 cm ⁻¹	Weak	Aromatic C-H
2922 cm ⁻¹	Weak-medium	Alkyl C-H
2237 cm ⁻¹	Weak	C≡N
1637 cm ⁻¹	Weak	C=C (aromatic)
1602 cm ⁻¹	Weak	C=C (non-aromatic)
1493,1453 cm ⁻¹	Medium	C-C
759,698 cm ⁻¹	Strong	Aromaticity

the two IR spectra, the changes are quite small, compared to the bulk of the ABS which remained unchanged. The IR spectra showed three key differences; in the functionalised spectrum, a small, sharp peak appeared at 3301 cm⁻¹, a series of small peaks appeared at 2390-2350 cm⁻¹, and the peak at 1637 cm⁻¹ had significantly increased in intensity. These important areas of change are shown in detail in Figure 5.11. While the peaks that appear in the silver functionalised ABS spectrum are small and the peak with increased intensity is also small, the percentage increase compared to the untreated ABS spectrum is over 100%, and so are deemed to be significant. The percentage increase of each changed peak is given in Table 5.3.

Table 5.3 Percentage increases of changed peaks in silver functionalised ABS ATR-FTIR spectrum compared to the untreated ABS ATR-FTIR spectrum.

Wavenumber of peak	Percentage increase
3301 cm ⁻¹	258%
2362 cm ⁻¹	273%
1637 cm ⁻¹	127%

The increased intensity of the peak at 1637 cm⁻¹ indicates a change in the C=C bonds in the material; while this peak has increased, the ratio of this peak compared to the peak at 1602 cm⁻¹ indicates less non-aromatic C=C bonds present in the functionalised sample compared to aromatic C=C bonds. The appearance of peaks at 3301 cm⁻¹ and 2362 cm⁻¹ can be attributed to the presence of C≡C-H and C≡C functionality, respectively. This indicates the formation of C≡C functionality and changes to the C=C functionality (potentially via some loss of non-aromatic C=C bonds) in the ABS during the silver functionalisation. Hence, this suggests that C=C bonds are being oxidised to C≡C bonds, while the Ag⁺ is being reduced Ag⁰. It is proposed that these non-aromatic C=C bonds are present in the butadiene monomer segments. As shown in Figure 5.12, butadiene can polymerise in a 1,2-addition fashion, leaving the second C=C double bond unperturbed and still present in the resulting branched polymer. It is proposed that these segments of butadiene with the C=C double bond intact, are responsible for the reduction of Ag⁺ to Ag⁰ nanoparticles in this treatment. However, as the changes in the spectra are quite

small and IR analysis is not definitive, this is not determined to be an absolute conclusion. It is also important to note the small decrease in intensity of the peak at 2237 cm^{-1} , attributed to $\text{C}\equiv\text{N}$ bonding. Silver has a known affinity for nitrogen, and so it is likely that the silver is associated to the nitrogen atoms in the polymer, causing this slight change in $\text{C}\equiv\text{N}$ peaks in the FTIR spectra.

Figure 5.12 Polymerisation reaction of butadiene showing different configurations of monomer segments in the polymer, after trans-1,4-addition, 1,2-addition, and cis-1,4-addition (resulting segments shown left to right, respectively).

5.2.4 CA and RoA

The CA values were measured for flat and structured samples with and without silver nanoparticle functionalisation and/or FAS functionalisation, these results are shown in Figure 5.13. It was found that the structured samples had significantly higher CA than the flat printed surface with the same treatments, for example, the untreated flat surface had a CA of 85° , whereas the untreated structured sample had a CA of 125° . This shows that the designed microstructured roughness has a large impact on the wetting behaviour, and the additional processing and printing serves to significantly increase the hydrophobicity. While the CA values of the untreated structured sample (Sample 2-5) produced here and in initial investigations were found to agree, the CA values of the structured sample treated with FAS measured here was found to vary slightly from the original measurement taken on the first sample produced and treated with FAS, in Section 5.1 (compare with Figure 5.3). This indicates that the variation is due to the non-uniform application of the FAS. However, the varying measurements do still agree within error margins. The treatments were seen to have the same effects and trends on both the flat and structured surfaces. The silver functionalisation alone was found to decrease the CA of the surfaces. This is due to the hydrophilic nature of silver and so the surface is rendered more chemically hydrophilic, decreasing the CA. As expected the FAS treatment alone increased the CA of both surfaces. But, the highest CA measured for each surface was that which was treated with both silver and FAS. The structured surface with both silver and FAS treatments was found to be the most hydrophobic with a CA of 143° .

Figure 5.13 Graph showing CA values of 3D printed flat and optimal droplet structure rough surfaces (Sample 2-5) functionalised with Ag and/or FAS compared to blank samples.

RoA values for these samples were also measured and are shown in Table 5.4. All flat printed samples with or without Ag and/or FAS treatments, were found to have the test water droplets pinned to the surfaces at angles greater than 90° . In the rough samples, the blank 2-5 sample and the sample treated with silver nanoparticles alone also showed pinning of test water droplets at angles greater than 90° . With regard to the rough samples treated with FAS, there was no difference in RoA values measured; the sample treated with FAS alone showed a similar RoA value to the sample treated with both silver nanoparticles and FAS ($25 - 30^\circ$). This indicates that the addition of silver nanoparticles has not had a measurable effect on the RoA value of the sample. As nanostructure contributes more to the RoA measurement than the CA measurement, it is unusual that a difference was measured in the CA values of the samples but not in the RoA values. However, the CA and RoA values were not measured at the same time. The RoA values were measured months after the CA values, and it is possible that the samples were somehow damaged in this time. This may have altered the physical nature of the printed structures, which would explain why no effect of the silver nanoparticles was observed in the measurement of the RoA values. While there was no decrease in RoA measured in the sample treated with both silver nanoparticles and FAS compared to the sample treated with FAS alone, there was no increase in RoA measured and the sample with both treatments was also found to have a slightly higher CA value. This shows that the use of the silver nanoparticle treatment with the FAS treatment can increase the hydrophobicity of

a surface with respect to CA and does not hinder the hydrophobicity with respect to RoA.

Table 5.4 Measured RoA values for flat and structured 3D printed samples functionalised with Ag and/or FAS.

	Flat	Structured
Blank	Pinned	Pinned
Ag	Pinned	Pinned
FAS	Pinned	25°
Ag + FAS	Pinned	30°

5.3 Conclusions

FDM printing was used to produce samples with designed micro-scale roughness. This roughness was specifically designed to achieve features smaller than the standard resolution of the printer. It was found that these samples had many levels of micro-scale roughness due to the designed structures and inherent roughness created during the printing process causing protrusions from each structure, as if torn from the printed filament. Varied roughness on the scale of a few hundred micrometres, down to just tens of micrometres, was achieved. Due to the high degree of surface roughness achieved in the printing process, these samples were fairly hydrophobic with respect to CA values, even without any chemical treatment, with CA values approaching 130°. However, the samples were found to be less hydrophobic with respect to RoA values. No RoA values could be measured as the surfaces displayed hydrophilic behaviour and test water droplets were found to be pinned to the surfaces. Hence, these surfaces were treated with FAS to increase their chemical hydrophobicity. This treatment was very successful in increasing the hydrophobicity of these samples, with respect to both CA and RoA values. After treatment, the samples were found to be highly hydrophobic; the most hydrophobic samples were found to have CA values of up to 143° and RoA values as low as 25°. Although these values do not strictly satisfy the criteria for superhydrophobic surfaces, they are very highly hydrophobic, without any added nano-scale roughness. This demonstrates that highly hydrophobic samples can be produced easily with only FDM printing and an aqueous FAS surface treatment.

Although highly hydrophobic samples were successfully produced with high CA and low RoA values, the most hydrophobic sample produced was investigated further to increase the already high level of hydrophobicity achieved. The most hydrophobic samples produced were further treated with silver nanoparticles to add nano-scale roughness to the high degree of micro-scale roughness achieved in printing. This

functionalisation was performed using a novel, facile, aqueous method with very few reagents. It is proposed that the reduction of Ag^+ to Ag^0 is achieved via the oxidation of $\text{C}=\text{C}$ double bonds to $\text{C}\equiv\text{C}$ triple bonds in butadiene segments present in the ABS polymer chain. After silver nanoparticle functionalisation and FAS treatment the CA value of the sample was increased by a few degrees, but no increase in RoA was measured. Although the nanofunctionalisation did not significantly increase the hydrophobicity of the sample, silver nanoparticles are widely known for their antimicrobial activity, and so the added functionality of these nanoparticles, adds value to the surface and it is possible that the functionalisation could be further tuned to provide more nanoroughness to significantly increase the hydrophobicity of the surface. Hence, although the conditions of superhydrophobicity were not fulfilled, the investigation successfully produced novel, highly hydrophobic and antimicrobial surfaces.

Chapter 6

Anisotropic 3D Printed Surfaces

In this chapter, samples produced with anisotropic surface roughness will be discussed. The aim of this work was to produce a surface with directionally dependent wetting behaviour using specifically patterned polymer surfaces generated by 3D printing. Surfaces with anisotropic roughness were produced in order to direct droplet movement across the surface in one direction. A method of further controlling the wettability of the surface was also investigated in order to create surfaces with closely controlled wettability that may vary between areas on one surface. These surfaces were not expected to show as extreme wetting behaviour as previous samples (such as those discussed in Chapter 5), as superhydrophobicity was not necessarily the focus, instead hydrophobicity allowing for droplet movement was considered sufficient for the surface to be fit for purpose.

Fused deposition modelling (FDM) 3D printing was used in this section as a method of rapid-prototyping in order to easily produce a large number of samples with different variables. Firstly, the inherent layering effect of FDM 3D printing was investigated in order to determine if this produced sufficient roughness to induce directional water flow/shedding from a surface. The size scale of the inherent layering in a 3D printed model is determined by the layer height resolution of the printer used. In this work, the MendelMax 2 printer was used with a layer height resolution of less than 100 μm . The standard layer height resolution of the MendelMax 2 printer is 100 μm but this resolution was increased by using non-standard parts on the printer, including a finer print head nozzle of 0.25 mm, instead of the standard 0.4 mm nozzle. Hence, the actual layer height resolution is not definitively known, but the limits of the printer resolution were tested in this investigation.

As it was found that the inherent layering of the printer was sufficient to induce

anisotropic wetting behaviour, but not able to produce directional water flow, further physically anisotropic surfaces were investigated. These surfaces had specifically designed anisotropic surface roughness patterns. These anisotropic patterns were based on the same line/channel pattern, with several protruding lines printed along the length of the sample in one direction. These lines and channels directed the wetting of water droplets in the direction parallel to the lines and was found to be able to induce water shedding in this direction and prevent water flow in the perpendicular direction, depending on the specific parameters set.

The optimal line/channel structure was determined that had the highest hydrophobicity while allowing water to flow in only the direction parallel to the structured lines. This surface was then investigated further with different patternable surface treatments in order to change the wetting behaviours of the surface. These surface treatments included FAS functionalisation and ion implantation using Ar^+ and C^+ ions. These surface treatments were found to have novel effects on the wetting behaviour of these surfaces.

6.1 Constant Thickness Varied Angle Samples

In addition to the samples discussed in Chapter 5, another set of samples was produced in collaboration with Liam Gilbertson, a summer research scholar from Victoria University of Wellington (VUW) School of Design (SoD). The purpose of investigating these samples was to determine the effect of the anisotropic roughness in 3D printed samples due to the inherent layering, and determine if this anisotropic roughness was sufficient to produce a surface capable of directing water droplet movement across the surface in one direction.

This inherent layering was investigated by printing samples vertically and testing the wettability of the upright surface of the print (see Figure 6.1). It was also possible to print models at an angle in order to offset the layers and in effect, increase the layer thickness and spacing in the samples. This allowed thorough investigation of the layering, with different variables. The roughness caused by this layering effect was expected to be on the scale of approximately 50 - 250 μm . Roughness on this scale was expected to affect the wetting behaviour on the surface and successfully introduce anisotropic behaviour, although this is relatively large scale roughness so the surfaces were not expected to be highly hydrophobic, as they lacked the smaller scale (nanoscale) roughness.

Figure 6.1 Schematic of normal and vertical print orientations, showing how layering creates a rough test surface in vertical prints.

6.1.1 Preparation

These samples were printed with the modified MendelMax 2 printer using PET+ filament. PET+ filament was chosen as it was easily accessible and PET was among the least hydrophilic polymers available as a filament. To allow greater manipulation of the layering, these samples were printed vertically, with the test surface on the upright side. This set comprised 16 samples with constant thickness. The two variables manipulated were print angle and layer height setting. The CAD model used to print these ‘constant thickness varied angle’ (CTVA) samples is shown in Figure 6.2.

Figure 6.2 CAD model of CTVA samples, showing series of different print angles used relative to the print bed (represented as area with axes and grid displayed).

Printing these samples at different angles, relative to the print bed, and with different layer height settings allowed for manipulation of the thickness and spacing of the printed layers, as shown in Figure 6.3. Samples printed at lower angles had greater spacing of the printed layers than samples at higher angles. Samples printed with greater layer height settings had thicker layers than those with lower layer height settings. It is important to note that while the layer height setting is given as a measurement in micrometres, the actual height of the printed layers is also dependent on a number of other print settings and so can differ from the measurement given. However, all other print settings were kept constant between samples so the quoted layer height setting still gives an accurate representation of relative layer height between samples in this series.

Figure 6.3 Schematic showing increase in test surface roughness with decreased print angle. At 90° print angle the test surface is nearly flat, compared to at 45° print angle where the off-set layers give a rough test surface.

6.1.2 SEM

SEM imaging was performed on four CTVA samples to determine the pattern and size of the roughness caused by the inherent layering of the 3D printing process. Representative images of the samples investigated are shown in Figure 6.4. It is clear that the print angle had an effect on the roughness of the layering. It can be seen that in samples printed at lower angles (45°) the layers are more staggered, with small dips clearly separating the layers, whereas than in samples printed at higher angles (90°), the layers sit flush against neighbouring layers, with only fine lines separating them. In SEI mode, the brightness can indicate the height of features in the sample being examined. In the samples printed at 90° it can be seen that there is little difference in height between the layers, represented by very fine, only slightly darker lines between layers, whereas in the samples printed at 45° the neighbouring layers begin and end at different heights, offset from each other, indicated by the thick dark lines between the layers and the gradient of brightness across each layer. This indicates that changing the print height has an effect on the surface roughness and lower print angles produce surfaces with greater microscale roughness. However, it was also found that the surfaces printed at higher angles had more defects than those printed at low angles. This also increases the roughness of the surface but in an unpredictable way.

The width of the layers was set by the relative layer height in the print, but it has been determined that the layer height setting does not necessarily represent the absolute height of the layers printed, as this also depends on other print settings. The height of the layers becomes the width of the layers when looking from the test perspective and this was measured using SEM images. For each sample measured, 10 layer width measurements were taken from random areas on the surface; the mean of these values was determined and this was taken as the average layer width. These values are given in Table 6.1. It was found that the layers in samples printed with a higher layer height setting were indeed thicker than those with a lower layer height setting. It was also found that samples printed with a lower layer height setting had much more irregularity in layer thickness than those printed with higher layer height settings, as shown by the standard deviations represented as percentages of the average value. In samples with $60\text{ }\mu\text{m}$ layer height setting the standard deviation was 29% of the average, whereas in samples with $150\text{ }\mu\text{m}$ layer height setting the standard deviation was 9-12% of the average.

SEM imaging clearly showed that the printing process alone causes anisotropic surface roughness on the microscale. It was also shown that this roughness was altered

Figure 6.4 SEM images of CTVA samples with print angles of 45° or 90° and layer height settings of 60 μm or 150 μm , showing width and spacing of inherent layers. Compare to Figure 6.3.

Table 6.1 Average layer widths of CTVA samples measured from SEM images, with standard deviations (Std Dev) and those standard deviations represented as a percentage of the average.

Sample		Layer width	Std Dev	Percentage
45° angle	60 μm	94 μm	28 μm	29%
	150 μm	214 μm	18 μm	9%
90° angle	60 μm	67 μm	19 μm	29%
	150 μm	155 μm	18 μm	12%

by changing the layer height setting and print angle of the printed samples.

6.1.3 CA Measurements

The static water CA of each sample was measured using the goniometer. Two measurements were taken of each sample, firstly with the sample observed parallel to the lines of the layers (CA_{Para}) and also observed perpendicular to the lines of the layers (CA_{Perp}), as shown in Figure 6.5. A summary of the measured values can be found in Table 6.2.

Table 6.2 Static water CAs of the CTVA samples observed in both parallel (CA_{Para}) and perpendicular (CA_{Perp}) directions.

Sample		CA_{Para}	CA_{Perp}
45° angle	60 μm	98°	76°
	100 μm	93°	69°
	150 μm	100°	76°
	200 μm	89°	63°
60° angle	60 μm	100°	67°
	100 μm	106°	69°
	150 μm	107°	74°
	200 μm	102°	67°
75° angle	60 μm	101°	73°
	100 μm	101°	69°
	150 μm	111°	72°
	200 μm	99°	67°
90° angle	60 μm	99°	68°
	100 μm	101°	70°
	150 μm	105°	71°
	200 μm	94°	61°

As expected, all measured CA_{Perp} values were found to be lower than the respective CA_{Para} values for each sample, and this was also observed with elongation of the test droplets, as shown in Figure 6.6. The surface was found to be only slightly hydrophobic or hydrophilic with CA_{Para} values less than 110°, and CA_{Perp} values as low as 61°. This indicates that the PET+ filament is not very hydrophobic and offers little benefit in terms of lowering surface tension. In these values we can clearly see the effect the anisotropy in the surface roughness has on the wetting behaviour. However, neither changing the print angle and hence the spacing of the roughness, nor changing the thickness of the layers had a significant effect on the CAs of the surface when viewed from either direction. As the CA values for these samples were found to be so low these samples were determined to be unsuccessful and no further testing was performed.

Figure 6.5 Schematic of an elongated water droplet on a chemically or physically anisotropic surface, showing parallel and perpendicular CA measurement perspectives.

Figure 6.6 Photograph of a 10 μL droplet on the surface of a CTVA surface (90° 150 μm), showing elongation in direction parallel to layering.

It was also found that this filament was quite difficult to print, as its low viscosity caused a lot of oozing and leakage from the hot extruder throughout the print. It was concluded that printing with the PET+ filament was too difficult and offered no chemical benefit and so other filament materials were investigated for further samples. No significant differences were observed in the wetting behaviours of these samples and no obvious trends were observed. Hence, it was determined that while the inherent layering of the 3D printed materials was enough to cause anisotropic wetting behaviour, this anisotropy was not significant enough to tune water droplet movement across the surface.

6.2 Channel Samples

The inherent layering of 3D printed surfaces showed that anisotropy can be easily induced into these surfaces but it was found that this inherent roughness was not sufficient to induce enough hydrophobicity to control the movement of droplets on the surface. Hence, further investigations were undertaken, which involved producing samples that were printed with deliberate, broader, anisotropic roughness patterns. This was achieved by designing samples as rectangular bases with protruding lines running the length of the sample in one direction along the top. This allowed for tuning of the thickness and spacing of the lines as well as variation of their cross-sectional shape. Two cross-sectional shapes were used, square and trapezoid. The square lines represented the most simple shape in terms of modelling and printing and this series of samples was expanded by also producing samples with trapezoidal lines which represented a similar structure to the square lines, but with an undercut

edge. As discussed in Section 1.2.6, an undercut edge can increase the barrier to movement and cause a higher RoA in the direction where the droplet approaches this edge. This facilitated investigation into the effects of larger anisotropic roughness on the wettability of a surface and on a droplets movement across such a surface.

6.2.1 Preparation

Samples were printed on the MendelMax 3 printer with ABS filament, using standard printing conditions as outlined in Section 2.3.2. ABS is a commonly used filament material for FDM printing and has a properties well suited to 3D printing (such as melting point and viscosity). ABS also has little chemical functionality, with only nitrile, aromatic and alkyl groups, so was anticipated to be quite hydrophobic. CAD models were produced of rectangular bases with protruding, square or trapezoid cross-sectional lines of varying size and spacing. Square cross-sectional line samples were printed with the lines and the spacings set to $250\ \mu\text{m}$, $500\ \mu\text{m}$, $750\ \mu\text{m}$, or $1000\ \mu\text{m}$, totalling 16 square samples, summarised in Table 6.3. As the cross-sections were square, the width of the lines also represents the height of the lines. Trapezoid cross-sectional line samples were printed with varying line and channel spacing, as well as varied line height and internal trapezoid angle. These dimensions were chosen as they are similar to the dimensions of the hydrophilic and hydrophobic areas on the back of the water harvesting *Stenocara* beetle, discussed in Section 1.6.2, shown in Figure 6.7. The hydrophilic bumps on the beetle's back are approximately $600\ \mu\text{m}$ in diameter and the spacing between them is approximately $400\text{-}1000\ \mu\text{m}$.⁵ Hence dimensions of $250\text{-}1000\ \mu\text{m}$ were used in order to achieve similar properties.

Figure 6.7 Image of a *Stenocara* beetle, showing the hydrophilic bumps surrounded by hydrophobic troughs on its back.

The samples were all named based on the dimensions of their lines and channels, as described in Figure 6.8. In square line structures, samples are called A x B, where A is the width of the spacing and B is both the height and width of the square line. In trapezoid line structures, samples are called A x B x C, where the lines are

always undercut and A is the width of the top of the trapezoid, B is the width of the top of the channels, C is the height of the trapezoid and D is the width at the bottom of the channels. In the trapezoid models, the A, B and C dimensions were specified and the D dimension was a factor of these three variables so while A, B and C were set to be round numbers, D values are more random. The dimension D of each trapezoid sample were measured and reported, but not used in naming. The dimensions of the trapezoid samples printed are summarised in Table 6.4.

Figure 6.8 Schematic showing dimensions of square and trapezoid lines and channels in channel structures. In square line structures, samples are called A x B. In trapezoid line structures, samples are called A x B x C.

Table 6.3 Sample names of all square cross-sectional line samples produced.

Sample names	250 μm Lines	500 μm Lines	750 μm Lines	1000 μm Lines
250 μm Spacing	250 x 250	250 x 500	250 x 750	250 x 1000
500 μm Spacing	500 x 250	500 x 500	500 x 750	500 x 1000
750 μm Spacing	750 x 250	750 x 500	750 x 750	750 x 1000
1000 μm Spacing	1000 x 250	1000 x 500	1000 x 750	1000 x 1000

Table 6.4 Sample names and dimensions of all trapezoid cross-sectional line samples produced.

Sample Name	A (mm)	B (mm)	C (mm)	D (mm)
1.5 x 0.5 x 0.5	1.5	0.5	0.5	1.1
1.5 x 0.5 x 1.0	1.5	0.5	1.0	1.95
1.5 x 1.0 x 2.0	1.5	1.0	2.0	2.15
0.75 x 0.5 x 1.0	0.75	0.5	1.0	1.35
1.25 x 0.25 x 1.25	1.25	0.25	1.25	1.15

6.2.2 SEM

SEM imaging was carried out on the 500 x 500 μm square line sample as a representative of this series of samples. As all samples were printed with the same print

settings and conditions and were not subjected to post-processing, the surface of this sample should represent the surface of all samples on the microscopic scale. Imaging was performed on the lower resolution SEM in low vacuum mode in order to image the unperturbed and uncoated surface of the sample. This limited the achievable magnification as at magnifications over 1000 times, the sample charged significantly and imaging was not possible. SEM images of the sample are shown in Figure 6.9. As expected, it was found that the surface of the sample had the larger scale, designed surface roughness in the form of the protruding lines atop the sample base, as well as inherent roughness from the layering effect of the printing process. However, it was also found that the sample had smaller scale roughness on the surface. This additional roughness was on the scale of a few micrometres, and was similar to that seen in the 3D printed samples discussed in Chapter 5. It is likely that this roughness is largely due to the behaviour of the polymer in the melting, extruding and solidifying phases of the printing process. Some larger striation-type roughness patterns were also seen on the surface, on the scale of tens of micrometres. This suggests that aside from the designed roughness and layered roughness from 3D printing, the printing process also induces smaller scale micro-roughness on the printed surfaces.

SEM imaging also allowed for measurement of the line and channel widths of this sample. It was found that the lines were slightly smaller than designed with an average width of $488\text{ }\mu\text{m}$ and the channels were slightly larger with a mean width of $518\text{ }\mu\text{m}$. This is likely due to the limitations of the printer and the extrusion process used in FDM. The printer must build the models using lines of extruded filament. These extruded lines are of a predetermined size and are optimised to be almost cylindrical, although some variation in relative height and width can occur due to the proximity of the print head to the print/print bed. The size of these extruded lines is predominantly based on the layer height setting. These samples were printed with a layer height setting of $150\text{ }\mu\text{m}$, but this absolute measurement is altered by other print settings, causing the actual layer height (and approximate width) to be slightly higher or lower than this set height. This determines the width of the filament extruded by the printer, and hence the thickness of the lines printed. Therefore, any printed feature must be of a size that is an integer multiple of the thickness of one extruded line. If a feature is modelled to a size that is not a printable size, it will be printed as close to the designed size as possible, using an integer multiple. In this case, it appears the width of the printed lines was approximately $244\text{ }\mu\text{m}$ and so the designed $500\text{ }\mu\text{m}$ features were printed with two lines, resulting in features that were $488\text{ }\mu\text{m}$ wide.

Figure 6.9 SEM images of 500 x 500 μm square line sample showing different levels of microscale roughness.

6.2.3 CA and RoA

The contact angles of all samples were measured, viewed from both parallel and perpendicular directions. These measurements are summarised in Table 6.5 and Table 6.6 for the square line samples. To aid in comprehension the highest values in each table are highlighted in yellow. The CA of flat, virgin ABS is approximately 90° .⁸¹ When considering the square line samples, it can be seen that two samples have shown among the highest CA values in both the parallel and perpendicular directions; these samples are 500 x 500 and 750 x 250. When comparing the CA values for these samples, the 500 x 500 sample can be designated as the most hydrophobic, with the highest CA values of all square line samples in both parallel and perpendicular directions.

Table 6.5 Parallel CA values of square channel samples. Highest CA values are highlighted in yellow.

	250 μm Lines	500 μm Lines	750 μm Lines	1000 μm Lines
250 μm Spacing	128°	129°	129°	124°
500 μm Spacing	135°	147°	130°	124°
750 μm Spacing	140°	140°	115°	123°
1000 μm Spacing	132°	124°	117°	144°

Table 6.6 Perpendicular CA values of square channel samples. Highest CA values are highlighted in yellow.

	250 μm Lines	500 μm Lines	750 μm Lines	1000 μm Lines
250 μm Spacing	94°	89°	85°	88°
500 μm Spacing	96°	105°	90°	106°
750 μm Spacing	103°	79°	82°	88°
1000 μm Spacing	85°	75°	85°	82°

The significant differences in parallel and perpendicular CA values was also observed in the elongation of the test droplets on some samples, in the direction parallel to the lines. This was especially apparent in the samples with the greatest hysteresis between parallel and perpendicular CA such as 750 x 500 and 1000 x 1000, as shown in Figure 6.10.

The RoA values of these samples were also measured in both the parallel and perpendicular directions. It was found that all test droplets were pinned to all sample surfaces in the direction perpendicular to the lines/channels. The measured RoA of each sample in the direction parallel to the lines/channels is shown in Table 6.7. With the goniometer used in this research, RoA can only be measured up to 70° . Samples which showed droplet movement at less than 70° were measured and their RoA values reported. Samples which did not show droplet movement at less than

Figure 6.10 Photographs of test droplets on square line samples, showing elongation of the droplets. All droplets are $10\ \mu\text{L}$, sample sizes vary.

70°, but showed droplet movement when manually held at 90° are labelled with 90°. Samples on which the test droplets remained pinned when tilted to greater than 90° are denoted as ‘pinned’. It was observed that some samples were also pinned in this parallel direction, but some surfaces successfully controlled the movement of the test droplets in one direction, and only allowed the droplets to roll in the direction parallel to the anisotropic roughness. It was also observed that the droplet movement was very slow for the samples with 250 μm spacing, even compared to those samples with 500 μm spacing. This was likely due to the increased liquid-solid contact in the samples with smaller spacings, inducing greater adhesion between the surface and the droplet. As with the CA measurements, the 500 x 500 sample was determined to be the most hydrophobic sample, as it was found to have the lowest measured RoA.

Table 6.7 Parallel RoA measurements of square channel samples.

	250 μm Lines	500 μm Lines	750 μm Lines	1000 μm Lines
250 μm Spacing	90°	55°	90°	Pinned
500 μm Spacing	60°	30°	90°	Pinned
750 μm Spacing	Pinned	50°	90°	Pinned
1000 μm Spacing	Pinned	Pinned	Pinned	90°

The CA and RoA values of the trapezoid line samples were also measured and are summarised in Table 6.8. Again, the highest values for each measurement are highlighted in yellow. These samples were found to be less hydrophobic than investigated square line samples, with parallel CA values of less than 132°, and as low as 92°, and perpendicular CA values of less than 100°. However, the trapezoid samples were on slightly larger size scales than the square line samples so direct comparison is difficult. Four out of the five samples were also found to have RoA values of 90° or higher. It was found that the sample with the smallest value for A (width of trapezoid) was overall the most hydrophobic with the highest parallel CA and lowest RoA. However, no trapezoid line sample was found to be more hydrophobic than the 500 x 500 square line sample.

Table 6.8 Measured parallel and perpendicular CA values and parallel RoA values of trapezoid cross-sectional line samples. Highest CA values are again highlighted in yellow.

Sample Name	CA _{Para}	CA _{Perp}	RoA
1.5 x 0.5 x 0.5	115°	80°	Pinned
1.5 x 0.5 x 1.0	127°	89°	90°
1.5 x 1.0 x 2.0	92°	96°	Pinned
0.75 x 0.5 x 1.0	132°	80°	44°
1.25 x 0.25 x 1.25	114°	96°	Pinned

Overall, some important points can be concluded from investigation into these samples. Firstly, it was found that samples with narrower lines tended to display more

hydrophobic behaviour, especially with regard to the RoA. This can be explained by considering the adhesive forces between the solid and liquid phases, which increases with increased contact area. Hence, samples with narrower lines have less contact with the droplet and therefore weaker adhesive forces, resulting in lower RoA values and more hydrophobic behaviour. Similar principles can be applied to the channel width. With increased channel width, the contact area between the droplet and the surface is reduced, increasing the hydrophobic behaviour of the surface. However, with widening channels, the problem of the droplet falling into a Wenzel state was seen to occur (refer to Section 1.2.2). Hence, it is necessary to keep the channels wide enough to keep liquid-solid contact to a minimum while still having the channels narrow enough to preclude the droplets from falling into them. It was also found that having an undercut edge, as was present in the trapezoid line samples, did not offer any benefit to the hydrophobicity of the surface, in the samples investigated here. However, investigation into trapezoid lines with similar dimensions to those of the most hydrophobic square line structures would be needed to confirm this. As the 500 x 500 μm square lines sample was found to be the most hydrophobic with respect to both the CA and RoA measurements, this was the designed surface roughness used for further investigations.

6.3 Ion Implantation Studies

Ion implantation (II) was investigated as a surface treatment through a collaboration with Dr Jérôme Leveneur using ion beam equipment at GNS Science. II has been used widely in the past to damage polymer surfaces and increase their wettability. Due to the shallow penetration depth of II, masks can easily be created in order to pattern a surface with the treatment. II was investigated as a surface treatment as it allows for facile chemical patterning of a surface. Therefore, when used in conjunction with 3D printed surfaces, it is possible to design areas of both chemical and physical heterogeneity, in order to closely modify and control the wetting behaviour of a surface across different areas. It was expected that the II treatment would cause increased hydrophilicity of the polymer surfaces and this was investigated by measuring the parallel and perpendicular CA values before and after II treatment. Due to the common occurrence of hydrophobic recovery in polymers treated with II, the CA of samples were not measured immediately after the II treatment, but after 10 days, to allow for some stabilisation of the CA. The perpendicular CA values were also measured again after five months to determine the stability and longevity of the effects of the treatment.

6.3.1 Preparation

Samples were initially prepared for ion implantation, based on results from previous investigations. All samples were 10 mm x 15 mm x 5 mm (length x width x height) rectangular surfaces with lengthwise 500 x 500 μm square cross-sectional channels, spaced 500 μm apart, as shown by the CAD model in Figure 6.11. This sizing and spacing of the lines and channels was chosen as it was found to be the most hydrophobic in Section 6.2. All samples were printed on a MendelMax 3 printer in ABS or PLA using standard printing conditions for each filament as outlined in Section 2.3.2. PLA was used in this section as well as ABS in order to investigate the effect of the ion implantation on more than one substrate. A total of 18 samples were printed. Six of these samples were printed in PLA, and 12 in ABS, with six ABS samples being post-treated with FAS. This FAS treatment was carried out using a 2 wt% solution of FAS.

Figure 6.11 Rendered CAD model of printed samples. Total height of sample is 5 mm, channels are 0.5 mm deep x 0.5 mm high x 15 mm long.

Ion implantation (II) was carried out at GNS Science with the help of Dr Leveneur. The first II samples were prepared using Ar gas with a fluence of 10^{14} , 10^{15} , or 10^{16} atoms cm^{-2} on each of the three kinds of substrate, totalling 9 samples. The second II samples were prepared using CO gas where the C^+ ions were isolated to achieve a fluence of 10^{14} or 10^{15} atoms cm^{-2} on each of the three kinds of substrate (ABS, ABS-FAS, and PLA), totalling 6 samples. Fluence of 10^{16} atoms cm^{-2} of carbon was also achieved on a PLA sample, but not ABS or ABS-FAS samples due to time restrictions. During the II treatment the samples are clamped in the sample holder. The sample holder set up is shown in Figure 6.12. It can be seen that where the clamp is holding the sample, the II cannot affect the surface; this allows for some of the surface to remain untreated for direct comparisons.

Figure 6.12 Schematic showing front and side view of sample holder used in II treatment, with clamp and holder, screws and sample with protruding anisotropic lines, showing how the clamp shadows an area of the sample which remains unaltered by the ion beam.

6.3.2 SEM

SEM and EDS analysis was performed on 5 samples, ABS 10^{16} Ar⁺, ABS 10^{15} C⁺, ABS-FAS 10^{16} Ar⁺, ABS-FAS 10^{15} C⁺, and PLA 10^{16} Ar⁺. The samples were analysed in low vacuum mode, so that the surfaces did not require a conductive coating to be added, allowing analysis of the unperturbed test surface. Due to severe electron beam damage to the PLA, only one PLA sample was analysed and only limited information could be obtained.

The ABS and ABS-FAS samples treated with 10^{15} atoms cm⁻² of C⁺ were found to have significant charging under the electron beam, suggesting poor conductivity of the surface. There was no obvious boundary mark at the top of the sample. There was no difference in the EDS maps of carbon and fluorine across the boundary areas. On both ABS and ABS-FAS samples treated with 10^{16} atoms cm⁻² of Ar⁺, a very clear difference was seen across the boundary of treated/untreated surface, as seen in Figure 6.13. The untreated surface was seen to be very much brighter under the electron microscope than the comparable II treated surface. This brightness is characteristic of charging on the surface when the electrons from the microscope's electron beam are not conducted across the surface and grounded. Hence, this difference in brightness indicates that the treated surface is more conductive than the untreated surface in both the ABS and ABS-FAS substrates treated with 10^{16} atoms cm⁻² Ar⁺. This suggests that the ion beam treatment has indeed carbonised the surface and caused this increase in conductivity. This increased conductivity is likely due to graphene-like carbon material produced on the surface during the II treatment.

EDS analysis of these boundary areas did not detect any difference in the elemental

Figure 6.13 SEM images of boundary between untreated (upper) and treated with 10^{16} atoms cm^{-2} Ar^+ (lower) surfaces areas of ABS (left) and ABS-FAS (right) samples.

composition of the areas before and after treatment, as shown in Figure 6.14. This result was found for both Ar^+ and C^+ treated samples. Line analysis from the untreated to treated area also did not detect any difference in the intensity of carbon or fluorine signals between the two areas, as shown in Figure 6.15.

The difference in surface roughness between treated and untreated areas on the surface of the 10^{16} atoms cm^{-2} Ar^+ ABS-FAS sample was investigated. Due to the high amount of charging in the untreated area the contrast and brightness of the two images is quite different, which makes assessing differences in roughness quite challenging. As seen in Figure 6.16, it seems that the treated area has less surface roughness than the untreated area. Both areas were seen to have unidirectional striation marks a few micrometres wide; these features are likely to have come about in the printing process. In addition to these striations there were numerous micro-scale bumps covering the surface in the untreated area. These bumps were still seen in the treated area but appear to be less defined and protrude less from the surface. However, this difference in appearance could be exaggerated by the difference in contrast and brightness between the two images so it cannot be conclusively determined if the surface roughness has been significantly altered.

Figure 6.14 SEM images (top) and EDS maps (centre and bottom) of boundary area between untreated areas and areas treated with 10^{16} atoms cm^{-2} Ar^+ . Left images: ABS substrate, carbon EDS map (centre). Right images: ABS-FAS substrate, carbon EDS map (centre) and fluorine EDS map (bottom).

Figure 6.15 SEM image (top) and carbon EDS map (middle) of boundary area between untreated area of ABS-FAS sample and area of same sample treated with 10^{16} atoms cm^{-2} Ar^+ , with line analysis profile of carbon (bottom) traversing this boundary showing no significant difference in the concentration of carbon between the two areas.

Figure 6.16 SEM images showing surface roughness of ABS-FAS sample before treatment (left) and after treatment with 10^{16} atoms cm^{-2} Ar^+ (right).

6.3.3 CA Measurements

Untreated Surfaces

Before II treatment the CA values of the samples were tested to determine the variation between replicates. This was done so that any change in measured CA after II treatment could be determined to be a true change due to the treatment and not due to any variation between prints. Below is a summary of the measured CA before II treatment and their 95% confidence intervals (Table 6.9 and Table 6.10).

Table 6.9 Average CA and variation for samples before II treatment, viewed parallel to channels. The column labelled Channels indicates the number of channels the droplet spans.

Sample	Channels	Average CA	95% CI
ABS	One	147°	6.0°
	Two	132°	10.1°
ABS-FAS	One	146°	10.3°
	Two	128°	8.8°
PLA	One	142°	7.1°
	Two	133°	6.6°

Table 6.10 Average CA and variation for samples before II treatment, viewed perpendicular to channels.

Sample	Average CA	95% CI
ABS	103°	1.3°
ABS-FAS	120°	4.2°
PLA	92°	2.9°

As discussed in Section 1.2.6, when comparing CA values measured from a parallel observation perspective, it is important to note how many channels the droplet spans as this can alter the shape, and hence the CA of the droplet. If a droplet

spans two channels as opposed to one channel it will be more spread out across the perpendicular direction and will appear to have a lower measured parallel CA, as shown in Figure 6.17. For this reason it is important to note the number of channels the droplet is spanning upon measurement and to only compare parallel CA values when the measured droplet is spanning the same number of channels.

Figure 6.17 Goniometer image showing difference in apparent parallel CA when droplet spans two channels compared to one channel.

Before II treatment the PLA was found to be the least hydrophobic sample and the ABS-FAS was found to be the most hydrophobic, with ABS slightly less hydrophobic than the ABS-FAS. After II treatment, the parallel and perpendicular CAs of each sample were measured again. These measurements were not taken immediately after treatment, in order to allow some stabilisation of the CA due to hydrophobic recovery. The samples were initially aged for 10 days before CA measurements were taken. It was found that for some of the samples treated with the highest fluence (10^{16} atoms cm^{-2}) the samples wetted and the droplets were in a full Wenzel state. This made measuring both the parallel and perpendicular CA values very difficult as the TCL was obscured or difficult to determine. When viewed from a parallel direction, the TCL was obscured by the edges of the channels. Similarly, when viewed perpendicularly, the edge of the droplet comes to a narrow point and hence it is difficult to determine where the droplet ends to define the TCL, as shown in Figure 6.18. Hence, no CA measurements were taken of these samples and they were denoted as ‘wetted’. However, in the samples that were found to be hydrophilic, some droplets were found to maintain a C-B state and not fully wet the surface. As it was not possible to average a measured CA value for these droplets with the unmeasured CA value of the Wenzel state droplets, neither value was measured and the samples were simply denoted as ‘wetted’. As this behaviour was not observed in any samples before the II treatment, it was deemed sufficient to note this change in behaviour from hydrophobic to hydrophilic, but the change in CA could not be quantified. The fact that water droplets have different wetting behaviour on different

areas of the surfaces suggests a non-uniform surface. Some initial inherent variation between samples and within the same sample was measured before II testing, due to the varied nature of 3D printing. However, this variation was found to be within quite a small range (less than 10%). Hence, it is difficult to conclude if this variation is due to the inherent initial variation in the surfaces from the 3D printing process behaving differently under the ion beam and being exaggerated in the final samples, or due to non-uniform II treatment causing differences across the surface in addition to the already existing variation.

Figure 6.18 Goniometer image of droplets in C-B and Wenzel states, showing difficulty in determining the TCL point when droplets are in the Wenzel state.

The effect of the II treatment was heavily dependent on the substrate, and as such the results of the treatment on each substrate will be discussed separately.

ABS Substrate After II Treatment

The II treatment on the ABS substrate caused an increase in hydrophilicity. This can clearly be seen in the perpendicular CA results, with a decrease in perpendicular CA after II treatment with either Ar^+ or C^+ . The parallel CA results are more complicated due to the added variables in measuring the parallel CA, but it was found that the parallel CA was decreased, greater than initial variation, after II treatment with the highest fluence (10^{16} atoms cm^{-2}) of Ar^+ . A summary of measured parallel and perpendicular CA values for ABS samples is presented in Table 6.11.

The perpendicular CA values indicate an increase in hydrophilicity after treatment but there is no indication of a trend between fluence and CA, with increased fluence resulting in similar CA values, see Figure 6.19. This could be due to a saturation point with regard to the change of surface chemistry. The Ar^+ ions were expected to damage the polymer backbone of the ABS and cause carbonisation and a more hydrophilic surface. These results suggest that even at the lowest tested fluence of 10^{14} atoms cm^{-2} , all of the ABS at the surface is completely damaged, to the point

Table 6.11 Parallel and perpendicular CA of ABS samples before and after II treatment. Channels column denotes how many channels the droplet spans in parallel view. Fluence is given in atoms cm⁻².

Treatment	Fluence	Channels	CA _{Para}	95% CI	CA _{Perp}	95% CI
Blank	0	One	147°	6.0	103°	1.3
		Two	132°	10.1		
Ar ⁺	10 ¹⁴	Two	122°	2.6	84°	3.1
Ar ⁺	10 ¹⁵	One	148°	3.7	86°	5.3
Ar ⁺	10 ¹⁶	One	124°	0.9	85°	5.6
Blank	0	One	147°	6.0	103°	1.3
C ⁺	10 ¹⁴	One	138°	2.1	90°	1.8
C ⁺	10 ¹⁵	One	141°	7.5	88°	7.0

where an increase in fluence has no effect, as it cannot further damage the surface. This indicates that ABS has a small threshold for damage by II and this has been reached with even the lowest fluence tested.

Figure 6.19 Graph of perpendicular CA of ABS samples before and after II treatment with Ar⁺ or C⁺.

ABS-FAS Substrate After II Treatment

The effect on the ABS-FAS substrate was much more obvious with a large decrease in perpendicular CA to the hydrophilic range (less than 65°) with high fluence of Ar⁺. This change was also noticeable by eye as it was observed that for the 10¹⁶ Ar⁺ sample, some droplets fell into a Wenzel state and wetted the surface. As seen in the table below, this caused the CA values to be unmeasurable. A summary of

measured parallel and perpendicular CA values for ABS-FAS samples is presented in Table 6.12.

Table 6.12 Parallel and perpendicular CA of ABS-FAS samples before and after II treatment. Channels column denotes how many channels the droplet spans in parallel view. Fluence is given in atoms cm⁻².

Treatment	Fluence	Channels	CA _{Para}	95% CI	CA _{Perp}	95% CI
Blank	0	One	146°	10.3	120°	4.3
		Two	128°	8.8		
Ar ⁺	10 ¹⁴	One	132°	9.9	100°	0.6
Ar ⁺	10 ¹⁵	One	140°	9.9	85°	0.8
Ar ⁺	10 ¹⁶	One	Wetted	-	Wetted	-
Blank	0	One	146°	10.3	120°	4.3
C ⁺	10 ¹⁴	One	141°	3.9	119°	0.9
C ⁺	10 ¹⁵	One	137°	11.2	92°	3.9

The samples with measurable parallel CA values do not suggest a trend towards higher hydrophilicity with increased fluence, in fact none of the measured values fall outside of the 95% confidence interval of the average parallel CA value of initial blank samples, within their respective error margins. However, we can draw the conclusion that the II treatment has effectively increased the hydrophilicity by looking at the perpendicular CA results and the visual assessment of the droplets sitting in a Wenzel state on the surface of the sample treated with the highest fluence. This Wenzel state can be seen in Figure 6.20. It was observed that droplets in the Wenzel state wetted and spread along the surface in the direction parallel to the channels more than the droplets in the C-B state.

The results of the perpendicular CA measurements suggest an inverse relationship between perpendicular CA and fluence, with samples treated with higher fluence exhibiting lower perpendicular CA values, see Figure 6.21. This trend can be seen especially well in the results from the Ar⁺ treatment as the highest fluence sample was found to exhibit truly hydrophilic behaviour, but a similar trend is also seen in the results for the C⁺ treatment. For the high fluence Ar⁺ sample, test droplets were found to wet the surface. This prevented an accurate measurement of the CA being taken and so this sample has been plotted in the graph with a CA value of 0° to show the dramatic increase in hydrophilicity.

When compared to the results of the ABS samples, the ABS-FAS samples show a significant difference. Before II treatment the ABS-FAS samples had a slightly higher perpendicular CA than the ABS samples, but the parallel CAs were about the same. After the treatment we can see a dramatic difference in the ABS-FAS samples being rendered hydrophilic by the high fluence Ar⁺ II treatment. Conversely, the same high

Figure 6.20 Top: Photographs of the same C-B and Wenzel state droplets showing greater spreading and increased wetting of Wenzel state droplet. Bottom: Goniometer view of parallel CA measurement showing the same C-B and Wenzel state droplets.

Figure 6.21 Graph of perpendicular CA of ABS-FAS substrates before and after II treatment with Ar⁺ or C⁺. Due to wetting, CA value not measured for 10¹⁶ Ar⁺ sample, plotted as 0° to show hydrophilicity.

fluence Ar^+ treatment on the ABS substrate caused a similar change as lower fluence II treatment and the samples remained overall generally hydrophobic. It is clear that the FAS surface treatment has changed the surface chemistry of the substrates and the results of the damage due to the ion beam are significantly different than the results of damage to the ABS substrate alone. It is reasonable to conclude that the damage to the FAS produces a more hydrophilic surface chemistry than the products of damage to the ABS. The other factor that could be causing this difference is if the damage to one substrate caused differences in the surface roughness between substrates, but SEM imaging suggested similar roughness between the two substrates after II treatment, so this explanation is unlikely.

PLA Substrate After II Treatment

The effect of II treatment on the PLA substrate was again different to the ABS substrate, but similar trends were observed as with the ABS-FAS substrate. The PLA samples were found to have varied changes in both parallel and perpendicular CA after treatment. A summary of measured parallel and perpendicular CA values for PLA samples is presented in Table 6.13. Some C^+ treated samples had CA values slightly higher than the average untreated values and many C^+ or Ar^+ treated samples had lower measured CA values but these still fell within the 95% CI of the initial untreated samples. The perpendicular CA values did show a decrease after II treatment, but no consistent trend was observed with respect to increased C^+ fluence (see Figure 6.22). However, as with the ABS-FAS substrate, high fluence Ar^+ was found to render the surface hydrophilic and test droplets were observed to wet the surface. With respect to the C^+ treatment, it is difficult to draw a conclusion on the effect of the treatment and the effect of higher fluence. However, it can be seen that high fluence treatment with Ar^+ has successfully increased the wettability and hydrophilicity of the surface, to the point where water droplets wet the sample and the droplets sit in a Wenzel state.

6.3.4 Longevity and Hydrophobic Recovery

As hydrophobic recovery is known to occur in polymer surfaces treated with II, it was necessary to determine the longevity of the effects of the II treatments and to determine whether the measured CA values of the surfaces after 10 days were stable. The chemical changes that occur after II treatment and how this can lead to

Table 6.13 Parallel and perpendicular CA of PLA samples before and after II treatment. Channels column denotes how many channels the droplet spans in parallel view. Fluence is given in atoms cm⁻².

Treatment	Fluence	Channels	CA _{Para}	95% CI	CA _{Perp}	95% CI
Blank	0	One	142°	7.1	92°	2.9
		Two	133°	6.6		
Ar ⁺	10 ¹⁴	Two	131°	10.8	80°	0.8
Ar ⁺	10 ¹⁵	One	137°	10.9	68°	2.3
Ar ⁺	10 ¹⁶	One	Wetted	-	Wetted	-
Blank	0	One	142°	7.1	92°	2.9
C ⁺	10 ¹⁴	One	143°	8.6	90°	6.3
C ⁺	10 ¹⁵	One	137°	12.6	73°	6.3
C ⁺	10 ¹⁶	One	143°	8.2	86°	2.2

Figure 6.22 Graph of perpendicular CA of PLA substrates before and after II treatment with Ar⁺ or C⁺. Due to wetting, CA value not measured for 10¹⁶ Ar⁺ sample, plotted as 0° to show hydrophilicity.

hydrophobic recovery are discussed in Section 1.5. As the most significant effect of II treatment was seen in perpendicular CA values, these values were remeasured five months after the initial measurements on the aged samples. These measurements are shown in Table 6.14, Table 6.15 and Table 6.16, and are summarised in Figure 6.23. All samples were stored in ambient conditions, in a partitioned, clear plastic box to protect the surfaces from dust, while they remained exposed to air and light.

Table 6.14 Perpendicular CA values of ABS samples before and after II treatment, measured 10 days or 5 months after II treatment. Fluence is given in atoms cm^{-2} . Blank samples were measured before II treatment.

Treatment	Fluence	CA _{Perp} 10 days	CA _{Perp} 5 months (Aged)
Blank		103°	-
Ar ⁺	10 ¹⁴	84°	91°
Ar ⁺	10 ¹⁵	86°	83°
Ar ⁺	10 ¹⁶	85°	85°
Blank		103°	-
C ⁺	10 ¹⁴	90°	100°
C ⁺	10 ¹⁵	88°	83°

Table 6.15 Perpendicular CA values of ABS-FAS samples before and after II treatment, measured 10 days or 5 months after II treatment. Fluence is given in atoms cm^{-2} . Blank samples were measured before II treatment.

Treatment	Fluence	CA _{Perp} 10 days	CA _{Perp} 5 months (Aged)
Blank		120°	-
Ar ⁺	10 ¹⁴	100°	104°
Ar ⁺	10 ¹⁵	85°	92°
Ar ⁺	10 ¹⁶	Hydrophilic	95°
Blank		120°	-
C ⁺	10 ¹⁴	119°	101°
C ⁺	10 ¹⁵	92°	106°

Table 6.16 Perpendicular CA values of PLA samples before and after II treatment, measured 10 days or 5 months after II treatment. Fluence is given in atoms cm^{-2} . Blank samples were measured before II treatment.

Treatment	Fluence	CA _{Perp} 10 days	CA _{Perp} 5 months (Aged)
Blank		91°	-
Ar ⁺	10 ¹⁴	80°	92°
Ar ⁺	10 ¹⁵	68°	81°
Ar ⁺	10 ¹⁶	Hydrophilic	Hydrophilic
Blank		91°	-
C ⁺	10 ¹⁴	90°	94°
C ⁺	10 ¹⁵	73°	92°
C ⁺	10 ¹⁶	86°	81°

For the ABS substrate it was determined that the samples had undergone hydrophobic recovery. It was determined that the samples treated with lower fluence were subject to more recovery than those treated with higher fluence. As discussed in

Figure 6.23 Graph of perpendicular CA of ABS (top) ABS-FAS (middle) PLA (bottom) substrates before and after II treatment with Ar⁺ or C⁺, measured 10 days or five months (Aged) after treatment. Due to wetting, CA value not measured for hydrophilic samples, plotted as 0° to show hydrophilicity.

Section 1.5, this is the expected recovery pattern of polymers treated with II. At high fluence, II can cause irreversible damage to the chemical structure of the surface, preventing hydrophobic recovery in samples treated with higher fluence. The threshold of fluence at which irreversible damage occurs, differs between polymer surfaces; for this substrate, it appears that the irreversible damage occurs at fluence of 10^{15} atoms cm^{-2} and higher, as only the samples treated with fluence of 10^{14} atoms cm^{-2} showed evidence of reversible damage and hydrophobic recovery. After recovery, these samples still showed signs of some remaining damage as the CA values remained lower than those measured before II treatment, but only by approximately $5 - 10^\circ$. Again, this is expected, as samples treated with II have a carbonised surface even after hydrophobic recovery. With respect to hydrophobic recovery, the chemistry of the ion beam was not seen to have a significant effect as samples treated with Ar^+ and C^+ were seen to give similar results.

Hydrophobic recovery was also measured for the ABS-FAS samples. However, this hydrophobic recovery was dependent on the ion used in the II treatment. All samples treated with Ar^+ were found to be subjected to hydrophobic recovery. This indicates that the threshold of sufficiently high fluence to cause irreversible damage to the chemical structure was not achieved. This is surprising as the sample treated with 10^{16} atoms cm^{-2} of Ar^+ was significantly affected by the II treatment and rendered generally hydrophilic, but after five months this hydrophilicity was lost and the sample was measured to have a perpendicular CA of 95° . After five months, all samples were measured to have approximately the same perpendicular CA value, but this value was approximately 20° less than the value measured before II treatment, again due to the carbonisation of the surface that occurs during II treatment. The ABS-FAS samples treated with C^+ were found to behave quite differently. Two samples of ABS-FAS substrate were treated with C^+ at fluences of 10^{14} atoms cm^{-2} or 10^{15} atoms cm^{-2} . The higher fluence sample was found to behave as expected, the decreased hydrophobicity measured 10 days after treatment was found to have recovered somewhat after five months, but the perpendicular CA remained approximately 15° lower than the untreated sample. Conversely, the sample treated with low fluence C^+ was found to have little to no change in perpendicular CA 10 days after II treatment. However, after 5 months, this sample was found to have a much lower perpendicular CA, a decrease of 20° . This was an unexpected result. It is proposed that this difference is due to defects in the sample. If this were the case, it would be possible that the when the sample was measured after 10 days and after 5 months, different surface areas were tested that had different surface properties. These potential defects could be due to a fault in the printing process of this sample or due to non-uniform application of FAS or II treatments, causing differences across the surface.

The PLA substrate was also found to be subjected to hydrophobic recovery in the expected pattern, whereby samples treated with lower fluence were seen to recover, but those treated with higher fluence did not. For the PLA samples there was a slight difference in hydrophobic recovery dependent on the ion used in the II treatment. For the samples treated with less than 10^{16} atoms cm^{-2} C^+ were found to recover significantly, to the same CA value as was measured before treatment. The sample treated with 10^{16} atoms cm^{-2} was found to have the same CA value after five months as was measured after 10 days, indicating that at this fluence, irreversible damage had occurred and so no hydrophobic recovery took place. For the samples treated with lower fluence Ar^+ (less than 10^{16} atoms cm^{-2}), hydrophobic recovery was found to occur. However, where the sample treated with 10^{14} atoms cm^{-2} was found to have the same CA value after 5 months as was measured before II treatment, the sample treated with 10^{15} atoms cm^{-2} was found to recover, but remained more hydrophilic than the untreated sample (CA decrease of approximately 10°). Lastly, the sample that was treated with 10^{16} atoms cm^{-2} Ar^+ was found to have been rendered hydrophilic 10 days after II treatment, and was found to be hydrophilic still after five months. This suggests that the threshold for irreversible damage is 10^{16} atoms cm^{-2} Ar^+ , and this sample did not undergo hydrophobic recovery. However, as the CA of this sample was not quantitatively measured, it cannot be determined if this sample has been subject to some degree of hydrophobic recovery while still remaining generally hydrophilic or if the sample has not been subject to hydrophobic recovery at all.

6.4 Conclusions

Anisotropy was first investigated using the inherent layering of the 3D printing process. This roughness was successfully created and varied by printing samples with different layer height settings at different angles. It was found that this roughness alone was sufficient to control the spreading of a droplet across the surface, where spreading was promoted in the direction parallel to the surface roughness. However, it was also found that this roughness was not sufficient to control the movement of a droplet across the surface in one direction.

Increased macro-scale roughness was achieved through designing line/channel structures and printing these atop simple bases. The width and spacing of the lines and channels was based on the size and spacing of features on the *Stenocara* beetle. This width and spacing was altered as well as the cross-sectional shape of the lines (and consequently the channels). It was found that using a trapezoid shaped line

to incorporate an under-cut edge did not have a significant effect on increasing the control of a water droplet on a surface on the size scales tested, and that square shaped lines were sufficient to induce this control. It was found that the spacing of the lines in relation to the size of the droplet was important as the spacing must be small enough to preclude the droplet from falling into a Wenzel state between the lines. It was also found that the width of the lines was important as an increase in line width represents an increase in solid-liquid contact area and hence, increased adhesion forces. For a 10 μL droplet, it was found that a sample with square lines 500 μm wide and 500 μm apart was the most hydrophobic surface. It was also found that this sample could most effectively control the movement of a droplet across the surface by prohibiting movement in the direction perpendicular to the lines/channels and promoting movement in the direction parallel, with a RoA of 30° in this direction.

Control of the wettability of the optimal 500 x 500 μm line/channel structure was further investigated using II surface treatment with Ar^+ and C^+ ion beams. Three substrates were tested, including ABS, ABS-FAS and PLA. It can generally be concluded that II treatment on 3D printed substrates increases the hydrophilicity of the surface. This was seen to occur to the greatest extent in the ABS-FAS and PLA samples with high fluence Ar^+ where hydrophilic surfaces were produced. However, some samples were subject to hydrophobic recovery and the hydrophilicity seen in the high fluence Ar^+ ABS-FAS sample was lost within five months of treatment. However, the hydrophilic surface of the high fluence Ar^+ treated PLA sample was retained for up to five months. With further investigations at higher fluence, the hydrophobic recovery of the other substrates could be halted after irreversible damage has occurred. Hence, with further research, it is possible that this long term, formal hydrophilicity could be achieved on all substrates. Evidence of long term increased hydrophilicity (decreased CA) was seen in all Ar^+ treated samples, but results for the C^+ treatment were somewhat varied and inconclusive. This shows that Ar^+ II can be used in conjunction with 3D printing to design surfaces with defined areas of particular chemical and physical properties affecting the hydrophobicity of the surface, allowing for great control over the wettability of such designed surfaces.

The results produced here are novel as existing literature does not report investigations into the effects of II treatment on substrates investigated here. Hence, this is a potential area for future research and development as the literature currently lacks information on the effects of II treatments on both ABS polymers and surfaces treated with FAS. In this work, the wetting behaviour of surfaces has been altered using both 3D printing and II treatments. The ease of patterning with both 3D printing and II treatments could allow for the specific design of wetting behaviours

across a surface. Hence, further development of this work could produce novel technologies for application in many industries where controlled wetting is required, such as refrigeration.

Chapter 7

Conclusions

7.1 Wool Fabrics

The hydrophobicity of wool fabrics was increased using both physical and chemical modifications. Firstly, investigations were carried out to develop a treatment to increase the hydrophobicity of wool fabrics involving only physical modifications, using only water and detergent. This led to the conclusion that hand-felting of the wool fabrics was successful in generally increasing the contact angle of the fabrics. This increase in contact angle was achieved through significant increase in the macro- and micro-scale roughness of the fabric surface. This increased roughness was crucial to increasing the hydrophobicity of the fabric, but compromised the desired soft texture of the wool. Subsequent trimming of the hand-felted samples was also investigated in order to restore the soft texture of the fabrics, but was found to lead to a lower CA than the original unmodified fabrics and so was deemed ineffective. While the rougher texture of the felted fabrics may limit the areas of application, hand-felting was found to successfully increase the hydrophobicity of wool fabrics and so felting was determined to be a potentially commercially viable treatment for increasing the hydrophobicity of wool fabrics for certain applications.

Due to the limited commercial applicability of hand-felted fabrics, further treatments were investigated using chemical modifications to increase the hydrophobicity of wool fabrics without compromising the soft texture of the wool fabric. The surface roughness of the individual wool fibres within the fabrics was increased by the addition of nano- or micro-particles to the fibre surface. This was first achieved through gold nanoparticle functionalisation of the wool fibres. This nanofunctionalisation successfully increased the surface roughness of the wool, but the effect of this

increase in surface roughness was outweighed by the increased chemical hydrophilicity of the metallic nanoparticles on the surface. Hence, this nanofunctionalisation treatment required a subsequent FAS treatment to render the surface chemically hydrophobic which led to a significant increase in hydrophobicity, compared to the untreated fabric and the fabric treated with FAS alone. While the use of gold nanoparticle functionalisation followed by FAS treatment was found to be successful in significantly increasing the hydrophobicity of the wool fabrics, the high cost of gold and necessity of the secondary FAS treatment were not commercially viable as industry treatments.

In following experiments Ag/AgCl functionalisation was investigated. The Ag/AgCl functionalisation was found to significantly increase the surface roughness of the wool fibres in the fabric, and the functionalised fabrics were found to have increased hydrophobicity, without the need for a subsequent FAS treatment. Although Ag/AgCl is also chemically hydrophilic, in this treatment the increase in surface roughness was sufficient to outweigh the effect of increased chemical hydrophilicity and result in a net increase in hydrophobicity, demonstrated by an increase in contact angle and decrease in roll-off angle. Ag/AgCl functionalised fabrics were also tested in an experiment more closely replicating situations encountered by commercial fabrics, to determine how water-repellent the fabrics would be in every-day use. The Ag/AgCl treated fabrics performed better in these tests than the untreated fabrics, indicating that the Ag/AgCl treatment could be useful as a commercial treatment to increase the water-repellency of wool fabrics. Ag/AgCl has been shown to be antimicrobial so not only are treated fabrics rendered more hydrophobic and more water-repellent, they are also rendered antimicrobial, further increasing the commercial potential for this treatment. However, the Ag/AgCl treatment also colours the fabrics and so another alternative functionalisation was investigated, CaCO_3 . CaCO_3 is a white, low-cost material that can be easily synthesised in a precipitation method similar to that used in the Ag/AgCl functionalisation. CaCO_3 functionalisation was found to increase the hydrophobicity of the wool fabrics with respect to contact angle and roll-off angle, but the treated fabrics did not perform well in tests more closely replicating every-day use.

Overall the process of felting was found to successfully increase the hydrophobicity of wool fabrics, but the consequent loss of the desired soft texture of the fabric could likely limit the potential applications of fabrics subjected to such a process. However, the functionalisation of wool fabrics with inorganic nano- and microparticles was found to also successfully increase the hydrophobicity of wool fabrics without compromising the texture of the surface. The CaCO_3 functionalisation was found to increase the hydrophobicity without altering other properties of the wool fabric

such as texture and colour, but the increase in hydrophobicity was not optimal. The Ag/AgCl functionalisation was found to increase the hydrophobicity to a greater extent than the CaCO₃ functionalisation, but also rendered the fabric a purple colour. However, while the Ag/AgCl treatment changed the colour of the fabric, it also added antimicrobial activity to the surface, so while the colour may limit the potential applications of fabrics treated with this process, other applications are made available by the incorporation of this antimicrobial activity.

7.1.1 Future Work

The results of the Ag/AgCl and CaCO₃ functionalisation treatments were very promising and further investigations into the optimisation of these functionalisations and properties of the functionalised fabrics would be of great value. As the CaCO₃ functionalisation does not negatively effect the appearance or texture of the fabric, optimisation of this process would be particularly useful. The current research only investigated the CaCO₃ functionalisation using one synthetic method and one concentration of CaCO₃, so optimisation of this process could allow for more significant increases in the hydrophobicity of the treated fabrics. If such an increase was possible with the CaCO₃ functionalisation, this process would show great promise in the commercial wool finishing industry, as it is cheap, facile and does not alter the other properties of the fabrics.

Ag/AgCl is known to be antimicrobial and so it is important to obtain accurate measurements of the antimicrobial activity of these Ag/AgCl treated fabrics in future research. Positive results of antimicrobial activity studies would add value to these fabrics in industry and increase the number of potential applications.

Further testing of the treated fabrics is also required. The fabric industry has a range of standardised tests to determine the performance of fabrics in different conditions for different purposes, such as durability and wash fastness. For these processes to be adopted into industry, the treated fabrics must meet the specified standards of the industry, and so these must first be tested for both the Ag/AgCl and CaCO₃ functionalisations.

7.2 3D Printed Polymer Surfaces

3D printing was used as a rapid prototyping method in developing both highly hydrophobic surfaces and surfaces with controlled wetting behaviour. First, FDM 3D printing was used to produce ABS surfaces with an array of specifically designed microscale features to achieve high levels of roughness and highly hydrophobic behaviour. This was done by operating the printer in a non-conventional way, to produce features of a smaller size. The nature of the extrusion itself also contributed to the obtained surface roughness by creating small striation-like features on the surfaces. The designed surface roughness in conjunction with the smaller striations gave a degree of hierarchy to the surface, and although this roughness was all on the microscale, high levels of hydrophobicity were achieved, with contact angle values of up to 143° measured after functionalisation with a fluoroalkyl silane (FAS). The size and spacing of the designed microscale roughness was optimised to give the highest level of hydrophobicity and an optimised sample was then also functionalised with silver nanoparticles and FAS. The silver nanoparticles added antimicrobial activity to the surface and the FAS restored the chemical hydrophobicity of the surface after the silver functionalisation. This produced a surface that was both highly hydrophobic and antimicrobial. With these properties, these surfaces can prevent the spread of dirt and bacteria. Such surfaces have applications in many industries, including healthcare and public transport areas, where cross-contamination and the spread of germs is an issue.

FDM 3D printing was also used to produce surfaces with anisotropic wetting behaviours. To achieve anisotropy in the wetting behaviour, these surfaces had anisotropic roughness, with surface features extended in one direction across the surface. Firstly, this roughness was produced by the inherent layering of FDM. This was found to successfully induce anisotropic wetting in the surface, with droplets observed to be elongated in the direction parallel to the lines of the layers. However, these samples were found to be only slightly hydrophobic, and so the use of more exaggerated roughness on a more hydrophobic polymer was investigated. This was done by printing protruding lines on top of a flat substrate. The size dimensions of these lines were based on the size dimensions of the features found on the *Stenocara* beetle. Different sizes and spacings of lines were investigated, as well as different cross-sectional shapes. These variables were optimised to produce a surface with high hydrophobicity and a low roll-off angle in the direction parallel to the lines but with a high roll-off angle in the direction perpendicular to the lines. Hence, the movement of water droplets across this surface could be controlled, as movement was allowed in the parallel direction, but halted in the perpendicular direction.

The wetting behaviour of the optimal anisotropic surface was then manipulated further, through subsequent physical and chemical treatments to alter the chemistry of the surface. Several replicates of this optimal sample were produced, and several combinations of physical and chemical treatments were investigated. Firstly, some surfaces were functionalised with FAS. This served to increase the chemical hydrophobicity of the surface, and alter the surface chemistry to be affected by the physical treatment. The surfaces were then treated with ion implantation (II) with Ar^+ and C^+ ions. The II treatment damaged the polymers at the surface and successfully decreased the hydrophobicity of the samples, especially those treated with Ar^+ ions. In some cases this decrease in hydrophobicity was sufficient to render the surfaces formally hydrophilic. However, after some months, hydrophobic recovery was found to have occurred in most samples and the surfaces were once again hydrophobic, but still less hydrophobic than before the II treatment. These results were completely novel, as there is no reported data on the effect of II treatment on FAS treated surfaces. The results obtained here suggest that the use of FAS functionalisation and II treatment together, may allow for the control of wetting behaviour of surfaces across many different substrates, allowing for the application of these processes in many different industries for many different purposes.

7.2.1 Future Work

While the highly hydrophobic sample produced in the first part of this work was successfully functionalised with silver nanoparticles, these nanoparticles did not have a significant effect on the hydrophobicity of the surface. Hence, it would be worthwhile to optimise the silver nanofunctionalisation method, in order to create more surface roughness and further increase the hydrophobicity of the functionalised surface. It is also important to quantitatively analyse the antimicrobial activity of these surfaces and their ability to reduce the spread of dirt and bacteria, through standardised industry testing. This would serve to increase the performance and value of these surfaces in industrial applications.

The use of II treatment to hydrophilise a surface showed great promise, and its effect on the FAS is of particular interest, as the FAS can be applied to many different substrate materials. However, the FAS functionalised surface was found to undergo hydrophobic recovery. Further investigation into the II treatment of FAS functionalised surfaces would be of great value. Firstly, it is important to determine if II treatment at higher fluence can prevent the hydrophobic recovery from occurring, so that a stable hydrophilic surface could be produced. Also, the effect of II treatment on different surfaces functionalised with FAS should be examined, to determine if

the chemistry of the underlying substrate affects the hydrophilisation. If the underlying chemistry was found to have no effect on the hydrophilisation, this would allow for the FAS and II treatment to be used on a number of different substrates for a number of different commercial applications, and would be a very valuable process to develop.

In addition, the II treatment used here can easily be applied through a mask, in order to selectively treat specific areas of a surface. Among numerous other potential applications, this allows for the design of a water harvesting device. Research into this could be done by printing a surface with the designed anisotropic line structures, functionalising the surface with FAS and then selectively treating some areas with II to create areas of hydrophilicity. This would result in a surface with areas of both hydrophilicity and hydrophobicity, with the hydrophobic areas preferentially directing the movement of water in one direction. Such a surface would be ideal as a water harvesting device.

Conference Presentations and Publications

Conference Presentations

Cook, M. J.; Gilbertson, L; Johnston, J. H.; Miller, T. “3D Printed Hydrophobic and Antimicrobial Nanofunctionalised Surfaces” *Nanotech France 2015 International Conference and Exhibition*, Paris, France, 15-17 June 2015.

Cook, M. J.; Johnston, J. H. “Investigation of the Wetting Behaviour of Nanofunctionalised Wool Fabrics” *CIMTEC 2016 the 5th International Conference on Smart and Multifunctional Materials, Structures and Systems*, Perugia, Italy, 5-9 June 2016.

Conference Presentations and Proceedings Publications

Cook, M. J.; Johnston, J. H.; Leveneur, J. “Anisotropic Wetting Behaviour of Modified 3D Printed Micro-Structured Polymer Surfaces for Water Harvesting” *TechConnect World Innovation Conference and Expo*, National Harbor, MD, United States of America, 14-17 May 2017.

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