Special Wettability Coatings, Films and Slippery Liquid Infused Porous Surfaces with Self-cleaning, Anti-icing and Anti-fogging Applications

by

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Declaration

I, Frances Heale, confirm that the work presented in this thesis is wholly my own. Where information has been derived or obtained from other sources, I confirm that this has been indicated as such.
Acknowledgements

Both the experimental and written parts of this doctorate would not have been possible without the practical, and at times emotional, support provided by the people I am proud to mention here.

Firstly, to my supervisors Claire and Ivan, I will always be grateful for your continual help over the past five, yes five, years. You both have been more than willing to share your knowledge, time, guidance and kindness. I have learnt a lot, and for that I am extremely thankful. Aside from contributing to the many successes of this project, I always felt that you both have had my best interests at heart, especially when things weren’t going quite as smoothly. I would also like to mention my appreciation for your support during what felt like my endless job hunt and my many failed conference trips. No thanks to broken ribs, chicken pox, Covid19, the list goes on. Finally, I hope you won’t mind me mentioning that I’ve come to consider you really good friends. Once again, thank you.

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Lastly, I’d like to formally thank EPSRC M3S and Akzonobel for funding my research and Dr Suraj Pawar for assisting me with all profilometry and digital microscopy measurements.
Abstract

This thesis presents research into the use of highly functional special wettability surface technologies for the enhancement of smart decorative paint formulation, self-cleaning materials and anti-icing and anti-fogging devices. Sample preparation via wet deposition, aerosol assisted chemical vapour deposition (AACVD) and lubricant spin coating afforded stain resistant superhydrophobic, self-cleaning water/ice/fog retardant and slippery liquid infused porous surface (SLIPS) materials respectively.

In answer to the paint industry’s desire for an economically viable self-cleaning decorative paint, low toxicity and reduced cost SiO$_2$ particles were incorporated into aqueous formulations containing octadecanoic acid (FA C$_{18}$), copolymer dispersant materials and an acrylic latex binder. Practical formulation workability was optimised using a refined FA C$_{18}$/SiO$_2$ ratio to produce hydrophobic painted surfaces. TiO$_2$ particle dopant studies were completed to assess the impact of multiple minerals on the resulting sample functionality.

Superhydrophobic and self-cleaning properties were further enhanced with CaCO$_3$ particles in octadecanoic acid (FA C$_{18}$) and acrylic latex containing aqueous systems. A range of TiO$_2$ dopant particle loadings were consequently introduced to achieve an optimised superhydrophobic drawn down paint, average water contact angle of 154±5°. Commercial paint additives including a thickening hydroxyethylcellulose Natrosol and a hydrophobic aminofunctional siloxane were explored prior to the draw down of said formulation as a self-cleaning top coat paint. Stain resistance testing identified samples that displayed the greatest resistance to red wine, tea and coffee staining.

Other special wettability surfaces with alternative anti-icing and anti-fogging applications have been produced via aerosol assisted chemical vapour deposition (AACVD). TiO$_2$-SnO$_2$ thin film composites were consequently spin coated with a Krytox lubricant. Resulting slippery liquid infused porous surfaces (SLIPS) had underlying intricate nano and micro protrusions, which contributed to the samples’ exceptional anti-icing and anti-fogging properties.

The final study stream focused on AACVD thin films that were transparent, superhydrophobic
and self-cleaning in nature. TiO$_2$ or SiO$_2$ particles were combined with a fluorinated and non-fluorinated polymer precursor mixture. Particle and polymer loadings and temperature variations were comprehensively explored to produce a final optimised thin film, with average contact angles reaching 167° that showed Cassie-Baxter water droplet rolling.
Impact Statement

Work conducted in this doctorate focussed on the production of facile and novel self-cleaning decorative paints and aerosol assisted chemical vapour deposition (AACVD) thin films with transparent superhydrophobic self-cleaning functional properties or with further slippery liquid infused surface modification for anti-icing and anti-fogging applications.

The addition of superhydrophobic inducing reagents to aqueous commercial paint formulations has been heavily under researched and favourable results have been limited. As such, the work conducted in this degree afforded water repellent octadecanoic acid (FA C_{18}) functionalised SiO$_2$ particle containing model commercial paints. Although water contact angles fell slightly short of the desired superhydrophobic functionality, as the mixed Cassie-Baxter/Wenzel surfaces had a maximum average of 130±8°, a significant step change towards the generation of a low cost and low toxicity self-cleaning decorative product had been achieved.

Superhydrophobic and self-cleaning characteristics were first realised in this research’s decorative aqueous paints using CaCO$_3$ particles with further FA C$_{18}$ modification. An exceptionally high average water contact angle of 154±5° was achieved on a TiO$_2$ particle doped, 50 wt%, CaCO$_3$ containing drawn down paint. Rheology modifiers and commercially viable siloxane hydrophobic coating additives were simultaneously incorporated without effecting a decrease in water repellency or cleaning properties. The same formulation was tested as a top coat on Dulux Trade Diamond Matt white paint. Red wine, tea and coffee stain resistance was noted and the formulation therefore had great appeal to industrial sponsors and coating specialists.

Special wettability surfaces generated via aerosol assisted chemical vapour deposition (AACVD) with subsequent slippery lubricant infusion were investigated for their exceptional anti-icing and anti-fogging performance. The first successful example of TiO$_2$/SnO$_2$ thin film composites for slippery liquid infused porous surface (SLIPS) production resulted in ice accretion prevention for >30 min in -10 °C conditions. Unique AACVD solvent systems afforded a variety of thin film surface morphologies and had a significant impact on surface porosity. The most intricate nano and mi-
cro flowered porous topographies, created from an ethyl acetate/dichloromethane solvent system, allowed substantial lubricant retention and therefore imparted exceptional anti-icing, anti-frosting and anti-fogging properties for potential transportation and packaging industrial use.

Final studies surrounded the generation of AACVD thin films from SiO₂ particles with 1H,1H,2H,2H-perfluorooctyltriethoxysilane (FAS C₈) and polydimethylsiloxane (PDMS) polymers. There are few literature examples of nanoparticle use in AACVD precursor solutions, however, their combination with said polymers in an ethyl acetate solvent generated first generation films with an average water contact angle of 167±2°. Water droplets bounced on these Cassie-Baxter type surfaces and exceptionally high light transmittance was recorded across the visible spectrum, 91%. The precise particle size control allowed fine tuning of superhydrophobicity, self-cleaning and transparent properties, which are of great use in the following applications: eye glasses, mobile phone screens, transportation wind shields, mirrors, solar cells, flooring and windows.

Therefore, substantial advancements to the special wettability surface field have been recorded in the four research streams presented in this thesis. Not only have the materials been developed from a research angle but intricate refinements have afforded near marketable coatings, especially in the case of the functional decorative paints.
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Abbreviations

AACVD  Aerosol assisted chemical vapour deposition
SLIPS  Slippery liquid infused porous surfaces
FA C\textsubscript{18}  Octadecanoic acid
PDMS  Polydimethylsiloxane
PTFE  Polytetrafluoroethylene
iCVD  Initiated chemical vapour deposition
UV    Ultraviolet
ESEM  Environmental scanning electron microscopy
SEM   Scanning electron microscopy
TEM   Transmission electron microscopy
TEOS  Tetraethyl orthosilicate
PMTFPS Polymethyltrifluoropropylsiloxane
POSS  Polyhedral oligomeric silsesquioxane
RAFT  Reversible addition fragmentation chain transfer
HBFP  Hyperbranched fluoropolymers
PEG   Poly(ethylene glycol)
LDPE  Low density polyethylene
PVA   Polyvinyl acetate
PET   Polyethylene terephthalate
TMOS  Trimethoxysilyl
PAA   Poly(acrylic acid)
CVD   Chemical vapour deposition
FAS C\textsubscript{8} 1H,1H,2H,2H-perfluorooctyltriethoxysilane
H-SiO\textsubscript{2} Hydrophobic-SiO\textsubscript{2}
P/M   Polymer/mineral ratio
XPS   X-ray photoelectron spectroscopy
XRD   X-ray diffraction
FT-IR  Fourier transform infrared
AFM   Atomic force microscopy
UV-Vis Ultraviolet-visible
Chapter 1

General Introduction

This thesis outlines the significant step changes towards production of water repellent and self-cleaning commercially viable decorative paints, slippery lubricant infused anti-icing, anti-frosting and anti-fogging materials and transparent superhydrophobic self-cleaning thin films. A detailed overview of background literature follows this preface and notable advancements to the described research fields have been documented in experimental Chapters 2-5.

Potential benefits to modern civilisation include the successful design and manufacture of special wettability materials that are capable of withstanding environmental challenges.¹⁻⁵ Water retardant ‘smart’ materials⁵ are currently central to a plethora of novel applications involving microfluidics,⁶ oil-water separation,⁴ self-cleaning surfaces⁷,⁸ and anti-icing/-fogging mechanisms.⁹,¹⁰ Extreme liquid-surface interactions often underpin these technologies and provide favourable alternatives to many energy intensive routes employed to achieve the efficient working and preservation of commercial devices, infrastructure and alike.

Self-cleaning surfaces draw significant attention because of their unique functional features and the variety of applications in which they can be implemented.¹¹,¹² Inspired by lotus leaf technology, whereby micro and nanoscale protrusions combined with a low surface energy material reduce water droplet adhesion, self-cleaning materials aim to maintain surface cleanliness and retain a degree of functionality when subjected to severe environmental conditions for extended periods.¹³,¹⁴ Textiles, construction, vehicles, solar cells and lavatories are some of the industries/products set to benefit from this type of surface technology. Current difficulties in the physical self-cleaning field center around designing more durable surfaces generated through facile methods using low cost materials.¹⁴,¹⁵

While many functional surface designs may withstand ambient longevity testing conditions, it
is widely accepted that special wettability surfaces’ mechanical robustness characterisation must either include or be tailored towards abrasion, corrosion, icing and fogging resistance. Ice accretion, in particular, is currently a separate area of particular concern for regions of colder climate; the transportation, construction and renewable energy sectors face serious economic threats and hazardous operational conditions due to ice accumulation and relentless freeze-thaw cycles. The aviation industry has been suffering the consequences of icing events since the 1940s and 1950s because during flight, supercooled water droplets impinge and then freeze on unheated/untreated areas of the aircraft body on which they impact. Aerodynamic performance is therefore substantially compromised due to increased drag and reduced lift. Renewable energy plants, notably wind farms, experience similar setbacks. Light icing increases turbine blades’ surface roughness, which in turn leads to increased drag, reduced aerodynamic efficiency and a diminished power output.

Conversely, material fogging is apparent in humid atmospheric conditions when condensed water vapour resides upon surfaces. Condensation build-up substantially impacts a material’s optical performance, which is problematic for a great number of industrial and domestic applications. Severe personal injury has also been known to result from fogging of vehicle and aircraft windscreens, with the majority of difficulties stemming from situations where high levels of light transmission are preserved but the image is completely distorted.

New generation surfaces with tailored water repellencies are continually being adapted to overcome icing or fogging concerns. In the case of ice accretion, a surface with reduced water wettability shows highly promising results while an anti-fogging surface tends to benefit from the sheeting action of water across the substrate’s surface. The passive anti-icing or anti-fogging characteristics have been realised based on said wetting behaviours but liquid repellency alone often is not sufficient. Slippery liquid infused porous surfaces (SLIPS) provide an extra lubrication dimension and are now revolutionising the way in which the potential impacts of harsh environmental conditions are managed.

1.1 Surface Wetting Behaviour

The topography and energy of a surface determines its wetting behaviour, a characteristic which is often measured in three ways. Firstly, the static water contact angle is recorded by placing a water droplet of $\sim 5 \mu L$ onto a material and measuring the angle, through the liquid, where the
liquid-vapour interface meets the solid surface. Figure 1.1 displays how water contact angles on superhydrophilic, hydrophilic, hydrophobic and superhydrophobic surfaces are classified as water contact angle \( \leq 5^\circ \), 5 < water contact angle \( \leq 90^\circ \), 90 < water contact angle \( \leq 150^\circ \) and water contact angle \( \geq 150^\circ \) respectively.\(^1\)^\(^5\)

![Diagram showing water contact angles on different surfaces.](image)

**Figure 1.1.** The static water contact angle on surfaces with different wettabilities. a shows a superhydrophilic surface, water contact angle \( \leq 5^\circ \), b displays a hydrophilic surface, 5 < water contact angle \( \leq 90^\circ \), c shows a hydrophobic surface, 90 < water contact angle \( \leq 150^\circ \) and d represents a superhydrophobic surface, water contact angle \( \geq 150^\circ \).\(^1\)

Secondly, a material’s water contact angle hysteresis describes the mobility of a spherical droplet and has been used to identify self-cleaning potential. It is described as the receding contact angle subtracted from the advancing contact angle, as seen in Figure 1.2. The receding contact angle is determined by placing a droplet on a horizontal substrate and removing some of the liquid, the angle is measured when the area of contact is first reduced. The advancing contact angle is established by adding some liquid to the droplet, when the contact area increases the angle is recorded.\(^5\)

Thirdly, the tilting angle is defined as the critical angle between the surface and the horizontal, below which the droplet begins to roll. It is a reflection of, but not equal to the contact angle hysteresis. A superhydrophobic surface with a tilting angle < 10° is regarded as self-cleaning.\(^5\)

When a solid is wetted, three interfacial boundaries are created with their own specific surface
energy content: solid-gas, solid-liquid and liquid-gas. During wetting the area of the liquid-gas interface is extended and the solid-gas interface is exchanged in equal amount with the solid-liquid interface. As with all other thermodynamic processes the magnitude of free energy change dictates whether the wetting could occur spontaneously and at what rate. As such, the surface (specific) energy content of a wetted water repellent solid interface would be larger than the dry surrounding area; droplets placed upon this surface should spontaneously form almost perfect spheres with identical surface energies inside and outside of the droplet. The same reasoning applies to any water loving surface where the wetted area has a lower specific energy; droplets on this material would spread spontaneously.

1.1.1 Young’s Model

Pioneering work describing the thermodynamic interactions between a liquid and solid, including wetting and non-wetting regimes, was first described by Thomas Young in 1805. Equation 1.1 explains the theory of wetting on an ideal surface and the forces that cause liquids and solids to behave in a predictable manor. \( \theta^Y \) is the water contact angle, \( \gamma_{SG} \), \( \gamma_{SL} \) and \( \gamma_{LG} \) are the interfacial free energies per unit area of the solid-gas, solid-liquid and liquid-gas interfaces respectively.\(^{22}\)

\[
\cos \theta^Y = \frac{\gamma_{SG} - \gamma_{SL}}{\gamma_{LG}}
\] (1.1)

Further developments in the early 1900s advanced Young’s work. They afforded understanding of wetting behaviour on non-ideal surfaces. Equation 1.2 defines surfaces roughness through comparison of the morphological with geometric surface areas, the former considers surface protrusions and features whereas the latter assumes a completely smooth planar surface.
If we consider a spherical water droplet that changes its shape, such as balling or spreading, in an identical fashion on both smooth and rough water repellent surfaces, a larger change in real solid-liquid area is observed on the high surface area/rough as opposed to the low surface area/smooth material. The rough surface will have the greatest net energy decrease upon droplet balling, favouring the reverse of wetting and would be regarded as a more water retardant surface. The same logic can be employed for either a smooth or rough water-loving surface. A bigger net decrease in energy occurs on a hierarchical material which more rapidly induces water spreading.\textsuperscript{1,23}

In either case, surface roughening amplifies the wetting performance of any given material. More pronounced surface protrusions cause an innately water repellent material to become more proficient at repelling water and a naturally water-loving surface to promote sheeting.\textsuperscript{1,23}

### 1.1.2 Wenzel and Cassie-Baxter Regimes

A magnification of wetting properties with increased surface roughness was outlined in Wenzel’s and Cassie-Baxter’s models. Figure 1.3 presents the contrasting ways in which water droplets can interact with hierarchical water repellant surfaces.\textsuperscript{1}

![Figure 1.3. Two possible superhydrophobic surface regimes; the Wenzel state where water droplets stick or adhere to the surface protrusions and the Cassie-Baxter state where droplets slip on a lubricating air layer trapped within surface structures.\textsuperscript{1}](image-url)
Wenzel’s regime describes a homogeneous system where a water droplet makes full contact with the surface it rests on; air is not trapped between surface asperities. Figure 1.3 represents said surface model where $\theta^W$ is the apparent water contact angle, $r$, corresponds to the roughness factor and $\theta^Y$ depicts Young’s angle. The linear relationship between roughness and contact angle hinges on the fact that liquid water strictly follows the morphology of the surface. This model suggests a large solid-liquid contact area; wettability characteristics are exacerbated but droplet mobility is greatly impeded. These surfaces experience water pinning whereby droplets are less likely to freely roll.

$$\cos\theta^W = r\cos\theta^Y$$

The Cassie-Baxter model was derived eight years later, in 1944, for non-homogeneous porous solids. A water droplet in this state assumes a position suspended on top of an air layer trapped within the surface topography. Therefore, the droplet only makes partial contact with the solid whilst gas pockets act as a lubricating layer upon which the liquid can slide. Equation 1.4 presents this research, where $\theta^C$ is the apparent water contact angle, $\theta^C$ describes the equilibrium water contact angle on a flat surface and $\phi_{SL}$ corresponds to the area fraction of solid-liquid contact.

Droplets in this state are highly mobile and commonly have tilting angles $<10^\circ$, the resulting exaggerated rolling action is fundamental to many self-cleaning mechanisms.

$$\cos\theta^C = \phi_{SL}\cos\theta^C + \phi_{SL} - 1$$

Many substrates exhibit characteristics that do not represent pure forms of either model. For these cases, intermediate hybrid states exist between the Wenzel and Cassie-Baxter regimes whereby water droplets are in partial contact with the surface protrusions. An amalgamation of equations 1.3 and 1.4 generate the Wenzel/Cassie-Baxter intermediate expression, labelled equation 1.5.

$$\cos\theta^{CW} = \phi_{SL}r\cos\theta^C + \phi_{SL} - 1$$

Despite its importance, surface roughness is not the sole consideration when designing special
wettability materials. Extreme functionality is only realised upon combination with necessary optimum surface energy adjustments. The previously mentioned inter-facial boundaries, solid-gas, solid-liquid and liquid-gas, that are created during wetting have their own associated specific surface energy content. The addition of surface water extends the liquid-gas interface area and the solid-gas interface is exchanged in equal amount with the solid-liquid interface. As with all other thermodynamic processes the magnitude of free energy change dictates whether the wetting could occur spontaneously and at what rate. As such, the surface specific energy content of a wetted water repellent solid interface would be larger than the dry surrounding area; droplets placed upon this surface should spontaneously form almost perfect spheres with identical surface energies inside and outside of the droplet. The same reasoning applies to any water loving surface where the wetted area has a lower specific energy; droplets on this material would spread spontaneously.

1.2 Special Wettability Material Classification

Surfaces can become covered in dust and dirt particles over time, which contributes to a diminished performance of the devices they cover. For a surface to be classified as self-cleaning, water droplets either roll or slide along the surface. Foreign particles are picked up by the moving droplet and are consequently removed. Superhydrophobic surfaces, with water contact angles $\geq 150^\circ$, are most suited to this process because the water adhesion strength is weak, $\leq 9.6 \text{ mJ m}^{-2}$, and there is also a reduction in the particle surface adhesion strength. The dominating forces between contaminant particles and the surfaces on which they reside include: the surface charge of the particles and substrate when the former are immersed in water, van der Waals interactions, capillary forces between the particles and the substrate and finally the line tensions between the particles-substrate and particles-water droplet. Alterations to the surface chemistry and/or surface morphology impact every described force between foreign particles and the substrate and therefore influence a water droplet’s ability to move across the surface. Surface variations notably change the water contact angle and therefore alter the geometry of the water-air boundary line tension as water covers/uncovers particles attached to the surface. The changed line tension either increases or decreases the forces acting on the particles and dictates whether detachment is likely to happen.

Special wettability surfaces also experience heterogeneous ice formation, ice crystallisation on a foreign material, when liquid water droplets come into contact with a surface at temperatures below 0°C. This situation is primarily realised in the case of freezing rain, which commonly af-
fects transmission lines, transport and infrastructure. Superhydrophobic surfaces are generally thought to be the ideal candidate for this type of ice accretion reduction due to their accentuated wetting behaviour. Ice nucleation is prevented by minimising the liquid-surface interaction time via droplet shedding and/or delayed through a combination of tuned surface roughness and energy. However, superhydrophobic surfaces can not always maintain their anti-icing properties in high relative humidity. The phenomenon of declining anti-icing performance due to the change in wettability can be alleviated to some degree when highly rough topographies are impregnated with a lubricating top liquid layer, also known as slippery liquid infused porous surfaces (SLIPS). Therefore, it is accepted that a material is unfavourable as an ice repellent when it is easy to wet the surface with water droplets and in order to retard wetting the surface should be endowed with durable hierarchical structure or coated in a slippery liquid.

While frost prevention requirements are frequently associated with low humidity environments, materials often suffer from severe fogging in highly humid regions. Surface-bound fog rapidly develops when water vapour condenses onto a surface as a result of temporary changes in humidity, temperature, or convection. In situations where condensed droplets fully wet a given material, formation of a near-continuous liquid film mitigates light scattering events and optical transmission is preserved. Alternatively, fogging can also be avoided through use of surfaces that rely on rapid removal of perfectly spherical droplets or slippery surfaces that prevent the sticking of discrete droplets that act as light scattering sites. Prompt condensate removal is particularly critical to the performance of thermal management systems as their effective running relies on maintained thermal conductance; a property compromised by water and frost accumulation. Parts 1.2.1, 1.2.2 and 1.2.3 consider the advantages and limitations of smooth, textured and slippery surfaces specifically targeted for either self-cleaning superhydrophobic or ice and fog evasion properties.

1.2.1 Smooth Surfaces

There is a common misconception that smooth surfaces are easier to clean than rough surfaces because containments rest on a flat substrate rather than becoming stuck between rough morphological features. However, there is indisputable evidence to suggest that naturally rough substrates, such as the lotus leaf, remain exceptionally clean as a consequence of their microscopic roughness and a waxy coating. The lotus leaf has a measured water contact angle of 161° and a tilting angle of 2° and it is an exceptional self-cleaning material. In contrast, low surface energy but smooth surfaces are generally unable to generate comparable contact angles, >110°, and display little to no
evidence of droplet rolling when the substrate is tilted. Therefore superhydrophobicity is consid-
ered a prerequisite of self-cleaning functionality and explains the absence of smooth self-cleaning
materials in the literature.\textsuperscript{26,39} Heckenthaler \textit{et al.} most succinctly supported this statement through
calculations that followed the investigation of multiple silicon wafers with differing topographies
and water repellencies. Their smooth hydrophobic substrate displayed an unfavourable elevated
adhesive force between unwanted surface particles and the silicon sample due to an increased con-
tact area between the two solids. Functional testing consequently identified a hydrophobic smooth
surface water contact angle of 110° and a water tilting angle of 40°; fluorescent imaging highlighted
that 81\% of particles were removed from said surface compared with 98\% on the equivalent rough-
ened sample. Greyer \textit{et al.} went on to monitor the removal of contaminants on a single-particle
level via micrometer scale confocal microscopy. The space- and time- resolved data was correlated
with friction force measurements. It was noted that the force required to clean a contaminated sur-
face is not substantially higher than the friction force the drop experiences over a pristine surface.
Interestingly, results also indicated that hydrophobic and hydrophilic contaminants had minimal
influence on sample wettability provided that the particle size was greater than either the pore
size or thickness and that the contaminant fell below the maximum height of the protrusions.\textsuperscript{40}
Wider literature trends indicated that experiment and theory aligned to highlight the stark issues
associated with using hydrophobic and smooth surfaces as self-cleaning materials.\textsuperscript{30,39}

Instead, low surface energy smooth surfaces were used in initial attempts to minimise ice ad-
hesion. Unstructured polydimethylsiloxane (PDMS) and polytetrafluoroethylene (PTFE) samples
with contact angles of 120° were proven effective ice-phobes in a study constrasting a variety of
smooth surface coatings.\textsuperscript{41,42} Peng and Petrenko coated gold and platinum metals with organic
compounds that were either strongly hydrophilic or hydrophobic. The contribution of hydrogen
bonding to ice adhesion was investigated by varying the degree of hydrophilicity/hydrophobicity
in self-assembled monolayers, Figure 1.4. The smooth monolayers consisted of similar length
molecules with the only difference being their outermost groups; recorded ice adhesion properties
could therefore be accurately contrasted with surface wettability. They determined that the sheer
strength of ice was increased with the amount of surface hydrogen bonding; this was further linked
to high surface-water affinity.\textsuperscript{43}

Bulk coatings are a different type of smooth topography surface that heavily feature in anti-icing
literature, Figure 1.4. Fluorodecyl polyhedral oligomeric silsesquioxane containing non-structured
coatings reduced the ice adhesion strength on bare steel discs by a factor of 4.2.\textsuperscript{44} In other work, ice
sheding properties of polydimethylsiloxane-polycarbonate block-copolymers films were studied. Jellinek found that adhesion on these surfaces were not only a function of the water repellency but were also dependent of the polysiloxane content, its block chain length and the glass temperature of the polymer, i.e. its dependent on the films’ rheology relative to ice.  

An ice-phobic bilayer surface was also developed by optimising the base layer for mechanical properties, while the top layer was designed to generate high water contact angles. Both components were formed sequentially in the same reaction chamber by initiated chemical vapour deposition (iCVD). The iCVD polymerization of divinyl benzene produced a cross-linked hydrocarbon base layer that was capped with a covalently-attached 10-40 nm poly-perfluorodecylacrylate ultra thin film. The high water contact angle, 150°, and low water contact angle hysteresis, 4, were thought to be a product of the thin top layer achieved via limiting surface reconstruction of the pendent perfluoro groups. This linker-free strategy provided the robust substrate-film adherence required in industrial applications whilst achieving a 6-fold reduction in ice adhesion strength.

<table>
<thead>
<tr>
<th>Self-assembled monolayers</th>
<th>Bulk coatings</th>
</tr>
</thead>
<tbody>
<tr>
<td>Environmentally tolerant</td>
<td>Environmentally tolerant</td>
</tr>
<tr>
<td>Poor surface compatibility</td>
<td>Durable and versatile</td>
</tr>
<tr>
<td>Low performance relative to state of the art</td>
<td>Low performance relative to state of the art</td>
</tr>
</tbody>
</table>

Figure 1.4. Comparison of smooth, dry surface structures for self-cleaning, anti-icing and anti-fogging applications.

Alternatively, Wang used the PDMS polymer, Sylgard 184, to determine the effect of coating thickness on ice adhesion strength at -10 °C. Peak removal stress decreased by a factor of 4 (457 to 115 kPa) with a coating thickness increase from 18 to 533 µm. These results supported those of Yorkgitis, who reported ice adhesion studies on an unfilled, platinum cured vinylpolysiloxane resin cross-linked with poly(methylhydro)siloxane. Despite cohesive failure of these weak/unfilled elastomers, ice removal energy reduced by a factor of 8, from 1.16 to 0.12 Jm⁻², with decreasing coating thickness.

Lai’s switchable superhydrophilic TiO₂ films are an example of smooth and non-lubricated
anti-fogging coatings. The work depicted a stable titanate nanobelt particle suspension that was generated with pre-hydrolysed surface fluoroalkylsilanes. Electrophoretic deposition on a conducting glass substrate originally produced a transparent cross-aligned superhydrophobic film. When heated to 500 °C the titanate nanobelt coating transformed into a porous TiO$_2$ film with superhydrophilic behaviour. Water on this surface immediately spread and shed giving it excellent anti-fogging properties.

Perfluorinated polyethylene glycol oligomers were covalently grafted to silica substrates which were first modified with a reactive isocyanate-silane. Resulting surfaces were oil-hating/water-loving and had improved robustness due to the resistance of covalent linkages to contaminants and solvents. Of the materials tested in Howarter’s study, the perfluorinated polyethylene glycol oligomers had the ability to prevent fogging after rapidly changing temperature and humidity conditions as well as being oleophobic in nature. This was noted as an advantageous characteristic as other high energy hydrophilic surfaces were ruined when contaminated with natural oils and airborne organic compounds. The hydrocarbon contaminants’ low surface energies made them difficult to remove thus forming a new high energy surface that induced fogging rather than preventing it. Further examples of effective hydrophilic anti-fog technologies have involved resin formation through esterification of acrylic or methacrylic acid and a short chain alcohol as well as cross-linking polyvinyl alcohol and poly-N-vinylpyrrolidone, Figure 1.4.

1.2.2 Textured Surfaces

The most fundamental principle associated with physical self-cleaning technology is the formation of spherical droplets that remove dust and dirt surface particles on droplet movement. A combination of hierarchical structure and low surface energy modification, characteristic of a superhydrophobic surface, provide essential self-cleaning conditions. Development of novel materials fitting of this description has been heavily influenced by nature’s unique wettability species. Like the lotus leaf, discussed in Part 1.2.1, rice leaves consist of micro and nano surface roughness. Papillae of 5-8 µm papillae are arranged in parallel to the leaf edge. With this knowledge, Zhao et al. produced a superhydrophobic surface using gold to mimic the rice leaf’s topography. Polydimethylsiloxane (PDMS) was the surface energy lowering coating subsequently applied to achieve a water contact angle of 136°. Gao et al. fashioned a rice leaf negative template in order to mimic its surface structure on a PDMS film. The PDMS template then imparted morphological features on a poly(N-isopropylacrylamide) film, which afforded a water contact angle in excess of 120° and
thermally responsive properties.\textsuperscript{54} In later work, Lu \textit{et al.} went on to develop a dual scale TiO\textsubscript{2} particle containing paint with a fluorinated polymer additive. A hard or soft coated surface showed self-cleaning characteristics even on emersion in oil. Commercial adhesives bonded the paint to a chosen substrate to promote durability, proven by the maintenance of water repellency after 40 sandpaper abrasion cycles.\textsuperscript{55}

Other species have evolved specialised features so to remain dirt free. Butterfly wings, pigeon feathers and fish scales have dual scale morphologies that cause water droplets to roll outwards and remove contaminants in the process.\textsuperscript{56–58} Soz \textit{et al.} designed a superhydrophobic surface that replicated these refined morphologies. A thermoplastic PDMS-urea copolymer with SiO\textsubscript{2} roughening particles produced a water contact angle of 150°. Zhang \textit{et al.} further advanced the designing of self-cleaning surfaces using butterfly wings as inspiration. They understood that water droplets easily rolled off in the radial outward direction, taking advantage of the body as the central axis, but stuck to the body along the radial inward direction. From this, they were able to identify the notable textural differences that resulted in these stark functional variations.\textsuperscript{57} Fish scales also display highly effective self-cleaning properties, exemplified in polluted sea water. Liu \textit{et al.} analysed a scale and recorded radial direction papillae lengths, 100-300 µm, and diameters, 30-40 µm, prior to replicating this topography with templates and polyacrylamide hydrogel. An exceptional water contact angle of 163° was recorded.\textsuperscript{58} In work conducted by Wang \textit{et al.}, robust superhydrophobic samples have been realised by structuring surfaces at two different length scales. Nanostructured designs provided water repellency while the microstructure imparted mechanical robustness. An interconnected frame of microstructure pockets that housed delicate water retardant nanostructures were imparted on silicon, metal, ceramic and transparent glass substrates. Superhydrophobic functionality remained after abrasion using both sandpaper and a sharp steel blade.\textsuperscript{59} Separately, a bottom up superhydrophobic preparation was designed by Pan’s research group. A mixture of fluorosilanes and cyanoacrylates were applied as thin films, which self-assembled into re-entrant hierarchical protrusions with low surface energies. Resulting samples were repellent to acids, bases, ultralow surface tension liquids, polymer solutions and solvents. Low roll of angles, transparent properties and anti-freezing properties qualified the surfaces as special wettability coatings.\textsuperscript{60} Flexible organic nanocomposite coatings generate by Peng \textit{et al.} showed a degree of mechanical robustness under Taber abrasion, cyclic tape peels and exposure to sodium hydroxide solution and aqua regia. Coatings also showed resistance to high-speed drops and turbulent jets, 35 ms\textsuperscript{-1} and a Weber number of 43000.\textsuperscript{61}
Despite the undisputed functional success of many textured self-cleaning materials, durability levels are still a concern in a commercial implementation context. The structural integrity of micro and nano scale protrusions typically reduces with time and surface degradation is commonly accelerated in acidic, alkaline, high ultraviolet (UV) light exposure, variable temperature and erosion causing environments. General observations have indicated that superhydrophobic surface generation methods that rely on facile surface material deposition, rather than chemical bonding between the functionalising agents and substrate, have lower durability potentials. For example, fresh samples produced through fatty acid grafting in a simple wet chemistry process that involved texturing aluminium samples with hydrochloric acid followed with a lauric acid modification were 20% likely to lose their superhydrophobic properties when subjected to 5 acid environment cycles, 60% likely after 5 alkali environment cycles had a 20% probability of not withstanding 5 UV exposure cycles. Clearly, the most accessible fabrication methods, most suited to industrial applications, have significant robustness drawbacks that require revision.

It is widely accepted that average water contact angles in excess of 120° are only attainable on highly structured low surface energy materials. This structure theory now extends to reduced ice adhesion as Ruan and colleagues coated FeCl$_3$ and HCl etched aluminium alloys with lauric acid to achieve water contact angles of 159°. Their anti-icing abilities were systematically investigated with a real-time control system based on a two stage refrigeration method which could accurately monitor temperature, humidity and pressure. Firstly, icing time was postponed from 406 s to 787 s when contrasting unmodified with modified substrates at -6 °C and secondly, droplet bouncing was visualised on these microstructured surfaces when sprayed with water at -8 °C, Figure 1.5.

Bahadur used a physics-based modelling framework to predict the extent of ice formation on microstructured superhydrophobic materials when impacted with supercooled water droplets. This approach integrated heat transfer, dynamics of droplet impact and heterogeneous ice nucleation submodels to comprehensively describe wetting interactions in freezing conditions. The model was validated with experimental findings that displayed prevention of droplet freezing at temperatures as low as 25°C.

Hydrophobic and superhydrophobic samples, with coatings comprising nanoparticles embedded in fluorinated polymers, were subjected to large supercooled water droplets and tested for ice accretion. Kulinich’s group agreed with the accepted theory that ice adhesion was directly related to the surface wetting hysteresis. The superhydrophobic, high surface area samples comprising micro and nanoscale roughening particles had the lowest wetting hysteresis; ice adhesion strength
was recorded as 5.7 times lower than on unstructured alternatives, Figure 1.5.\textsuperscript{65}

<table>
<thead>
<tr>
<th>Microstructured</th>
<th>Nanostructured</th>
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<td>- Droplet balling and rapid shedding, which prevents ice nucleation</td>
<td>- Droplet balling and rapid shedding, which prevents ice nucleation</td>
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<td>- Poor humidity and pressure tolerance</td>
<td>- Improved humidity and pressure tolerance</td>
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<td>- Low durability</td>
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![Figure 1.5.](image)

\textbf{Figure 1.5.} Comparison of textured, dry surface structures for superhydrophobic self-cleaning, anti-icing and anti-fogging applications.\textsuperscript{2}

Unfortunately, the complex structuring associated with these extreme wettability surfaces introduce vulnerabilities. Protrusions and voids between asperities are fragile and experience degradation within relatively short time frames. Doubts surrounding the use of textured superhydrophobic materials as icephobes were further highlighted in Varanasi’s work. When these freezing surfaces were subjected to water vapour, frost formed indiscriminately on all available structures. The wetting regime consequently changed from a Cassie-Baxter to Wenzel state and the samples became hydrophilic. Environmental scanning electron microscopy (ESEM) visualisation proved that frost nucleation occurred, without preference, on all peaks and troughs of the originally superhydrophobic surface. Ice adhesion measurements on water retardant surfaces susceptible to frost formation indicated increased adhesion over smooth surfaces with a strong linear trend linking the total surface area.\textsuperscript{66}

Surface roughness incorporation has also had profound effects on anti-fogging functionality, Figure 1.5. For example, superhydrophobic surfaces prepared via HCl etching of aluminium substrates followed by modification with lauric acid generated superior wetting characteristics. Varshney’s materials had water contact angles of 172°, displayed thermal stability up to 250°C and were UV stable. Anti-fogging tests were conducted by placing coated and uncoated substrates into a refrigerator for 5 h before storing in ambient conditions. Within a few minutes, water from the air immediately collected on the bare aluminium substrates; an absence of condensate on the functional sample ensured preservation of optical properties.\textsuperscript{67}

A topography-controlled ZnO nano-petal array was generated on a Ga\textsubscript{75.5}In\textsubscript{24.5} liquid metal
The liquid metal was first achieved by melting Ga and In metals under 150°C for 24 h. The ZnO crystals were then generated through the addition of a Zn(NO$_3$)$_2$$\cdot$6H$_2$O growth liquid at 90°C for 1-18 h. Scanning electron microscopy (SEM) identified a ZnO nano-layer after 3 h of reaction time; by 7 h, nano-petals formed micro-clusters on the liquid metal surface and afforded a surface capable of preventing condensation accumulation.68

In contrast, superhydrophilic Fe doped TiO$_2$ films developed for photocatalysis were noted to be effective anti-fogging devices. Fe$^{+3}$ doped TiO$_2$ coatings were applied to glass substrates via a photosensitive sol-gel method; resulting anatase micro and nanoscale crystallite surface displayed rapid water droplet spreading. Rigorous fogging tests proved that glass coated in a non-patterned TiO$_2$ control film rapidly fogged and experienced a decrease in optical transmittance. The corresponding patterned film induced complete and continuous wetting which inhibited unwanted light scattering.69

This well documented evidence indicates that superhydophobic self-cleaning surfaces rely heavily on dual scale morphologies, ice prevention is widely attributed to hydrophobic textures and anti-fogging devices made use of both hierarchical hydrophilic and hydrophobic surfaces. Despite many of the described advantageous functionalities, concerns surrounding material lifespan and mechanical robustness have prompted the development of alternative smart surface models.

### 1.2.3 Slippery Surfaces

Slippery liquid infused porous surfaces (SLIPS), generated through the infusion of lubricant oil into porous structures, have garnered attention due to their ability to cause other fluids to easily slide off of their interfaces. The theory of SLIPS can be understood using Robbins et al.’s idea of interfacial friction, which refers to the friction produced when molecules and atoms slide on the surface on an ideal smooth crystal.70 It was explained that the friction is a product of intermolecular forces that arise from interactions between atoms that form a material’s surface and foreign surface atoms/molecules. Relative motion can come into effect when the two solids have inequivalent microstructures and a random superposition of intermolecular interaction potentials. In said case, the lowest energy potential valley is not formed when the two solids are static, relative to each other, and therefore a slippery property is instead realised.70

Natural examples of slippery surfaces include the Nepenthes plant. This carnivorous species attracts insects with a sweet scent and consists of two slippery parts: the peristome and the slippery zone beneath. Insects are prone to slide in both mentioned regions because of the waxy crescent
shaped microstructured topography. Aizenberg’s group imitated this morphology by fabricating a silanised surface based on epoxy resin that comprised a network of Teflon nanofibrous membranes. A low surface tension perfluorinated oil was finally added to afford extreme liquid repellence with a water tilting angle of $<5^\circ$. This synthetic surface also displayed a self-healing ability, whereby the lubricating liquid refilled areas of surface damage to restore functionality. Zhao et al. also looked to nature to report the presence of a self-sustaining thick lubricating layer on earthworm’s skin to permit movement through sticky soil without becoming contaminated. Deep surface skin grooves, covered in a dense microscale texture, result in a gap between the worm’s surface and surrounding soil to provide space for the collection of secreted body fluid. This coupling effect was found to minimise the friction coefficient during movement and reduced the adhesion properties of foreign materials on the body surface.

SLIPS generated for liquid self-cleaning applications do not display superhydrophobic properties owing to the relatively large surface lubricant-water droplet area of contact. Further to this, SLIPS experience disadvantages that surround the depletion of their lubricant layer. Volatilisation, contamination and migration of the lubricant fluid greatly limit potential applications with cross-linked siloxane polymer networks and smeared NaCl surface layers currently providing flimsy lubricant locking solutions at best.

The escalating demand for superior yet durable ice-phobic materials has also led to the development of specialised SLIPS. These coatings suppress ice accretion by eliminating moisture from an inert continuous slippery film prior to ice nucleation. A closed-cell architecture is not only thought to eradicate ice accretion but could also maximize mechanical robustness in order to promote mechanical stability, Figure 1.6.

The lubricant impregnation of structured surfaces is also known to dramatically reduce ice adhesion strengths, 10-150 kPa. In many cases these surfaces fall in the upper threshold for self-removal of accreted ice via wind or natural vibrations, $<20$ kPa. Subramanyam’s work indicated that ice adhesion was dependent on the level of surface lubrication as increased accretion was linked to lubricant depletion below the maximum height of surface structures. Somewhat counterintuitively, the authors argued that close spacing of micro and nanoscale protrusions, and by extension an increased solid surface area, mitigated the issue surrounding lubricant depletion. They reasoned that ice adhesion was prevented as a result of high crack initiation site densities at the protrusion edges; other suggestions include the superior lubricant retention within closely spaced structure voids due to heightened Laplace pressure.
Lubricated polymer-based systems have demonstrated exceptional ice repellent properties. Both lubricant-infused polymer systems and infused polymers have the ability to maintain low levels of ice accretion even after lubricant depletion; a phenomenon made possible due to the polymer’s naturally smooth and low energy characteristics.\textsuperscript{83} Wang’s research group built upon this theory to fabricate a liquid paraffin infused polydimethylsiloxane (PDMS) network with an extraordinarily low ice adhesion strength, 1.7 kPa at -70°C. The amount of ice build-up was also significantly decreased when silicone oil was mixed with PDMS prior to curing and when the polymer network was swelled with compatible oils, Figure 1.6.\textsuperscript{41,83–85}

Research into ice formation identified the presence of a thin, slippery, liquid-like transition layer at the ice surface. Although the presence of a friction- or pressure-induced liquid layer are popular reasoning for the low friction on ice, these explanations have been disregarded in favour of theories that attribute interfacial disordering and entropic effects to the presence of the quasi-liquid surface film.\textsuperscript{45,86,87} This effect has been explored in order to reduce ice accretion on hydrated surfaces; the aqueous lubricant layers are favoured as they mitigate the need for additional oils that become depleted over time.\textsuperscript{81,88,89}

Examples of slippery surfaces for anti-fogging applications have been under-researched despite the fact that many of the advantages to their use as icephobes may still apply. A variety of superhydrophobic surface designs excelled in humid environments owing to their ability to quickly shed water. However, topography degradation and poor longevity made them ineffective choices in extreme weather conditions and thus initiated investigation into highly specific SLIPS. Aqueous layers on anti-fogging surfaces are expected to solve lifespan issues through lubricant replenishment from environmental moisture; innate hydrophilicities should afford droplet spreading and, more critically, maintain optical properties.
Surfaces comprising hydrophobic lubrication systems are thought to yield even more promising fog retardant functionalities. Whilst expectations are once again limited by longevity, the anticipated optimisation of morphological length scale, surface chemistry and lubricant composition shall minimise these concerns. The empirical refinement of these parameters is desired but a deeper understanding of the interaction energetics between the components of the system is important to the advancement of this field.

Finally, infused polymers are thought to offer improved robustness compared with structured alternatives due to the presence of excess oil in their bulk polymer network. Heightened anti-fogging properties would still be maintained upon surface lubricant disruption as this form of degradation would only result in exposure of the functional, low-surface energy, smooth polymer. Thorough understanding of the successes and failures of different technologies may allow incorporation of features from different strategies to enhance the overall smart surface characteristics. The integration of these novel techniques with real-life applications are still in initial development stages but SLIPS based self-cleaning, ice-phobic and fog-phobic materials may well be the suitable solution to climate-centred material performance failings.

1.3 Special Wettability Material Design

The fundamental research outlined in Section 1.2 has led to important advancements in the development of special wettability material design. Importantly, understanding how these materials can be implemented in select applications, that function under specific environmental conditions, is of great value to a range of industries. Therefore, biological wetting mechanisms have inspired either bottom-up synthesis or substrate modification techniques that afford both desired surface topographies and chemistry. The variety of applications enabled by extreme interfacial interactions include self-cleaning materials, anti-icing surfaces, anti-fogging surfaces, atmospheric water collection, corrosion control, chemical shielding and biological adhesion mitigation. Despite the wealth of industrial outlets, the remainder of this chapter sheds light on the opportunity associated with engineering tuned surface wetting properties for self-cleaning, anti-icing and anti-fogging systems.
1.3.1 Self-cleaning Surfaces

Different reagents and material designs have been examined for the preparation of self-cleaning surfaces. Traditional fabrication methods involve the use of dip-coating, chemical deposition, layer by layer assembly, spray coating, spin coating, electrospinning, chemical etching and painting techniques. Not only is there considerable focus on developing a highly functional material, but ease of production, economic and environmental costs and durability.

Dip-coating methods afford high quality films that comprise complex and/or large structures through a process separated into five phases: dipping, start-up, deposition, drainage and evaporation. In result, high quality films comprising complex and/or large structures are produced. Sundaresan et al. have used the cost effective, low thermal energy and low pressure sol-gel method to generate nano sized TiO$_2$ particles for cotton fabric dip-coating. The group went on to investigate the self-cleaning, antimicrobial and ultraviolet (UV) protection abilities after 32-36 functional robustness washing cycles. Kumar et al. utilised tetraethyl orthosilicate (TEOS) and glycidoxypropyltrithoxysilane reagents in the sol-gel method to produce coatings able to maintain hydrophobic properties after the top layer was removed via a accelerating scrape test. The final abraded material had 96% self-cleaning capability. Furthermore, low density polyethylene coated SiO$_2$ particles were incorporated into Satapathy’s dip-coating mixture. A durable, porous, superhydrophobic and self-cleaning coating was realised when applied to a glass substrate.

Chemical deposition is another successful processing method for self-cleaning materials. Micro and nano scale translucent superhydrophobic coatings were generated through aerosol chemical vapour deposition (AACVD) of tetrafluoroethylene. Performance testing identified the thin film’s surface had a water contact angle of 168°, a tilting angle of $>1^\circ$ and a visible light transmittance of $>90\%$. It was the extremely low tilting angle that gave rise to self-cleaning functionality; further testing realised anti-corrosion properties. Benefits of the AACVD technique include the ability to tune film thickness at atmospheric pressure with a controlled reagent stoichiometry. Drosos et al. highlighted some of the challenges and benefits associated with atmospheric pressure CVD, using vanadium dioxide precursors, which have been directly transferable to the optimisation of superhydrophobic self-cleaning film thickness. Li et al. and Tombesi et al. consequently designed translucent films with enhanced functionalities due to careful selection of silicon based precursors, reagent loading, temperature and deposition time. The successful development of transparent superhydrophobic self-cleaning films achieved via AACVD influenced the studies carried out.
in Chapter 5. This coming chapter describes the development of thin films using TiO$_2$ and SiO$_2$ nanoparticle containing precursor solutions in the presence of both fluorinated and non-fluorinated polymers.

Layer by layer assembly of nanoscale films have received attention in recent years due to development in the obtainable resources and manufacturing technologies. A nanoparticle filling method was employed by Zuo et al. to fabricate a polydimethylsiloxane (PDMS) superhydrophobic deposition on a glass substrate with water tilting angles less than 5°. Yi’s research also afforded exceptional self-cleaning films via self-assembly of porous SiO$_2$ particles that were chain-like in nature. Mechanical robustness was assessed through purposefully causing damage to the films’ surface. In both literature examples, the water repellent films quickly regenerated after the abrasion had occurred and provided a new route in tackling low durability issues.

Spray coating of SiO$_2$ nanoparticles mixed with dodecyltrimethoxysilane was coated on glass and stainless steel substrates. The fluorine free coatings were able to maintain their water repellency after being scratched with a knife and abraded with sandpaper for 50 cycles. Self-cleaning ability was a consequence of the low water tilting angle of 12°, which was qualitatively displayed via cleaning tests in both air and oil mediums. Bake et al. went on to develop transparent superhydrophobic surfaces with a water contact angle of 170° and a tilting angle of 1°, the surfaces had a 90% transmittance of light with 800 nm wavelength. Sample robustness was promoted through the bonding of methyltrimethoxysilane and (3-glycidyloxypropyl)trimethoxysilane to functionalised SiO$_2$ nanoparticles and then to the chosen substrate. Physical surface stability was proven on exposure to a pressurised jet wash, UV radiation and abrasive processes.

The electrospinning coating technique has been utilised by Radwan et al. in the preparation of Al$_2$O$_3$ nanocomposites. The optimum conditions needed to produce a Al$_2$O$_3$ coating with the most extreme superhydrophobic properties, water contact angle of 155°, were 0.25 wt% and 2.50 wt% of Al$_2$O$_3$ and polystyrene respectively. Other experimental conditions include an applied potential of 25 kV and a solution flow rate of 1.5 mL h$^{-1}$ at 35 °C. Corrosion resistance on the electospun surface was recorded three orders of magnitude higher than an uncoated aluminium alloy substrate. Furthermore, a superhydrophobic coating containing ultrathin fibers was also prepared via electrospinning. Subsequent steps involving electrospraying nanostructured SiO$_2$ microparticles produced a surface with a water contact angle of 157° and a tilting angle of 8°, indicating self-cleaning ability.

Chemical etching has been an alternative facile self-cleaning surface generation method. Brass
substrates have been etched using an amalgamation of HCl and HNO$_3$ solutions and then treated with lauric acid. Surface microstructures were realised across the entirety of the metal surface and were fundamental in achieving water contact and tilting angles of 173° and <10° respectively. The durability of the self-cleaning coating was shown through chemical, thermal and mechanical stability tests. Self-cleaning superhydrophobic polycarbonates were also fabricated through a simple HNO$_3$ treatment to obtain yellow polycarbonate, after which a surface modification using methyltrichlorosilane afforded water repellent properties. Water droplets rolling down this surface are easily able to remove dust particles and there was no loss in functionality after several water jet impacts.

Decorative paints with self-cleaning functionality are greatly desired in the coatings industry. Il’darkhanova et al. devised a method of generating nanostructured and hydrophobised paint coatings. Carbon nanotubes and carbon nanofibers were preliminarily treated with surfactants and separately added to an epoxy silicone resin. The functionalising slurry was then combined with a commercial paint and applied to steel substrates. The paint films were dried to a thickness between 30 µm and 40 µm. There was an increase in water contact angle from 72°, on the uncoated film, to 88°, on the carbon nanotube containing paint, and 98° when carbon nanofibers were incorporated in paint. Unfortunately, the Cassie-Baxter wetting regime was not realised so self-cleaning properties were not observed. Durability was another issue for this material because the film formed was not chemically bonded to the paint coating and therefore did not last for any substantial period, particularly when subjected to a stream of water.

Simpson et al. filed a patent that encompassed superhydrophobic paints and epoxies that comprised the use of oil loving particles, which had a hydrophobic coating layer deposited thereon. An example of said paint coating was formed from a slurry mixture that included fluorinated SiO$_2$ particles (3 wt%) and a urethane binder (2 wt%) in acetone (95 wt%). Further adaptations to dried films, such as the addition of a lubricating oil that resided within the porous particle network were explored in this work. Detrimental functional impacts of surface abrasion were reduced through consistent particle arrangements moving from the surface to the bulk of the paint film. Another patent, from Baumann et al. describes the production of a self-cleaning paint coating. A base layer of polyester-epoxy resin was initially applied to an aluminium sheet and either gelled or cured to form a 300 µm film. The top layer was formed using SiO$_2$ particles and an alcoholic solution of tridecafluorooctyltriethoxysilane. Drying and curing resulted in a lacquer coating that was resistant to scratching and was self-cleaning in nature, water tilting angle of <3°.
In other work, Carneiro et al. created a nanodispersion of methacryloxypropyl-tri-methoxysilane functionalised SiO$_2$ particles.$^{115}$ Water was the solvent of choice, therefore an alcohol ethoxylate surfactant was required. The described hydrophobic mixture was combined with an aqueous commercial acrylic resin. Water contact angle results showed an unfavourable outcome as the coatings displayed hydrophilic properties. This work indicated the difficulties associated with making a superhydrophobic self-cleaning paint from cheaper non-fluorinated polymers and in industrially suited aqueous conditions. $^{115}$ Yang et al. had more success in generating a super water retardant blue-grey solar reflective paint. The paint contained water, styrene-acrylic emulsion, rutile TiO$_2$, Cromophtal orange, cobalt aluminate blue, anti-foaming agent and coalescent. The water contact angle was initially measured at 122°, which increased to 155° when the surface was physically roughened using sandpaper. Artificial roughening also saw a decrease in water tilting angle, 2°, and therefore self-cleaning functionality was achieved. Disadvantages of this coating were focused around robustness as accelerated weathering tests proved that the surface was destroyed on the periodic spraying of water, 400 h total spray duration.$^{116}$

An extremely promising water contact angle, 158°, was afforded on Jafari et al.’s paint coatings. Their experimental involved the use of octadecanoic acid (FA C$_{18}$), CaCO$_3$ microparticles, copolymer of styrene and acrylate, water and acetone. This facile method allowed coatings to be produced within an hour and at low temperatures, 30 °C. Disappointingly, spray coated paints were not tested for self-cleaning properties and water tilting angles were not recorded. While this work provided a step change towards achieving a low cost and low toxicity superhydrophobic decorative paint, the presence of an organic solvent and the absence of required paint additives, such as rheology modifiers, left a lot to be desired.$^{117}$ It was therefore noted that the literature lacked a low cost, low toxicity, facile approach to the creation of a superhydrophobic, self-cleaning aqueous decorative paint and inspired the work completed in Chapters 2 and 3.

### 1.3.2 Anti-icing Surfaces

Many material design strategies have sought to overcome complications associated with ice accretion in cold climates. As ice consists of polar molecules, hydrogen bonding, van de Waals forces and electrostatic interactions are directly responsible for the adhesive forces between a surface and frozen water. It is understood that surfaces with lower permittivity would substantially reduce ice adhesion. Therefore, a range of materials have been produced using low surface energy polymers.$^{118,119}$ As high water contact angles have been linked to low ice adhesion strengths,
fluoride containing polymer coatings have been investigated. Farzaneh et al. deposited polytetrafluoroethylene (PTFE) colloidal nanoparticles on on anodised aluminium in order to increase surface roughness. The functionalised samples had ice adhesion strengths around four times lower than on uncoated aluminium substrates that had been anodised for 90 min alone. Yang and group then looked to monitor the icephobic characteristics of PTFE plates, sandblasted PTFE plates, fluorinated vulcanised silicone rubber coatings and fluorinated polyurethane coatings. It was determined that smooth fluorinated polymer coated materials most successfully retarded ice adhesion. Surprisingly, they found that the fluoropolymer materials with more intricate surface topographies had increased ice adhesion strengths, a property linked to the reduction in hydrophobicity with a temperature reduction and elevated humidities. Gleason et al. went on to report the inclusion of the highly cross-linked poly(divinyl benzene) network below a thin layer of polyperfluorodecylacrylate, which stopped the inward reorientation of fluorine groups when exposed to water. This top layer chain linking prevented any surface remodelling, which ultimately resulted in a six-fold ice adhesion strength reduction compared with the untreated steel or silicon substrates.

Silicone based polymer materials have also shown anti-icing properties. Yuan et al. explored the relationship between ice adhesion strength and the surface structure of copolymers; the use of polydimethylsiloxane (PDMS)-polyacrylate copolymers as anti-icing agents was also investigated. Microphase separation was identified when different molecular weights of polyacrylate-\textit{b}-PDMS and polyacrylate-\textit{g}-PDMS were synthesised. PDMS chains aggregated on the surface of the polymer material, which was found to weaken polymer-ice interactions and therefore reduced ice accretion. Obvious differences between hard ice and the soft polymer surface have been thought to result in strain mismatch when a force is exerted to shed ice. Polymethylmethacrylate displayed negligible thickness of coating dependence on ice adhesion strength, which was in contrast to some research carried out on the PDMS elastomer. In this second example, shear removal force was reduced four times when the coating thickness increased from 18 \( \mu \text{m} \) to 533 \( \mu \text{m} \). Golovin et al. tailored the cross-link density of PDMS elastomeric coatings. By enabling interfacial slippage, they systematically designed samples with extremely low ice adhesions, 0.2 kPa. This mechanism allowed for rational design of icephobic coatings with a predetermined ice adhesion strength. Said materials were extremely durable, as they showed significant resistance to mechanical abrasion, thermal cycling, acid and base exposure and accelerated corrosion. Similarly, He’s work focused on the facile preparation of PDMS based sandwich-like sponges with low ice adhesion strengths. Weight ratios of PDMS prepolymer to the curing agent were adjusted to produce a lower elastic
modulus and surface energy. PDMS sponge structures subsequently afforded macroscopic crack initiators at the solid-ice interface and therefore reduced ice adhesion, which remained constant over 25 freezing cycles.\textsuperscript{126}

Both PDMS and fluoropolymers have been independently utilised in ice retardant applications. Therefore a combination of both materials, working in synergy, was expected to further diminish ice adhesion strength. Yuan’s research group managed to delay icing time by 186 s in -15 °C conditions when polymethyltrifluoropropylsiloxane (PMTFPS)-\textit{b}-polyacrylate was synthesised with PMTFPS macroazoinitiator via free radical polymerisation. The ice shear strength was recorded at 300 kPa, which was substantially lower than the 800 kPa value associated with polyacrylates.\textsuperscript{127} Alternatively, polyhedral oligomeric silsesquioxane (POSS) organic/inorganic hybrid molecules have unique nanosized caged structures. POSS molecules have advantages that include: ease of incorporation into various polymer assemblies provided there is substituent group compatibility, facilitation of microphase separation, immobility of low surface energy fluoropolymer chains at the material-air interface and generation of nanoscale roughness.\textsuperscript{128,129} Ice retardant fluorinated polymethylsiloxane and octavinyl-polyhedral oligomeric silsesquioxane hybrid films were generated using hydrosilylation methods in work carried out by Li \textit{et al}. The film with roughness of 90.2 nm performed most favourably with an ice adhesion strength of around 180 kPa.\textsuperscript{130} The icephobicity of another fluorosilicone POSS methacrylate copolymer was synthesised using reversible addition fragmentation chain transfer (RAFT). Ice adhesion results indicated that the fluorosilicone block copolymer material decreased ice accretion but did not encourage water droplet sliding.\textsuperscript{129} Unfortunately, solvent use and the degradation of fluoropolymers carries an environmental toxicity risk that could cause harm to humans and wildlife; it therefore needs to be limited in anti-icing coating application.

Liquid infused porous surfaces (SLIPS) form a separate research area that has had success in retarding ice adhesion. Porous surfaces can be infused with either aqueous or oil lubricating liquids, both of which shall be reviewed as follows. Work published by Wang \textit{et al} involved the production of many anti-icing coatings with aqueous lubricating layers on porous cross-linked hyaluronic acid, poly(acrylic acid) or hydrophilic polyurethane particles.\textsuperscript{131,132} Hygroscopic polymers, infused with poly(ethylene glycol diacrylate), were shown to swell when water was absorbed. At sufficiently low temperatures, water migrated out of the microporous polymer network forming a self-lubricating aqueous liquid surface layer. The ice adhesion strength was measured to be 60 kPa at -15 °C.\textsuperscript{133} Polyurethane and dimethylolpropionic acid lubricated surfaces were generated
via spin-coating and thermal curing. The ice accretion strength was recorded at 30 kPa and was maintained down to -53 °C. To maximise ice adhesion strength other factors, such as film thickness, temperature and monomer molar ratios were taken into account.  

Wang et al. made anti-icing surfaces that comprised hyaluronic acid and dopamine aqueous lubricant layers. The lowest ice adhesion strength, 61 kPa, was achieved when the film was 20 nm deep and the ratio of hyaluronic acid to dopamine was 0.33.  

Wooley et al. examined the molecular interactions that occurred between hyperbranched fluoropolymers (HBFP)/poly(ethylene glycol) (PEG) and water. They found that the cross-linked HBFP-PEG network film had the ability to reduce the freezing temperature of water and therefore displayed ice retardant properties.  

Chernyy and group developed super-hydrophilic polyelectrolyte brushes that included monovalent, bivalent and trivalent ions to afford anti-icing functionality. Li⁺ and Na⁺ ions most strongly disrupted hydrogen bonds in water and depressed the ice adhesion strength to 100 kPa and 200 kPa at -10 °C, respectively.  

Oil lubricated SLIPS coatings, such as the perfluorinated oil that Varanasi et al. studied, greatly reduced frost and ice formation. It was thought that surface oil migrated from the substrate interface to a surface water droplet, and subsequently inhibited ice formation. Furthermore, ice adhesion strength was decreased with increased microtexture density and ice nucleation was retarded due to the chemically homogeneous surface oil that eliminated potential nucleation sites. Yin et al. produced a Fe₃O₄ nanoparticle-PDMS surface via a polystyrene microsphere-assembled template, followed by fluorinated polyether lubricant impregnation. The Fe₃O₄ nanoparticles displayed a highly efficient photothermal effect when irradiated with near-infrared light, which contributed to rapid melting of accumulated ice. Other studies saw the deposition of highly mobile and low surface energy silicone oil on porous PDMS coatings. A favourably low 50 kPa ice adhesion strength was recorded for the surface described, 3% of that observed on bare aluminium standards. Wang et al. saw to the preparation of a durable anti-icing organic gel. Cross-linked PDMS integrated liquid paraffin networks effected a low ice adhesion strength, <10 kPa in -30 °C conditions, which was preserved after 35 icing/de-icing cycles. The durability of the oil lubricant posed the biggest challenge to oil-infused porous surfaces as lubricants were commonly depleted through evaporation or repeated icing cycles. Work carried out in Chapter 4 sought to address these issues by synthesising a highly porous composite thin film via aerosol assisted chemical vapour deposition (AACVD).
1.3.3 Anti-fogging Surfaces

Windows, vehicle windsheilds, eyewear and mirrors are types of transparent glass and polymer materials that have important applications in daily life. Due to the condensation of water vapour on solid substrates, these surfaces undergo fogging during normal operating conditions. This phenomenon reduces optical performance as light transmittance is compromised and gives rise to hygiene, aesthetic and safety issues. Work completed by Briscoe et al. highlighted the relationship between water contact angle and the described post fogging optical properties in question. It was concluded that light transmittance was almost unchanged at 90% on fogged surfaces with a water contact angles \(<40^\circ\). When the water contact angle was between 40 and 90\(^\circ\), residual surface fog reduced the normal incident light transmittance from 90% down to 50%. A slight transmittance recovery was observed on polyethylene films with water contact angles in excess of 90\(^\circ\). Surfaces with flatter condensed droplets resulted in transmittance curves that were most similar to transparent substrates with a continuous water layer. Therefore, detrimental fogging effects were prevented on materials with water contact angles below 40\(^\circ\).

Depositing organic thin films has been one of the simplest ways to equip any transparent material with anti-fogging properties. Introzzi et al. developed polysaccharide based anti-fogging coatings for packaging. A two step method for pullulan coatings on low density polyethylene (LDPE) produced favourable anti-fogging results; a consequence of the 24\(^\circ\) water contact angle. After moist environment exposure at 4 °C for 7 days, optical property assessments confirmed pullulan coatings had better visual characteristics than the LDPE film standard. The haze, 6.09%, and light transmission, 85.24%, values were comparable to non-fogged LDPE films and substantially better than commercially available anti-fogging plastics. Li et al. produced cellulose nanocrystal films for polyethylene terephthalate and oriented polypropylene. Water contact angles were in the range of 10-20\(^\circ\) and so visible light transmittance was high, >90\%, and haze was low, 3-4\%. Synthetic water soluble polymers, such as polyvinyl acetate (PVA), were thermally crossed linked on plasma treated polyethylene terephthalate (PET). PVA concentrations between 0.5 wt% and 10.0 wt% prevented surface fogging and had light transmissions of >84.3%. This was found to exceed light transmittance of non fogged PET standards, 83.0%. Poly(ethylene glycol) (PEG) has also been used as an anti-fogging material because of its hydrophilic nature and its chemical and mechanical stability generating crosslinking capability. Monila and group created PEG coatings with hybridised end-chain functionalisation with (3-isocyanatopropyl)triethoxysilane. The films had a
low water contact angle, 20°, which corresponded to the preserved transparency of modified glass after boiling water exposure. The hydrophobic nature of the uncoated glass standards, explained the resistance to water spreading and caused visual blurring.144

Dissolution of hydrophilic organic material based coatings can unfortunately compromise durability, as such inorganic polymers have been considered a more mechanically stable alternative. As SiO$_2$ nanoparticles are intrinsically hydrophilic, due to surface silanol groups (Si-OH), a single layer of nanoparticles has been deposited on glass through a dip coating process. UV irradiation in ozone and 1 h of 500 °C calcination afforded a water contact angle close to 0°. Light scattering water prevented when the sample was placed over hot water, which was quantitatively proven as visible light transmittance averaged at 95%. Thompson et al. fabricated a similar SiO$_2$ nanoparticle containing coating via dipping glass substrates into a 5 wt% suspension. UV irradiation was not required in this facile procedure. Samples remained superhydrophilic after dark room storage for 150 days and were able to transmit 4.3% more solar radiation than blank glass.146 TiO$_2$ inclusive coatings have also frequently been employed for anti-fogging applications. The material displays an unusual switch from a hydrophobic to superhydrophilic when subjected to UV light as TiO$_2$’s photocatalytic activity results in an increase in the number of surface hydroxyl groups. Miyauchi created superhydrophilic TiO$_2$/WO$_3$ films after UV irradiation. The most hydrophilic film was achieved when doped with only 1 wt% of WO$_3$.147 In other work, Chen et al. made porous TiO$_2$/ZnO coatings. A 10 mol% ZnO doped coating produced water contact angles of 2° on calcination for 30 min at 500 °C. Optical transparency was recorded at 95% when coated glasses were suspended over boiling water.148

Organic-inorganic coating synthesis involved combining both organic and inorganic components at the nanoscale. Crosslinked polymers with hydrolysed trimethoxysilyl (TMOS) groups have produced SiO$_2$ nanoparticle based anti-fogging coatings with a mechanical robustness. When TMOS was hydrolysed, polymer Si-OH groups reacted with silanol surface groups on the SiO$_2$ nanoparticles. The particles were consequently immobilised in the polymer network on formation of Si-O-Si bridges and the TMOS component also allowed for nanocomposite anchoring onto ceramic and polymer substrates.149,150 In separate studies, three alternate mesoporous SiO$_2$ nanoparticle/poly(diallyldimethylammoniumchloride) depositions built high performance anti-fogging coatings on quartz substrates. The sample superhydrophilicity mitigated light scattering as visible light transmittance was increased from 93% to 99% after functionalising quartz materials.151 ZnO flower nanostructures have also been utilised as building blocks in the development of poly(acrylic acid)
(PAA)/polyethyleneimine polyelectrolyte mediated layer by layer assembly. Water contact angles decreased with the increasing number of PAA/ZnO bilayers and light scattering was avoided when three bilayer samples were moved into a humid environment after storage at -20 °C.\textsuperscript{152}

Surface physical modification for anti-fogging surfaces has involved increasing surface specific area to achieve more extreme hydrophilic wettabilities. Myoung and group created nanoflakes on glass substrates after liquid etching in KOH solutions at 95°. Resulting topographical features afforded a 94.5% visible light transmittance after 1.5h of alkaline treatment. A 480 nm etching depth ensured transparency was retained on exposure to steam after sample storage in -10 °C conditions.\textsuperscript{153} \(\text{H}_2\text{SiF}_6\) vapour etching at 5-20 °C and subsequent low pressure \(\text{O}_2\) plasma treatment decreased water contact angles from 35.4° to 3.2°. Surface Si-F groups had been converted into Si-OH groups and was attributed to a maximum sample transmittance of 98.9% at 475 nm when placed over 80 °C water.\textsuperscript{154}

Surface chemistry modification has fine tuned anti-fogging functionality without affecting any of the material’s bulk properties. Copolymerisation has involved the covalent bonding of a hydrophilic monomer to a more hydrophobic backbone. This irreversible attachment ensured that anti-fogging functionality was maintained for extended periods. Yao \textit{et al.} generated linear low density polyethylene (LLDPE) with grafted monstearic acid monomaleic acid glycerol. Transparency increased with the degree of grafting and the concentration of hydrophilic monomer. Water contact angles were reduced from 62° to 23° when grafting was elevated from 0.52% to 1.31%, bulk properties were preserved and light scattering was alleviated.\textsuperscript{155} The biodegradable and biocompatible agar, alginate and collagen blends created by Wang \textit{et al.} were not only highly transparent but displayed anti-bacterial and UV-screening characteristics when Ag nanoparticles were included. Fogging was not observed throughout condensate testing and water contact angles did not exceed 49°.\textsuperscript{156} Other anti-fogging films of PET were synthesised via low pressure Ar/\(\text{O}_2\) plasma, which produced hydrophilic OH, COH and COOH groups. Water contact angles dropped from 95° to near 0° after the described treatment, which translated into optically clear samples when subjected to high relative humidity.\textsuperscript{157} Despite a vast range of methods and materials employed for this type of surface preparation, slippery liquid infused porous surface (SLIPS) modifications have not been investigated. Studies described in Chapter 4 address this absence and identify whether lubricant modification can override the need for extreme water spreading in order to prevent condensate accumulation.

This doctoral research addresses the shortcomings that surround the production of low cost,
low toxicity, self-cleaning model paints, categorised as a formulation containing water, additives (pH modifier or dispersants), extenders (functional particles), pigments (coloured particles) and a polymer binder or latex. The desired model paint substantially differs from existing research, in that it goes beyond the fabrication of a simple functional coating and focuses on the generation of a comprehensive commercial paint. Further to this, the use of AACVD permitted direct comparisons between a sample’s morphology and its impact on icing, frosting and fogging for SLIPS modified materials. Finally, the first example of transparent thin films, again via AACVD, have been produced using nanoparticles in a fluoroalkylsilane/PDMS precursor solution to allow for a new type of morphological control. In consequence of the described work, considerable advancement to the special wettability surface field have been realised.
Chapter 2

Towards Superhydrophobic and Self-cleaning SiO$_2$ based Decorative Paints

2.1 Background

Surfaces capable of self-cleaning are of huge interest to industry; as a commercial product their potential is significant and their market far reaching. Hydrophobic and hydrophilic coatings are known to display self-cleaning abilities through water action. The former is a physical process that makes use of rolling spherical droplets that collect surface debris while the latter carries dirt away from the chemically active material through water sheeting in the presence of UV light. Coatings and paints developed in this chapter solely focus on the development of extreme water retardant formulations inspired by lotus leaves,$^{158}$ water strider legs,$^{159}$ butterfly wings$^{160}$ and alike.

As for any superhydrophobic surface, physical self-cleaning coatings require hierarchical surface structure and epicuticular hydrophobic wax. The desired outcome of said combination is an ultraphobic surface: superhydrophobic water contact angle of $>150^\circ$ and a very low water tilting angle, $<5^\circ$.\textsuperscript{161} The final commonly used descriptor is the contact angle hysteresis, it is defined as the difference between the advancing and receding contact angles when the droplet is force to move on a tilted surface. Droplets are typically pinned to materials with high tilting angles/contact angle hysteresis so therefore low values, where rolling is facilitated, are preferred.\textsuperscript{25} These functionality values are partly reliant on surface roughness, categorised by two models: Cassie-Baxter\textsuperscript{25} and Wenzel.\textsuperscript{162} In accordance with the information provided in Part 1.1.2, water droplets on sticky Wenzel regimes heavily contact surface roughening structures and fully penetrate topographical cavities. Instead, the Cassie-Baxter model comprises an air layer that is trapped within these sur-
face cavities to maximise the liquid-solid interface area and minimise the equivalent liquid-gas area. This enables droplets to pick up microbes and foreign dust and dirt particles as they roll on the gaseous lubricant, giving rise to the self-cleaning terminology.  

While both wetting models account for the increase in water contact angle with surface roughness, they fail to adequately justify dynamic water droplet behaviour. It is hypothesised, however, that a Cassie-Baxter/Wenzel transitional state may also occur somewhere between the independent models’ roughness extremes. This is supported by the tendency of some surfaces to display both droplet pinning and rolling depending on the degree of tilt. The theoretical ambiguity surrounding self-cleaning states clearly indicates that average tilting angle testing is the only reliable method of identifying wetting state and therefore self-cleaning ability.

### 2.1.1 Superhydrophobic Self-cleaning Coating and Paint Technology with SiO$_2$ and/or TiO$_2$ Particles and/or Fatty Acids

Chemical vapour deposition (CVD), hydrothermal techniques, electrospinning and chemical etching are prevalent self-cleaning coating generation processes; specific examples of facile, wet chemistry formulation coating or paint production methods are not currently so widely researched.

SiO$_2$ and TiO$_2$ surface structure imparting particles are industrially favoured due to their availability, low toxicity and inert properties. However, associated drawbacks to their use must be considered and, where necessary, appropriately counteracted. Photocatalytic TiO$_2$ particles are known to undergo photoinduced hydrophilicity when irradiated with UV light; the sunlight initiated reduction of hydrophobic Ti$^{4+}$ to hydrophilic Ti$^{3+}$ ions result in smaller water contact angles on superhydrophobic coatings with insufficient polymer top coat coverage. In alternative SiO$_2$ systems, silanol groups are readily formed on the SiO$_2$ solid-gas interface. Materials are rendered hydrophilic due to hydrogen bonding between these hydroxyl groups and incoming polar water droplets. Consequently, the successful use of innately hydrophilic SiO$_2$ particles requires particle functionalisation or dehydration steps prior to final formulation inclusion. A functionalisation modification example is detailed in Part 2.4.1 and provides hydrophobicity enhancement, by way of lowering the surface energy of SiO$_2$ particles, via attaching non-polar groups to existing silanol groups.

Benefits to the use of SiO$_2$ and TiO$_2$ particles outweigh their drawbacks, as proved by Heale
et al. They designed a superhydrophobic and oleophilic separation surface that made use of dual scale TiO$_2$ and SiO$_2$ particles in a 1H,1H,2H,2H-perfluoroctyltriethoxysilane (FAS C$_8$)/polydimethylsiloxane (PDMS) polymer mixture. An average water contact angle of 151±7° was recorded on a coated metal mesh substrate. Lu et al. achieved contact angles of 168° on a paint containing two sizes of TiO$_2$ particles in an FAS C$_8$/ethanol solution. Further functional testing identified that water droplet bouncing was an additional feature of these superhydrophobic surfaces. Self-cleaning properties were then visualised by pouring water over MnO dust powder covered samples to produce clean surfaces. From this, it is clear that fluorinated species have the potential to generate highly superhydrophobic surfaces, yet their industrial use is limited due to toxicity and expense. Instead, attention has turned to non-fluorinated materials, such as fatty acids. Varesano et al. coated cotton fabrics in a polypyrrole-oleic acid emulsion to create electrically conductive hydrophobic materials. Oleic acid has also been applied to nanorod structures for anti-stick and anti-contamination coatings with water contact angles of 155°. Water contact angles of 155° were measured on hydroxyapatite/stearic acid composite coatings for the treatment of magnesium alloys. The extreme water repellency film was shown to improve the corrosion resistance of magnesium alloys. Mohammad et al. went on to develop sustainable and economical superhydrophobic coatings using magnesium silicate nanoparticles functionalised in fatty acids extracted from myristica and cinnamon. Dip-coating on metal substrates in addition to absorbent fabrics and glass produced apparent water contact angles of 160°. Agrawal et al. combined ZnO particles (24 nm diameter) with acid in a hydrothermal process to fabricate self-cleaning coatings with water tilting angles of 8°.

Having discussed the advantages of selecting low toxicity and cost reagents for the formulation of water retardant and self-cleaning materials, a streamlined approach to facile functional paint generation methods was considered. Il’darkhanova et al. researched methods of hydrophobisation through nanostructuring paint surfaces. An epoxy silicone resin modified with carbon nanotubes and carbon nanofibers was painted onto a surface treated with fluoroisilane; water contact angle values were recorded between 112 and 115° after fine cloth polishing. Superhydrophobic testing results were not realised but the result was over 40° higher than that of the non-modified base paint.
alone. Water contact angles in excess of 150° and a water tilting angle of 10° were achieved after grinding a solar reflective orange-grey paint with emery paper. The initial paint formulation was produced using styrene-acrylic emulsion, TiO$_2$ particles, CoAl$_2$O$_4$ particles, Cromophthal Orange, water, a wetting agent, a dispersant, an antifoaming agent and a suspending agent. It is important to note that the contact angle prior to surface roughening via grinding was much lower at 110°. Finally, Cui et al. prepared hierarchically modified epoxy paint surfaces by microstructure sandblasting followed by SiO$_2$ nanoparticle anchoring. An aminopropyl terminated polydimethylsiloxane epoxy adhesive top coat contributed to the final average contact angle result of 168°.

A clear deficiency in research surrounding superhydrophobic and self-cleaning model paint that comprises industrially viable materials, such as SiO$_2$, TiO$_2$, CaCO$_3$ or CaMg(CaCO$_3$)$_2$ particles with fatty acid modification, while also ensuring a consumer friendly end application provided inspiration for the work outlined in Chapters 2.5 and 3.

2.2 Aims

Experiments in this chapter aim to develop superhydrophobic and self-cleaning interior decorative model wall paints that incorporate low toxicity and cost SiO$_2$ structuring particles with a low surface energy octadecanoic acid (FA C$_{18}$) component. Functional material inclusion ratios and weight percentages should be optimised prior to addition of dopant extenders and typical commercial paint additives.

2.3 Experimental

With heavy influence on minimising toxicity and cost, routes towards the production of self-cleaning and superhydrophobic decorative model paints were explored. Water repellent slurries comprising surface roughening SiO$_2$ particles and surface energy lowering octadecanoic acid (FA C$_{18}$) were dried to powder or slurry coatings for functional testing purposes. Optimised material combinations and weight ratios were selected and trialled as part of organic and/or aqueous solvent slurry system variation evaluation. Final steps included the incorporation of selected functional slurries with common paint components, such as pH control and dispersant additives, prior to the addition of a chosen acrylic latex. Particle doping subsequently identified the benefits, if any, of introducing other industrially viable minerals as surface structure enhancing entities.
2.3.1 Materials

Aerosil OX50 fumed SiO\(_2\) particles (45 nm diameter) were purchased from Evonik. 1H,1H,2H,2H-perfluorooctyltriethoxysilane (FAS C\(_8\)) \(\text{NaOH}\) were acquired from Sigma-Aldrich. Laboratory grade solvents were supplied by Fisher Scientific. Dolomites, \(\text{CaMg(CO}_3\text{)}\)\(_2\), dispersants and latex materials were provided by Akznobel. All chemicals were of analytical standard and used as received.

2.3.2 Hydrophobic Fluoroalkylsilane and Fatty Acid Stock Mixture Generation

Four water-ethanol mixtures were generated with 0:1, 1:3, 1:1, 3:1 and 1:0 ratios, in a bid to move from an organic to aqueous solvent system. 1H,1H,2H,2H-perfluorooctyltriethoxysilane (FAS C\(_8\)) was added to each of these water-ethanol mixtures to generate four different FAS C\(_8\) (15 wt\%) stock mixtures. A separate FAS C\(_8\) (4 wt\%) stock was produced using the 0:1 water-ethanol mixture.

Subsequent experiments required four octadecanoic acid (FA C\(_{18}\)) (4 wt\%) stock mixtures generated from the original 0:1, 1:3, 1:1, 3:1 and 1:0 water-ethanol mixtures. Vigorous magnetic stirring, elevated temperature (30 °C) and an alkaline environment (pH = 8 via addition of \(\text{NaOH}\) (2.00 mol dm\(^{-3}\)) solution) promoted dissolution of FA C\(_{18}\) in the presence of water. A separate FA C\(_{18}\) (2 wt\%) stock was produced using the 0:1 water-ethanol mixture.

2.3.3 H-SiO\(_2\) Particle Generation

Non-fluorinated and fluorinated varieties of hydrophobic-SiO\(_2\) particles (H-SiO\(_2\)) were fabricated by magnetically stirring one portion of Aerosil OX50 fumed SiO\(_2\) particles (10 wt\%) in a 1H,1H,2H,2H-perfluorooctyltriethoxysilane (FAS C\(_8\)) (4 wt\%) stock mixture using the 0:1 water-ethanol ratio described in Part 2.3.2 and the other portion of SiO\(_2\) particles (10 wt\%) in an octadecanoic acid (FA C\(_{18}\)) (2 wt\%) stock mixture, again using the 0:1 water-ethanol ratio, for 20 mins.

H-SiO\(_2\) particles were later generated using aqueous conditions. Water was heated to 75 °C prior to the addition, with magnetic stirring, of FA C\(_{18}\) (2 wt\%). \(\text{NaOH}\) (2.00 mol dm\(^{-3}\)) was then added dropwise until the suspension reached pH 8. Aerosil OX50 SiO\(_2\) particles (10 wt\%) were then added in small amounts and magnetically stirred for a further 30 min. The suspension was placed in a 120 °C oven and only removed on complete powder dryness.
2.3.4 Hydrophobic Slurry Generation Using H-SiO₂ Particles

Hydrophobic-SiO₂ particles (H-SiO₂) (6 wt%) were separately magnetically stirred, 60 mins, in both the fluorinated and non-fluorinated stock solutions with 0:1, 1:3, 1:1, 3:1 and 1:0 water-ethanol ratios, Part 2.3.2. In every case the Aerosil OX50 fumed SiO₂ particles were pre-treated with the corresponding functionalising agent in which they were finally dispersed. Particle coagulation was noted in mixtures with a higher water content despite the addition of NaOH (2.00 mol dm⁻³), which afforded a pH 8 environment. The H-SiO₂/octadecanoic acid (FA C₁₈) slurries with 3:1 and 1:0 water-ethanol ratios did not form homogeneous mixtures upon 20 mins of magnetic stirring. Instead particle clumping was observed and uniform coatings were not produced when the following film application method was employed: (super)hydrophobic slurries (1 mL) were pipetted onto glass substrates covered in double sided Scotch tape (25x30 mm). FA C₁₈ coatings were oven dried at 60 °C for 20 mins to prevent recrystallisation, all other coatings were dried overnight at room temperature and pressure. In a separate trial, all coating slurries were dried at 120 °C for 6h prior to film application. FA C₁₈ containing samples produced powders that were pressed onto Scotch tape covered glass slides. 1H,1H,2H,2H-perfluorooctyltriethoxysilane (FAS C₈) based samples produced thick pastes which had to be discarded.

Issues that surrounded dispersing H-SiO₂ particles in 1:0 water-ethanol ratio solvent systems were overcome through process amendments and the use of dispersants. Water was heated to 75 °C prior to the addition, with magnetic stirring, of FAS C₈ or FA C₁₈. NaOH (2.00 mol dm⁻³) was then added dropwise until the suspension reached pH 8. To aid particle incorporation, Orotan 371-A-ER (sodium salt of a carboxylate polyelectrolyte pigment dispersant) or Orotan CA2500 (hydrophobic copolymer dispersant) was magnetically stirred into the formulation (x0.02 wt% of H-SiO₂ particles). H-SiO₂ particles were then added in small amounts and magnetically stirred for a further 30 min. The suspension was placed in a 120 °C oven and only removed on complete powder dryness. A table of key sample formulations, including trials centred around varying FAS C₈ or FA C₁₈/H-SiO₂ particle ratios (polymer/mineral or P/M ratios), have been outlined in Table 2.1.

In order to qualify as model paint formulations, a latex component was incorporated via the following method: water was again heated to 75 °C prior to the addition, with magnetic stirring, of FA C₁₈. NaOH (2.00 mol dm⁻³) was then added dropwise until the suspension reached pH 8. To aid particle incorporation, Orotan CA2500 was magnetically stirred into the formulation (x0.02 wt%
of H-SiO$_2$ particles). H-SiO$_2$ particles were then added in small amounts and magnetically stirred for a further 30 min. The appropriate amount of slurry was mixed with either of Akzonobel’s 1052, 1070 or 1080 acrylic latex components using a 400 rpm overhead stirrer for 30 min. Texanol was subsequently added to 1052 and 1070 latex systems (x0.05 wt% of 1052 or 1070 latexes) and left to stir for a further 10 min. Model paint formulations were applied to glass substrates using a draw down bar (304.8 µm clearance or wet film thickness of 6 mL) and left to dry overnight at room temperature and pressure, Table 2.2.
Table 2.1. Formulation table of oven dried powder films of either FAS C₈ or FA C₁₈ H-SiO₂ particles dispersed in an aqueous mixture of the respective long chain functionalising agent. Orotan 371-A-ER and CA2500 dispersants were explored and P/M ratios were varied.

<table>
<thead>
<tr>
<th>P/M ratio</th>
<th>Polymer/wt%</th>
<th>H-SiO₂ particles/wt%</th>
<th>Water/wt%</th>
<th>Dispersant/wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>FAS C₈</td>
<td>FA C₁₈</td>
<td></td>
<td>Orotan 371-A-ER</td>
</tr>
<tr>
<td>0.17</td>
<td>1.00</td>
<td>0.00</td>
<td>6.00</td>
<td>92.88</td>
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<tr>
<td>0.22</td>
<td>4.00</td>
<td>0.00</td>
<td>18.00</td>
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Table 2.2. Formulation table of model paint systems containing FA C\textsubscript{18} H-SiO\textsubscript{2} particles dispersed in an aqueous mixture of FA C\textsubscript{18}, Orotan CA2500 dispersant and latex (1052, 1070 or 1080). P/M ratios were varied and the resulting slurries were drawn down onto a glass substrate.

<table>
<thead>
<tr>
<th>P/M ratio</th>
<th>FA C\textsubscript{18}</th>
<th>H-SiO\textsubscript{2} particles/wt%</th>
<th>Water/wt%</th>
<th>Orotan CA2500/wt%</th>
<th>Latex/wt%</th>
<th>Texanol/wt%</th>
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2.3.5 Hydrophobic Slurry Generation Using H-SiO$_2$ Particles with Dopant

The use of particle dopants were explored to assess their functional impact on octadecanoic acid (FA C$_{18}$) functionalised SiO$_2$ (hydrophobic-SiO$_2$ (H-SiO$_2$)) particle containing model paints, Table 2.3. Water was heated to 75 °C prior to the addition, with magnetic stirring, of FA C$_{18}$. NaOH (2.00 mol dm$^{-3}$) was then added dropwise until the suspension reached pH 8. To aid particle incorporation, Orotan CA2500 was magnetically stirred into the formulation (x0.02 wt% of formulation particles). H-SiO$_2$ particles along with either TiO$_2$ (250 nm diameter), dolomite GMR20180904 (41 nm diameter) or dolomite GMR20180906 (80 nm diameter) dopant particles, in 5 wt%, 10 wt%, 25 wt% or 50 wt% dopant level amounts, were then added in small portions and magnetically stirred for a further 30 min. The appropriate amount of slurry was mixed with a 1052 latex component using a 400 rpm overhead stirrer for 30 min. Texanol was subsequently added (x0.05 wt% of 1052 latex) and left to stir for a further 10 min. Model paint formulations were applied to glass substrates using a draw down bar (304.8 µm clearance or wet film thickness of 6 mL) and left to dry overnight at room temperature and pressure.
Table 2.3. Particle doped model paints. H-SiO$_2$ particles and various wt% of a dopant, TiO$_2$ (250 nm diameter) and GMR20180904 (41 nm diameter) and GMR20180906 (90 nm diameter) dolomite particles, were embedded in FA C$_{18}$ and 1052 latex mixtures before being drawn down on glass substrates (wet film thickness of 6 mL) and then dried. Orotan CA2500 was the dispersant used to generate mixtures with a 0.67 P/M ratio.

<table>
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<tr>
<th>P/M ratio</th>
<th>FA C$_{18}$</th>
<th>Particle/wt%</th>
<th>Water/wt%</th>
<th>Orotan CA2500/wt%</th>
<th>1052 Latex/wt%</th>
<th>Texanol/wt%</th>
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<td>86.71</td>
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<td>0.12</td>
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<td>0.12</td>
<td>3.35</td>
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<td>86.71</td>
<td>0.12</td>
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<td>H-SiO$_2$ 5.50 TiO$_2$ 0.29 Dolomite (41 nm) 0.00 Dolomite (80 nm) 0.00</td>
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<td>86.71</td>
<td>0.12</td>
<td>3.35</td>
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2.3.6 Material Characterisation Techniques

X-ray photoelectron spectroscopy (XPS) was carried out using a Thermo Scientific X-ray photoelectron spectrometer with a monochromated Al-Kα X-ray source (8.3381 Å). Peaks were modelled using CasaXPS software and binding energies were adjusted for adventitious carbon (284.5 eV). X-ray diffraction (XRD) patterns were obtained using a Bruker D8 Discover diffractometer with monochromated Cu-Kα radiation (1.5406 Å). Fourier transform infrared (FT-IR) spectroscopy was carried out using Bruker alpha platinum ATR equipment between 400 and 4000 cm⁻². Raman spectra were recorded between 100 and 3000 cm⁻² on a Reinshaw 1000 spectrometer equipped with a 514.5 nm laser. Surface topographies were investigated using a JEOL JSM-6301F scanning electron microscope (SEM) with an acceleration voltage of 5 or 10 kV; films were gold coated prior to SEM analysis to negate charging effects. Transmission electron microscopy (TEM) was performed using 100 kV JEOL CX100 equipment. Finally, profilometry mapping was achieved by Dr Suraj Pawar at Akzonobel (Slough) on a Keyence VHX-5000 digital microscope with a 1 μm tolerance, 500x500 μm coating areas were measured.

2.3.7 Functionality and Performance Testing Techniques

Three water contact angles were measured per coating at ambient temperature via the sessile-drop method using a FTA 100 optical contact angle meter (13.00 μg water droplet). An average value and associated error, from three measurements, were calculated for each sample stored in ambient conditions at 0, 3 and 6 month intervals where appropriate. The tilting angle, defined as the angle at which a water droplet readily slides off a slanted surface (fixed droplet weight of 0.5000 g), was recorded using a digital angle finder. Averages and standard deviations were again calculated for each sample stored in ambient conditions in slide holders at timed intervals where appropriate.

2.4 Results and Discussion

Basic interior decorative wall paints have historically been developed with four primary features in mind: aesthetics, toxicity, durability and production cost. Paint companies are now looking towards adding a fifth primary feature, such as surface functionality, to gain a competitive edge in the increasingly saturated interior paints market. This chapter documents the various trials towards formulating a functional self-cleaning model paint. As with many physical self-cleaning coatings documented in the literature, superhydrophobic Cassie-Baxter regimes are desired due to the fact
that near spherical water droplets are able to pick up dirt and dust particles as they roll across the angled surface. Firstly, low toxicity and low cost paint formulation compatible surface roughening and energy lowering materials were combined in ethanol solvent. A range of organic solvent systems were then explored prior to adopting a process that would facilitate dispersing water retardant materials in water based formulations. The addition of all other essential paint additives, such as a latex binder component, was the penultimate step before investigating the use of particle dopants.

2.4.1 Material Characterisation

In order to understand the functional properties of the water repellent coatings generated according to Part 2.3, thorough surface characterisation was carried out as follows. X-ray photoelectron spectroscopy (XPS) data was collected to identify material composition, preferred oxidation states and chemical environments. Firstly, C1s, Si2p and O1s XPS data for the oven dried powder film of octadecanoic acid (FA C\textsubscript{18}) hydrophobic-SiO\textsubscript{2} particles (H-SiO\textsubscript{2}) (6 wt%) originally dispersed in a FA C\textsubscript{18} stock (4 wt%) solution comprising 1 part water and 3 parts ethanol was modelled. Peaks at 284.5 eV, 285.9 eV and 288.4 eV in the C1s scan were artefacts of surface carbon contaminant species coupled with the long FA C\textsubscript{18} hydrocarbon backbone,\textsuperscript{177} the C-O(OR) ester environment\textsuperscript{178} and the C-O(OH) acid environment,\textsuperscript{179} respectively. The C-O(OR) environment confirmed the presence of SiO\textsubscript{2}-FA C\textsubscript{18} ester linkages. A peak identified at 103.4 eV in the Si2p scan established that the surface roughening SiO\textsubscript{2} particles were present and that Si was in the 4+ oxidation state.\textsuperscript{180} The O1s scan contained a single peak that further proved oxygen was bonded to Si. Based on modelled XPS data and the fluoroalkysilane-silanol group dehydration mechanism proposed by Crick et al., an ester linkage between FA C\textsubscript{18} and SiO\textsubscript{2} particles’ silanol groups was hypothesised.\textsuperscript{1} A schematic of said reaction is depicted in Figure 2.1.

The superhydrophobic functional properties of dried H-SiO\textsubscript{2}/FAS C\textsubscript{8} and H-SiO\textsubscript{2}/FA C\textsubscript{18} water containing formulations provided reason to believe that water retardant samples could be generated from an aqueous medium. Figures 2.2, 2.3 and 2.4 present XPS scans of the oven dried powder film: FA C\textsubscript{18} H-SiO\textsubscript{2} particles dispersed in FA C\textsubscript{18} aqueous stock solution with the Orotan CA500 dispersant, fatty acid to H-SiO\textsubscript{2} particle (P/M) ratio was equal to 0.67. The spectra were recorded 12 weeks after powder deposition and all SiO\textsubscript{2} particles were originally functionalised in an ethanol solvent system. The peaks at 284.5 eV, 286.6 eV and 288.5 eV in the C1s scan were again characteristic of surface carbon contaminant species coupled with the long FA C\textsubscript{18} hydrocarbon backbone,\textsuperscript{177} a C-O(OR) ester environment\textsuperscript{178} and the C-O(OH) acid environment\textsuperscript{179} respectively.
Figure 2.1. Proposed reaction mechanism, at 120 °C, between octadecanoic acid and silanol-terminated SiO₂ particles.¹

The C-O(OR) environment highlighted SiO₂-FA C₁₈ ester linkages and surface roughening SiO₂ particles were consistently present in the 4+ oxidation state. A single peak was identified in the O1s region, further proving that oxygen species were bonded to the Si metal. No noteworthy spectral difference was identified on interchanging this film dispersant for Orotan 371-A-ER.

Figure 2.2. XPS C1s scan of the oven dried powder film of FA C₁₈ H-SiO₂ particles dispersed in FA C₁₈ aqueous stock solution containing the Orotan CA500 dispersant. The ratio of fatty acid to H-SiO₂ particles was equal to 0.67 and the spectrum was recorded 12 weeks after powder deposition. All SiO₂ particles were originally functionalised in an ethanol solvent system.

Assessment of functional testing results, Part 2.4.2, allowed identification of optimum P/M ratios for future formulation investigation. In order to transform these formulation coatings into
Figure 2.3. XPS Si2p scan of the oven dried powder film of FA C\textsubscript{18} H-SiO\textsubscript{2} particles dispersed in FA C\textsubscript{18} aqueous stock solution containing the Orotan CA500 dispersant. The ratio of fatty acid to H-SiO\textsubscript{2} particles was equal to 0.67 and the spectrum was recorded 12 weeks after powder deposition. All SiO\textsubscript{2} particles were originally functionalised in an ethanol solvent system.

Figure 2.4. XPS O1s scan of the oven dried powder film of FA C\textsubscript{18} H-SiO\textsubscript{2} particles dispersed in FA C\textsubscript{18} aqueous stock solution containing the Orotan CA500 dispersant. The ratio of fatty acid to H-SiO\textsubscript{2} particles was equal to 0.67 and the spectrum was recorded 12 weeks after powder deposition. All SiO\textsubscript{2} particles were originally functionalised in an ethanol solvent system.

model paint systems, water, additives (pH modifier or dispersants), extenders (functional particles) and pigments (coloured particles) had to be combined with a polymer binder or latex. The XPS data of a H-SiO\textsubscript{2} particle-FA C\textsubscript{18}-1052 latex paint system, P/M ratio 0.67, contained signature SiO\textsubscript{2} environments in the Si2p and O1s scans at 103.6 eV\textsuperscript{180} and 532.4 eV\textsuperscript{181} respectively. Expected peaks in the C1s scan at 284.3 eV (-CH\textsubscript{2}CH\textsubscript{2}),\textsuperscript{177} 286.0 eV (C-O(OR))\textsuperscript{178} and 288.7 eV
were also visualised. This finding indicated that the 3.35 wt% of latex binder did not produce additional peaks and therefore suggested that there was a minimal associated chemical functionality on the paint surface. TiO$_2$ (250 nm diameter), dolomite GMR20180904 (41 nm diameter) or GMR20180906 (90 nm diameter) particles were added into the optimised H-SiO$_2$ particle-FA C$_{18}$-Orotan 2500-latex 1052 paint system in accordance with Table 2.3. In the case of the paint drawdown containing H-SiO$_2$ and TiO$_2$ particles in equal parts, the Si2p scan consisted of a single SiO$_2$ environment at 104.2 eV. TiO$_2$ and SiO$_2$ components were identified in the O1s scan at 530.9 eV and 533.1 eV respectively, the Ti2p scan was deconvoluted into a 458.6 eV TiO$_2$2p$^{1/2}$ and a TiO$_2$2p$^{3/2}$ 464.4 eV environment and the C1s scan contained three peaks at 285.0 eV, 286.6 eV and 288.8 eV that represented hydrocarbon, carbonyl and ester groups respectively. The Ti2p and O1s scans are shown in Figures 2.5 and 2.6. Paint films containing H-SiO$_2$ particles with dolomite dopants contained identical peaks to those in the nondoped data; additional modelled peaks featured in the Ca2p and Mg1s scans due to the dolomite presence. In accordance with the dopant’s chemical formula, CaMg(CO$_3$)$_2$, CaO$_2$2p$^{3/2}$ and CaO$_2$2p$^{1/2}$ peaks were realised at 347.6 eV and 351.4 eV respectively. A lone peak at 1305.2 eV in the Mg1s spectra was representative of the full CaMg(CO$_3$)$_2$ structural environment.

Figure 2.5. XPS Ti2p scan of the model paint containing H-SiO$_2$ particles and 50 wt% of a TiO$_2$ (250 nm diameter) particle dopant embedded in FA C$_{18}$ and 1052 latex mixtures before being drawn down on a glass substrate (wet film thickness of 6 mL) and then dried. Orotan CA2500 was the dispersant used to generate the mixtures with a 0.67 P/M ratio.

The X-ray diffraction (XRD) pattern for the powder thin film sample of oven dried H-SiO$_2$ particles (6 wt%) dispersed in a FA C$_{18}$ (4 wt%) stock solution with a 1:3 water-ethanol ratio is
Figure 2.6. XPS O1s scan of the model paint containing H-SiO$_2$ particles and 50 wt% of a TiO$_2$ (250 nm diameter) particle dopant embedded in FA C$_{18}$ and 1052 latex mixtures before being drawn down on a glass substrate (wet film thickness of 6 mL) and then dried. Orotan CA2500 was the dispersant used to generate the mixtures with a 0.67 P/M ratio.

shown in Figure 2.7. As expected, amorphous SiO$_2$ particles did not produce diffraction peaks but the peak contribution from FA C$_{18}$ aligned with inorganic crystal structure database standards. High intensity crystalline fatty acid peaks were identified at 16° (700), 22° (402), 24° (602) and 40° (813). Near identical peaks were visualised in the XRD patterns of oven dried powder films: FA C$_{18}$ H-SiO$_2$ particles dispersed in FA C$_{18}$ aqueous stock solution with the Orotan 371-A-ER or CA500 dispersant, fatty acid to H-SiO$_2$ particle (P/M) ratio was equal to 0.67. The spectra were recorded 12 weeks after powder deposition and all SiO$_2$ particles were originally functionalised in an ethanol solvent system.

Functional groups associated with SiO$_2$ particles, FA C$_{18}$ and oven dried FA C$_{18}$ (H-SiO$_2$) (6 wt%) dispersed in FA C$_{18}$ (4 wt%) stock solution with a 1:3 water-ethanol ratio were compared using Fourier transform infrared (FT-IR) analysis. Medium to broad peaks in the SiO$_2$ precursor particle spectrum at 1080 cm$^{-1}$, 800 cm$^{-1}$ and 450 cm$^{-1}$ were characteristic of Si-O-Si asymmetric transverse optical stretching, symmetric Si-O-Si stretching and symmetric Si-O-Si bending; it followed that positionally similar peaks, of lower intensity, were also visualised in the SiO$_2$ containing oven dried powder film sample. The strongest -CH asymmetric and symmetric alkane stretches were respectively identified around 2920 cm$^{-1}$ and 2850 cm$^{-1}$ in both FA C$_{18}$ and the powder film sample. A C=O carboxylic acid stretch was found in the FA C$_{18}$ containing spectra at 1700 cm$^{-1}$, a C-O stretching band appeared at 1430 cm$^{-1}$ and the notable absence of a broad O-H symmetrical
Figure 2.7. XRD pattern for the powder thin film sample of oven dried FA C\textsubscript{18} H-SiO\textsubscript{2} particles (6 wt\%) dispersed in FA C\textsubscript{18} (4 wt\%) stock solution with a 1:3 water-ethanol ratio. Peaks consistent with FA C\textsubscript{18} have been referenced in red.

stretch at 3000 cm\textsuperscript{-1} was indicative of acid dimerisation.\textsuperscript{188,189}

Figure 2.8 displays FT-IR spectra of key formulation precursors and the oven dried powder films: FA C\textsubscript{18} H-SiO\textsubscript{2} particles dispersed in FA C\textsubscript{18} aqueous stock solution with the Orotan CA500 dispersant, fatty acid to H-SiO\textsubscript{2} particle (P/M) ratio were equal to 0.17, 0.33 and 0.67. Bands in the H-SiO\textsubscript{2} particle containing samples’ spectra at 1063 cm\textsuperscript{-1}, 774 cm\textsuperscript{-1} and 760 cm\textsuperscript{-1} were again indicative of Si-O-Si asymmetric transverse-optical stretching, symmetric Si-O-Si stretching and bending respectively. Powder samples with FA C\textsubscript{18} generated spectra that included a C-H bending vibration at 721 cm\textsuperscript{-1}, another C-H bending vibration at 1473 cm\textsuperscript{-1} and a -CH\textsubscript{2} symmetric alkane stretch at 2850 cm\textsuperscript{-1}. The 946 cm\textsuperscript{-1} and 1299 cm\textsuperscript{-1} bands were associated with C-O carboxylic acid bending and stretching respectively. Lastly, a C=O carboxylic acid stretch at 1701 cm\textsuperscript{-1} was characteristic of a FA C\textsubscript{18} containing sample but the lack of a broad O-H stretch at 3000 cm\textsuperscript{-1} confirmed acid dimerisation in the condensed state. Contrasting the spectra of dried formulations, increased intensity of the characteristic FA C\textsubscript{18} bands was observed from low to high P/M ratios. The reverse is true of the characteristic SiO\textsubscript{2} band intensities. From this the desired P/M ratios have been preserved through the preparative steps. The absence of a broad O-H band at 3000 cm\textsuperscript{-1} also indicated water had evaporated from powder surfaces on drying.\textsuperscript{188,189}

Raman spectra of SiO\textsubscript{2} particles, FA C\textsubscript{18} and the oven dried powder films of H-SiO\textsubscript{2} particles dispersed in FA C\textsubscript{18} aqueous stock solution containing the Orotan CA500 dispersant with 0.17, 0.33 or 0.67 P/M ratios are shown in Figure 2.9. In keeping with previously described studies,
Figure 2.8. FT-IR spectra of: SiO$_2$ particles, FA C$_{18}$ and the oven dried powder films of H-SiO$_2$ particles dispersed in FA C$_{18}$ aqueous stock solution containing the Orotan CA500 dispersant. The spectra of 0.17, 0.33 and 0.67 fatty acid to H-SiO$_2$ particle ratios were recorded 12 weeks after powder deposition. All SiO$_2$ particles were originally functionalised in an ethanol solvent system.

SiO$_2$ particles produced bands in the Raman spectra at 204, 262, 353 and 469 cm$^{-1}$ and all FA C$_{18}$ associated modes <1200 cm$^{-1}$ represented C-C skeletal stretches. Additional FA C$_{18}$ alkane chain modes were also seen at 1295 cm$^{-1}$ (-CH$_2$)$_n$ in-phase twist), 1437 cm$^{-1}$ (CH$_3$ antisymmetric bend), 2846 cm$^{-1}$ (CH$_2$ symmetric stretch), 2882 cm$^{-1}$ (symmetric -CH$_3$ stretch) and 2966 cm$^{-1}$ (antisymmetric -CH$_3$ stretch) and a weak C=O carboxylic acid dimer band was recorded at 1630 cm$^{-1}$. It was not appropriate to directly contrast band intensities from different P/M ratio samples as SiO$_2$ and FA C$_{18}$ are not equally effective Raman scatterers. However, variations in relative intensities could be explored. From the spectra of dried formulations, decreased intensity of the characteristic 469 cm$^{-1}$ SiO$_2$ band relative to the FA C$_{18}$ modes was observed from low to high.
P/M ratios.\cite{188,189}

Figure 2.9. Raman spectra of: SiO$_2$ particles, FA C$_{18}$ and the oven dried powder films of H-SiO$_2$ particles dispersed in FA C$_{18}$ aqueous stock solution containing the Orotan CA500 dispersant. The spectra of 0.17, 0.33 and 0.67 fatty acid to H-SiO$_2$ particle ratios were recorded 12 weeks after powder deposition. All SiO$_2$ particles were originally functionalised in an ethanol solvent system.

As previously mentioned, innately hydrophilic SiO$_2$ particles required functionalisation with FA C$_{18}$ prior to formulation incorporation. Transmission electron microscopy (TEM) was utilised to identify the coated particle reagent size. Figure 2.10 suggests that particle diameters prior to functionalisation were consistently <100 nm, the smallest of which were recorded at 25 nm. These figures are loosely in keeping with Evonik’s average particle size value of 45 nm. After functionalisation, the average value rose to 100 nm, due to the surrounding acid layer, with the maximum measurable particle diameter equalling 145 nm.

The surface topography of the powder thin film sample of oven dried H-SiO$_2$ particles (6 wt%)
Figure 2.10. Particle size determination via TEM of as received SiO$_2$ particles and FA C$_{18}$ functionalised SiO$_2$ particles.

dispersed in a FA C$_{18}$ (4 wt%) stock solution with a 1:3 water-ethanol ratio was assessed using scanning electron microscopy (SEM). Areas of mixed scale surface protrusions were formed through combination of nano particle deposits and micron sized agglomerates (>10 µm); a key requirement for superhydrophobic functionality. This powder film’s favourable surface hierarchy contributed to an average water contact angle of 156±8°, as shown in Figure 2.17 from Part 2.4.2.

High magnification SEM images in Figure 2.11 depict the dried powder sample generated from the formulation comprising H-SiO$_2$ particles dispersed in a FA C$_{18}$ aqueous stock solution containing the Orotan CA500 dispersant. A P/M ratio of 0.67 was utilised for this sample. Multiscale particle clusters (5 µm) were present in combination with nanosized particles (100 nm) to produce the desired rough surface landscape that minimised the water droplet-coating surface area contact. While it was noted that sample morphology was exaggerated in the lowest P/M containing samples, a higher wt% of FA C$_{18}$ was needed to lower surface energy and improve hydrophobicity. It follows that the reverse is true of the powder coating with the highest P/M ratio; particles appeared embedded in a thick acid layer. Therefore, the optimum ratio of 0.67 managed to preserve surface structure and sufficiently lowered surface energy.

The transition from a slurry coatings to a model paint system, relies on the integration of a polymer binder/latex with water, additives (pH modifier or dispersants), extenders (functional particles) and pigments (coloured particles). Latex 1052 was added to the optimised H-SiO$_2$-FA C$_{18}$ formulations with further trials exploring the use of latex in TiO$_2$ (250 nm diameter), dolomite GMR20180904 (41 nm diameter) or GMR20180906 (90 nm diameter) particle doped H-SiO$_2$-FA C$_{18}$ systems, Table 2.3. The SEM images shown in Figure 2.11 correspond to the previously
described undoped dried coating slurry with a P/M ratio equal to 0.67. This high magnification imaged surface was found to be visually indistinguishable from the corresponding 1052 latex containing model paint; the latex (3.35 wt%) was considered to have had negligible surface structure influence. It was noted that H-SiO$_2$ particles displayed no evidence of coalescence, instead the latex was thought to have increased surface hardness. Similar surface topography was also seen upon doping with TiO$_2$ (250 nm diameter) particles, Figure 2.12. A relatively high average water contact angle of 135±9° and evidence of a mixed Cassie-Baxter/Wenzel droplet rolling regime was achieved on this dried drawdown; likely due to the variation in agglomerated particle size and shape. Many roughly spherical particles were visualised at 200 nm in diameter and clusters of highly structured micro features were suspected artifacts of the SiO$_2$ functionalisation process. As the minerals utilised in this sample were of similar size, and in equal parts, it was difficult to differentiate between the two particle types in SEM analysis. Figure 2.13 presents SEM images of H-SiO$_2$-FA C$_{18}$ formulations containing latex and the dolomite GMR20180904 (41 nm diameter) particle dopant. The hydrophobicity of dolomite doped model paint films were dramatically reduced at levels between 5 wt% and 50 wt%. The 5 wt% doped sample SEM images displayed characteristically spherical H-SiO$_2$ particles (200 nm) with few dolomite plate-like structures. Many more agglomerated flat plates were visualised as the dopant weight percentage was increased; further compromising surface hierarchy and therefore hydrophobicity.

Figure 2.14 depicts the profilometry mapping data that again corresponds with the oven dried
Figure 2.12. SEM images of the model paint containing H-SiO$_2$ particles and 50 wt% of a TiO$_2$ (250 nm diameter) particle dopant embedded in FA C$_{18}$ and 1052 latex mixtures before being drawn down on a glass substrate (wet film thickness of 6 mL) and then dried. Orotan CA2500 was the dispersant used to generate the mixtures with a 0.67 P/M ratio.

Figure 2.13. SEM images of the model paints containing H-SiO$_2$ particles and 5 wt% or 50 wt% of a dolomite GMR20180904 (41 nm diameter) particle dopant embedded in FA C$_{18}$ and 1052 latex mixtures before being drawn down on a glass substrate (wet film thickness of 6 mL) and then dried. Orotan CA2500 was the dispersant used to generate the mixtures with a 0.67 P/M ratio.

powder films originally formulated using hydrophobic-SiO$_2$ particles (H-SiO$_2$) dispersed in octadecanoic acid (FA C$_{18}$) aqueous stock solution containing the Orotan CA500 dispersant. Various maps of the 0.22, 0.67 and 1.00 fatty acid to H-SiO$_2$ particle (P/M) ratio samples are displayed for comparison purposes. The average water contact angles, at the time of mapping, were $130 \pm 4^\circ$, $151 \pm 11^\circ$ and $151 \pm 1^\circ$ respectively. Due to the relatively high wt% of particles versus low acid coverage, the 0.22 powder sample produced the most textured film with the highest roughness factor (33.5 µm). The reverse was true of the P/M = 1.00 sample where surface features appeared rounded and were less abundant per unit area; the roughness factor was 9.2 µm. Therefore it followed that
the 0.67 sample was able to produce a maximum contact angle of 162° because surface features remained well defined and in sufficient quantity. The FA C₁₈ component of this surface did not significantly mask the structural scaffold but imparted adequate surface energy lowering fatty acid chains, as supported by the previously described SEM analysis.

**Figure 2.14.** Profilometry mapping of oven dried powder films originally formulated using H-SiO₂ particles dispersed in FA C₁₈ aqueous stock solution containing the Orotan CA500 dispersant. Various maps of the 0.22, 0.67 and 1.00 fatty acid to H-SiO₂ particle ratio samples were recorded 12 weeks after powder deposition. All SiO₂ particles were originally functionalised in an ethanol solvent system.

The most useful characterisation techniques were those that investigated surface morphology. Coatings or model paints that comprised a combination of nano and micro sized particle deposits had a tendency to display more hydrophobic functionalities. This was realised in H-SiO₂ containing
dried slurries with optimised P/M ratios and H-SiO$_2$ model paints and those doped with TiO$_2$ particles. Conversely, dolomite dopant particles contributed flat/plated surface structures, which qualitatively reduced roughness and resulted in hydrophilic tenancies.

2.4.2 Functional Properties and Performance Testing

The self-cleaning ability of a surface, through physical process, is dependent upon a Cassie-Baxter wetting regime; a phenomenon that can be confirmed through average water contact and tilting angle analysis. Therefore, the slurry and powder coatings characterised in Part 2.4.1 underwent varying degrees of these functional and performance testing methods depending on sample viability. Where appropriate, three water contact and tilting angles were measured per coating and then averaged. These values were commonly measured 24h after sample generation but timed studies required additional readings to be recorded at subsequent 3 month intervals.

Low surface energy 1H,2H,2H-perfluorooctyltriethoxysilane (FAS C$_8$) hydrophobic-SiO$_2$ particles (H-SiO$_2$) (6 wt%) were separately magnetically stirred, 60 mins, in FAS C$_8$ (15 wt%) stock solutions with 0:1, 1:3, 1:1, 3:1 and 1:0 water-ethanol ratios. Particle coagulation was noted in mixtures with a higher water content despite the addition of NaOH (2.00 mol dm$^{-3}$), which afforded a pH 8 environment. The resulting slurries were pipetted onto double sided Scotch tape covered glass substrates and dried overnight; average water contact and tilting angles were consequently determined for each film sample. The degree of hydrophobicity achieved across all water-ethanol stock ratio containing samples was consistent within experimental error, a maximum average value of 151$\pm$3$^\circ$ was realised on the dried 0:1 water-ethanol film and a minimum of 144$\pm$8$^\circ$ on the equivalent 3:1 sample. Despite the promising water contact angles, the level of sonication required to successfully disperse the hydrophobic particles in the 0:1 to 3:1 water-ethanol ratio stocks was dramatically increased from 20 to 60 mins respectively. In the most extreme case, H-SiO$_2$ particles floated when added to the 1:0 water-ethanol stock solution so a coating could neither be generated or functionally tested. Average water tilting angle data highlighted a transition from the Cassie-Baxter to a mixed Cassie-Baxter/Wenzel regime with increasing slurry water content. Water droplets were able to freely roll on the samples originally containing 0:1 and 1:3 ratio stock solutions, average tilting angle values of 3$\pm$3$^\circ$ were calculated. The 1:1 and 3:1 water-ethanol based film samples produced contrasting average water tilting angle values of 28$\pm$5$^\circ$ 42$\pm$3$^\circ$ respectively.

From this data, it can be deduced that the dispersion of H-SiO$_2$ particles in FAS C$_8$ based formulations relied on the presence of the non-polar ethanol solvent. It is believed that slurries with
a larger ethanol component afforded greater fluorinated polymer dispersion and therefore enhanced surface water repulsion. The increased water repulsion likely offered a feasible route to substantial air accumulation within the voids found between morphological surface structural features. Upon this air layer, water droplets freely rolled.

Due to the high cost and toxicity associated with fluorinated polymer use, water retardant octadecanoic acid (FA \text{C}_{18}) was investigated as an industry-approved functional alternative. H-SiO$_2$ (6 wt%)/FA \text{C}_{18} (4 wt%) slurries with 0:1, 1:3, 1:1, 3:1 and 1:0 water-ethanol ratios, adjusted to pH 8, were applied to double sided tape covered microscope slides. It was found that the slurries containing water-ethanol ratios of 3:1 and 1:0 contained considerable particle agglomerates and uniform films were not easily achieved. Figures 2.15 and 2.16 display the average water contact and tilting angle data for the described study. There was no significant trend associated with increasing water content in the FA \text{C}_{18} formulations and the average water contact angle recorded for their dried slurry films. Values of 142±6°, 164±8°, 145±1° and 144±11° corresponded to the use of 0:1, 1:3, 1:1 and 3:1 water-ethanol ratio stocks respectively; as before the 1:0 ratio was not successful as H-SiO$_2$ particles could not be dispersed in a 100% water based stock solution. Average water tilting angles tended towards lower or more favourable values on dried slurries derived from ethanol alone, 16±2°. Alternatively, these FA \text{C}_{18} formulations were dried at 120 °C for 6h to produce water repellent powders that were pressed onto Scotch tape covered glass slides. It is useful to mention that this process was not possible with FAS \text{C}_8 based samples as they generated unworkable thick pastes that had to be discarded.

Figures 2.15 and 2.16 incorporate the functional testing data for this deviation in preparation route. It was apparent that the powder films resulted in significantly reduced hydrophobic functionality. The lowest average contact angle was recorded on the powder film derived from the 0:1 water-ethanol based stock solution, 46±3°. Powder samples that originally contained ethanol generated values that fell below the hydrophobic threshold and were similar within experimental error. This contradicted the belief that ethanol’s volatility would accelerate sample drying and lead to minimised residual water contents. Average water tilting angles were less favourable than their dried slurry counterparts and showed little variation between samples generated from the 0:1, 1:3, 1:1 and 3:1 water-ethanol stock solutions, averages centred around 40° indicative of a mixed Cassie-Baxter/Wenzel surface wetting regime.

The initially disappointing functional dried powder testing results, likely due to incomplete sample drying, were further monitored in a timed study. The dried powder samples were stored at
Figure 2.15. Average water contact angles of oven dried powder films and thin slurry films of FA C_{18} H-SiO_{2} particles (6 wt%) dispersed in FA C_{18} (4 wt%) stock solutions with 0:1, 1:3, 1:1, 3:1 and 1:0 water-ethanol ratios.

Figure 2.16. Average water tilting angles of oven dried powder films and thin slurry films of FA C_{18} H-SiO_{2} particles (6 wt%) dispersed in FA C_{18} (4 wt%) stock solutions with 0:1, 1:3, 1:1, 3:1 and 1:0 water-ethanol ratios.

room temperature and pressure and functionally tested at 3 and 6 months from the initial deposition date, Figures 2.17 and 2.18. After 3 months, elevated average water contact angles of 51±4°, 156±8°, 155±13° and 152±8° supported the theory that further sample drying had the potential to yield desired superhydrophobic surface properties. The dried powder film of the 3:1 water-ethanol stock containing formulation showed the most substantial increase in water repellency with an average water contact angle increase of 85°; an intuitive result as this mixture originally contained the highest water content and therefore had an increased drying potential. It was hypothesised that
the greater the water content, the longer to complete sample dryness. The reverse was expected to be true of samples containing higher percentages of volatile solvent. As complete sample dryness is a generally accepted requirement for droplet balling, the previous statements provide some explanation as to the observed water contact and tilting angle trends. Film hydrophobicity showed no additional improvement between the 3 and 6 months period from deposition. In the case of the 3:1 water-ethanol stock containing formulation, an average decrease of 42° was observed in this 3 month time frame and was attributed to surface degradation. Slight reductions in average values also noted in the 1:3 and 1:1 water-ethanol stock containing formulations but were not large enough to be deemed significantly different due to experimental error. The most drastic finding attributed to the later part of this timed study was the apparent switch from a mixed Cassie-Baxter/Wenzel to a Cassie-Baxter surface wetting regime. Water droplets were able to bounce and roll upon the 1:3, 1:1 and 3:1 water-ethanol stock containing formulations when applied as powder films. This was the first and an extremely promising example of a superhydrophobic, Cassie-Baxter type film generated from SiO₂ particles, FA C₁₈ and a water containing solvent system. Despite the issues surrounding the floating of H-SiO₂ particles on 1:0 water-ethanol based mixtures, this result indicated that the generation of a water repellent material from a water based solvent system was entirely feasible.

Figure 2.17. Average water contact angles of dry powder films at time = 0, 3 and 6 months. Oven dried slurries of FA C₁₈ H-SiO₂ particles (6 wt%) dispersed in FA C₁₈ (4 wt%) stock solutions with 0:1, 1:3, 1:1, 3:1 and 1:0 water-ethanol ratios afforded said powders.

These superhydrophobic functional testing results provided evidence to suggest that highly water repellent samples could be generated from a partial aqueous base. The difficulties associated
Figure 2.18. Average water tilting angles of dry powder films at time = 0, 3 and 6 months. Oven dried slurries of FA C<sub>18</sub> H-SiO<sub>2</sub> particles (6 wt%) dispersed in FA C<sub>18</sub> (4 wt%) stock solutions with 0:1, 1:3, 1:1, 3:1 and 1:0 water-ethanol ratios afforded said powders.

with dispersing H-SiO<sub>8</sub> particles in 1:0 water-ethanol solvent systems were mitigated using either Orotan 371-A-ER (sodium salt of a carboxylate polyelectrolyte pigment dispersant) or Orotan CA2500 (hydrophobic copolymer dispersant). These dispersants primarily lowered the interfacial tension between the liquid media and the hydrophobic particles whilst keeping particles apart from one another via stearic or electronic repulsion mechanisms, or a mixture of both. As outlined in Table 2.1, Orotan 371-A-ER was added to aqueous systems containing FAS C<sub>8</sub>-H-SiO<sub>2</sub> particles with polymer/mineral (P/M) ratios of 0.17, 0.22, 0.33, 0.67 and 1.00 and dried to powders for film testing purposes. Initial average contact angle values were 133±4°, 155±3°, 150±3°, 165±4° and 164±4° for these powder film samples respectively. A correlation between increasing P/M ratio and enhanced superhydrophobicity was loosely identified; all samples with a P/M ratio of 0.22 or greater were found to be characteristic of Cassie-Baxter type surfaces. The switch to the hydrophobic copolymer Orotan CA2500 resulted in slightly reduced water repellent properties. Respective P/M ratio samples had average contact angle values of 152±1°, 146±1°, 149±3°, 147±5° and 159±3°; all samples were typical of the Cassie-Baxter regime. The use of higher P/M ratios was thought to afford more favourable functionalities due to the increased surface energy lowering component per unit area of surface roughening particles.

Similarly, the use of Orotan 371-A-ER was explored in non-fluorinated FA C<sub>18</sub>-H-SiO<sub>2</sub> particle formulations with 1:0 water-ethanol solvent systems. Powder film reagents are listed in Table 2.1 and their resulting average water contact and tilting angle results, over a 12 week period, are
plotted in Figures 2.19 and 2.20. The initial sample drying process was deemed adequate as average water contact angles were generally consistent for a selected P/M ratio over the course of this timed study. A P/M ratio of 0.33 produced the most water repellent powder film samples with average water contact angle values of 143±16°, 141±5° and 143±5° at weeks 4, 8 and 12 from deposition respectively. The 0.33 P/M ratio samples also tended towards lower average tilting angle results, a value of 36±7° was realised 12 weeks from deposition. Missing data points in Figure 2.20 correspond to entirely Wenzel regime surfaces whereby droplets remained pinned to vertical coatings; values were in excess of 90°. While these non-fluorinated powder film results were a promising step towards achieving the contact angles typical of formulations comprising aqueous solvent systems, 99-143°, superhydrophobicity had not been achieved.

Figure 2.19. Average water contact angles of dry powder films at time = 0, 4, 8 and 12 weeks. Oven dried slurries of FA C_{18} H-SiO_{2} particles dispersed in FA C_{18} aqueous stock solutions. Orotan 371-A-ER was the dispersant used to generate mixtures with 0.17, 0.22, 0.33, 0.67 and 1.00 P/M ratios. Average water contact and tilting angles on dry powder Orotan CA500 containing films 0, 4, 8 and 12 weeks from deposition are displayed in Figures 2.21 and 2.22. As with all previous systems, H-SiO_{2} particles were generated via an ethanol based functionalisation process prior to their use in subsequent solvent systems. Again, FA C_{18}-H-SiO_{2} particle containing formulations with P/M ratios of 0.17, 0.22, 0.33, 0.67 and 1.00 were explored. There was an apparent increase in average water contact angle 4 weeks after powder film deposition, which indicated that improved hydrophobicity relied on the time taken for residual water to evaporate from film surfaces. At this time stage a value of 159±5° was calculated on the 0.67 P/M ratio containing sample; water repellency stabilised thereafter. This exceptional superhydrophobic result was thought to be a result
Figure 2.20. Average water tilting angles of dry powder films at time = 0, 4, 8 and 12 weeks. Oven dried slurries of FA C\textsubscript{18} H-SiO\textsubscript{2} particles dispersed in FA C\textsubscript{18} aqueous stock solutions. Orotan 371-A-ER was the dispersant used to generate mixtures with 0.17, 0.22, 0.33, 0.67 and 1.00 P/M ratios.

The described hydrophobicity testing outlined in Part 2.4.2 has been focused on the use of H-SiO\textsubscript{2} particles generated in ethanol solvent systems. A switch to aqueous conditions provided an opportunity to reduce cost and toxicity. As such, the water based SiO\textsubscript{2} particle functionalisation method described in Part 2.3.3 was the initial procedure for production of new generation dry powder Orotan CA500 containing films with FA C\textsubscript{18}-H-SiO\textsubscript{2} particle P/M ratios of 0.17, 0.22, 0.33, 0.67 and 1.00. Unfortunately, this functionalisation process adaptation had negative repercussions on average water contact and tilting angle data. Immediately after powder deposition average water contact angles values were calculated between 37-87°, as opposed to 79-141° upon the samples with the ethanol SiO\textsubscript{2} functionalisation step. There was an increase in hydrophobicity 4 weeks from sample preparation, a value of 112±8° was realised on the aqueous solvent formulation with a P/M ratio of 1.00. Stability in water repellency was noted for all P/M ratio samples after 4 weeks from dry powder film coating. As before, the lag time associated with functional stability was attributed
Figure 2.21. Average water contact angles of dry powder films at time = 0, 4, 8 and 12 weeks. Oven dried slurries of FA C_{18} H-SiO_{2} particles dispersed in FA C_{18} aqueous stock solutions. Orotan CA500 was the dispersant used to generate mixtures with 0.17, 0.22, 0.33, 0.67 and 1.00 P/M ratios.

Figure 2.22. Average water tilting angles of dry powder films at time = 0, 4, 8 and 12 weeks. Oven dried slurries of FA C_{18} H-SiO_{2} particles dispersed in FA C_{18} aqueous stock solutions. Orotan CA2500 was the dispersant used to generate mixtures with 0.17, 0.22, 0.33, 0.67 and 1.00 P/M ratios. The absence of data for the 0.17 P/M ratio sample at 0 weeks from deposition was indicative of droplet adhesion.

to time taken for complete evaporation of residual surface water. The Wenzel wetting regime was consistently observed throughout this study and it was theorised that the water based solvent system did not allow for sufficient SiO_{2} particle-FA C_{18} interaction, which resulted in insufficient particle coating.

Identifying optimum particle roughening and surface energy lowering agent combinations and
ratios have been useful in producing the most water repellent powder films or coatings within experimental constraints. However, for a coating formulation to be considered a model paint the following components are required: water, latex, additives, extenders and pigments. Previous systems have contained water, additives (pH modifiers or dispersants), extenders (functionalising reagents) and pigments (coloured particles) but lacked a polymer binder or latex. Latex inclusive formulations were consequently produced according to the procedure in Part 2.3.4. H-SiO$_2$-FA C$_{18}$ mixtures were added to 1052, 1070 or 1080 latex systems before being drawn down on glass substrates (wet film thickness of 6 mL) prior to drying. P/M ratios of 0.67 or 1.00 were chosen due to their propensity towards superhydrophobic material production and Orotan CA2500 was the dispersant used in all latex trials as its functionality outperformed alternative additives. Figure 2.23 indicates that water repellency was maximised on dry paints containing the 1052 latex. Average water contact angles of 130±8° and 140±2° and average water tilting angles of 47±4° and 43±8° were recorded on drawdowns with P/M ratios of 0.67 and 1.00 respectively. 1052 was the only latex inclusive formulation that resulted in non-adhered water droplets on vertical painted substrates; a mixed Cassie-Baxter/Wenzel surface had been created. Average water contact angles between 93° and 111° were achieved when the 1070 and 1080 latexes were used in comparable samples proving coating functionality had been dramatically reduced. These results proved that 1052 latex was most suited to use in SiO$_2$ systems and that 1.00 P/M ratio based paints gave more favourable testing results than their 0.67 alternatives. Unfortunately, the higher mineral content made slurries extremely viscous and unworkable so further investigations involved incorporating P/M ratios of 0.67 in latex 1052. High speed video snap shots of various sized water droplets were recorded hitting the P/M ratio = 0.67 drawdown containing 1052 latex. Water droplet beading can be observed but bouncing or rolling was not detected due to the hydrophobic functionality, Figure 2.24.

Having concluded the best choice of dispersant, P/M ratio and latex, the change in physical and chemical film drawdown properties were monitored with the addition of various dopant minerals. TiO$_2$ (250 nm diameter), dolomite GMR20180904 (41 nm diameter) and dolomite GMR20180906 (90 nm diameter) particles were chosen to impart additional nanosized surface structure and/or innate chemical advantages. In accordance with Figure 2.25, TiO$_2$ particles were doped into the optimised H-SiO$_2$ particle-FA C$_{18}$-Orotan 2500-latex 1052 system with a P/M ratio of 0.67. Average water contact angles of 99±2° and 92±3° corresponded to model paints containing 5 wt% and 10 wt% TiO$_2$ dopant levels; a significant drop in hydrophobicity compared with the undoped
Figure 2.23. Average water contact angles of model paints. H-SiO$_2$ particles with FA C$_{18}$ mixtures were added to 1052, 1070 or 1080 latex systems before being drawn down on glass substrates (wet film thickness of 6 mL) and then dried. Orotan CA2500 was the dispersant used to generate mixtures with 0.67 and 1.00 P/M ratios.

Figure 2.24. High speed camera snap shots of water droplets hitting a formulation coating. H-SiO$_2$ particles with FA C$_{18}$ were added to a 1052 latex system before being drawn down on a glass substrate (wet film thickness of 6 mL) and then dried. Orotan CA2500 was the dispersant used to generate the paint mixture with a 0.67 P/M ratio.

value of 130±8°. Slight functional improvements, from the 0 wt% baseline, were measured on paints containing 25 wt% and 50 wt% dopant levels. Water droplets rolled on these coatings when tilted by 50° and the average water contact angles were 137±1° and 135±9° respectively. The use of dopant dolomite GMR20180904 particles (41 nm diameter) again forced a reduction in average contact angle in comparison with the original undoped system. The average water contact angles with dopant levels between 5 wt% and 50 wt% were between 68° and 100°. This flat/plated particle dopant addition was unfavorable and there was no clear pattern that linked dopant wt% to hydrophobicity. It was therefore unsurprising that the milled dolomite GMR20180906 particles (80 nm diameter) had an equally negative effect on average water contact angle results. From 5 wt% to 50 wt% of dopant additive, water contact angles did not exceed 101° on any surface portion tested. Water droplets remained pinned on any dolomite containing surface so showed little promise for application in self-cleaning decorative paint applications.

Particle doped systems had the potential to elevate model paint hydrophobicity by introducing
new surface dimensions, textures and chemistries. However, it was determined that mineral choice was crucial and high wt% dopant levels were needed to realise additional low-level functional benefits, as seen in the TiO$_2$ dopant study. With that said, the work completed in this chapter surpassed literature based comparable model paint systems. An example of a singular formulation coating that required minimal subsequent physical surface modification, such as polishing, was only able to afford water contact angles of 115°. This clearly highlights the functional step change of work completed in this research stream; major breakthroughs included the use of water repellent materials in aqueous systems and the absence of fluorinated reagents. Chapter 3 goes on to cover the even more successful use of CaCO$_3$ particles in model paint systems. Favourable sets of functional results were generated and samples displayed notable self-cleaning abilities.

### 2.5 Summary

Superhydrophobic, Cassie-Baxter wetting regime model paints were unfortunately unachievable using low toxicity and low cost SiO$_2$ particles with octadecanoic acid (FA C$_{18}$) containing aqueous systems. However, important step changes towards generating workable and highly functional model paint formulations were realised.

FA C$_{18}$ functionalised SiO$_2$ (H-SiO$_2$) particles (6 wt%) were initially dispersed in FA C$_{18}$ (4
wt%) stock solutions with various water-ethanol ratios. Exceptionally high average water contact angles, 164±8°, and mixed Cassie-Baxter/Wenzel wetting models were achieved on dried slurry films. Timed functionality testing was carried out on dried powder samples with the previous particle and surface energy lowering FA C₁₈ combination (P/M ratio = 0.67). After 3 months of powder film drying at room temperature and pressure the average contact angle almost matched those of the original dried slurry and the full Cassie-Baxter wetting regime was observed. This proved complete sample drying was crucial and should be monitored with periodic functional testing.

In order to further reduce toxicity and cost, the next study focused on interchanging mixed water-ethanol based solvent systems for entirely aqueous formulations. An Orotan CA2500 dispersant was added to disperse water repellent H-SiO₂ particles in aqueous systems. Dried powder films with P/M ratios of 0.17, 0.67 and 1.00 consistently displayed superhydrophobic functionalities during the 4-12 week period from deposition and the Cassie-Baxter wetting regime was again observed.

For model paint classification, the optimised water based superhydrophobic slurries subsequently required the addition of a latex binder. Practical formulation workability was achieved using the P/M ratio = 0.67 and the 1052 latex combination; an associated average water contact angle of 130±8° was recorded but there was complete Wenzel model wetting. The incorporation of TiO₂ dopant particles (50 wt%) worked to increase the average water contact angle, 130±8°, and water droplets rolled when coatings were tilted by 50°. It was thought that the innate hydrophobic tendency of the TiO₂ spherical particles resulted in the a more favourable mixed Cassie-Baxter/Wenzel surface model. It was concluded that surface cleaning properties would only be realised for similar aqueous FA C₁₈-Orotan CA2500-1052 latex systems with a particle base that deviates from H-SiO₂ particles.

The work in Chapter 3, goes on to make use of CaCO₃ particles in FA C₁₈ model paint systems. CaCO₃ reagents not only fulfil industry’s criteria of low toxicity and cost commercial products but also produced favourable sets of functional results with samples displaying notable self-cleaning characteristics.
Chapter 3

Towards Self-cleaning, Superhydrophobic CaCO$_3$-based Decorative Paints

3.1 Background

Following Chapter 2, a physical self-cleaning superhydrophobic surface requires both hierarchical surface structure and a top layer of epicuticular hydrophobic wax, or equivalent. The resultant functional outcome of the described surface feature combination are: a superhydrophobic water contact angle of $>150^\circ$ and a low water tilting angle, $<5^\circ$. Roughened special wettability materials are also commonly characterised as having a Cassie-Baxter or Wenzel type wetting regime. Water droplets on sticky Wenzel surfaces are known to fully contact surface morphological peak and valley contours whereas the Cassie-Baxter model consists of an entrapped air layer that resides within surface cavities, therefore maximising the liquid-solid interface area and minimising the equivalent liquid-gas area. The latter model promotes droplet rolling; dynamic droplets pick up microbes and foreign dust/dirt particles as they roll on the gaseous lubricant and give rise to the self-cleaning effect.

3.1.1 Superhydrophobic Self-cleaning Coating and Paint Technology with CaCO$_3$ Particles

Examples of superhydrophobic self-cleaning surfaces generated through predominantly facile formulation application processes, such as painting, spray coating or dip coating, have been reviewed and produced as documented throughout Chapter 2. While SiO$_2$ and TiO$_2$ particle based coatings are of low toxicity, low cost and in many cases have produced highly functional
coatings, their compatibility with commercial paint components was determined suboptimal.

In response, the easily accessible and economically viable CaCO$_3$ mineral was investigated as an alternative roughening agent. Literature searches indicated that Chen et al. had successfully prepared CaCO$_3$ nanoparticles with hydrophobic properties. The particles in this work were generated by a carbonation route in the presence of dodecanoic acid. It was observed that increasing weight percentages of dodecanoic acid, up to monolayer coverage, improved the water contact angle of the resulting particles. The hydrophobic value of 120° remained unchanged beyond this point; thought to be due to the complete CaCO$_3$ surface coverage of the cubic particles.$^{190}$ Similarly, Wang et al. created hydrophobic CaCO$_3$ particles via an in situ carbonation method using a Ca(OH)$_2$ slurry and an ethanol solution of oleic acid. By increasing the weight ratio of oleic acid, to 2.7 wt%, the surface property of the particles was changed from hydrophilic to hydrophobic. A maximum water contact angle value recorded at 108°.$^{191}$

Coatings have also been afforded through CaCO$_3$ particle inclusion. In the work carried out by Atta et al., superhydrophobic CaCO$_3$ particles were fabricated through carbonation and then modified with a range of fatty acid solutions. The acid covered particles were then dispersed in an epoxy resin and spray deposited onto brushed glass slides or carbon steel. The presence of epoxy groups were found to substantially increase the sample water repellency as a contact angle of 161° and tilting angle of 1° was measured. The low water tilting angle was indicative of a Cassie-Baxter type surface and therefore self-cleaning abilities were assumed.$^{192}$ A very low cost and facile method for achieving a superhydrophobic surface was produced by Hu et al. using precipitated CaCO$_3$. The mineral was first dispersed in an oleic acid/water mixture and then dried in 120 °C for 2 hours. The resulting modified power was evenly applied to double sided tape for water contact angle testing. Values of 164° and 163° were measured on the advancing and receding contact angles respectively. Tilting angles were also low enough to satisfy self-cleaning functionality requirements.$^{193}$ Similar work was conducted by Zhang et al. through spin coating a suspension of nano and micro scale particles followed by further addition of an octadecanoic acid monolayer. The self-assembled monolayer helped produce an average contact angle of 153° and tilting angle of 8° and consequently displayed self-cleaning characteristics.$^{194}$

The following research most closely resembled the use of CaCO$_3$ minerals in paint like formulations. Firstly, water resistance was achieved on paper by superhydrophobic modification with a calcium carbonate/fatty acid formulation, designed by Hu et al.. Their research outlined a paint generation method using micro sized particles, octadecanoic acid and a polymer latex, compris-
ing a 50 wt% copolymer of styrene and acrylate in water. Formulation application was achieved through a dip coating process to afford a water contact angle near 150°.\textsuperscript{195} Whereas Wu \textit{et al.} studied the effects of nano CaCO\textsubscript{3} particle incorporation, when used in combination with micro fillers in architectural paints. It was found that the emulsion paint prepared with the described additives showed many favourable features: improved wet-state storage stability and abrasion resistance and lower roughness and wettability when compared to a conventional paint standard. Water contact angles were not measured in a traditional method but were assumed to have reached 90°.\textsuperscript{196}

The above findings suggest that CaCO\textsubscript{3} particles in combination with long chain fatty acids have the desired features required for superhydrophobic surface generation. However, there are clear difficulties when trying to incorporate these constituents into pre-existing paint formulations and remains a key exploration area and therefore the basis for the novel studies documented in this chapter.

3.2 Aims

Experiments in this chapter aim to advance superhydrophobic and self-cleaning interior decorative model wall paints with the first instance of low toxicity and cost CaCO\textsubscript{3} structuring particles in combination with a low surface energy octadecanoic acid (FA C\textsubscript{18}) component. Optimised material inclusion ratios and weight percentages are to be guided by the work completed in Chapter 2 and should be explored in combination with further rheology modifiers and hydrophobising agents, dopants and top coat applications.

3.3 Experimental

Aqueous SiO\textsubscript{2} paint formulations towards superhydrophobic decorative model paints, generated in Chapter 2, provided a slurry basis for further mineral inclusion trials. This coming chapter explores the use of CaCO\textsubscript{3} particles as the new predominant formulation mineral. CaCO\textsubscript{3} particles are an industrially suitable structure generation alternative as they are readily available and have a low associated toxicity and cost. A surface energy lowering octadecanoic acid (FA C\textsubscript{18}) component was required to induce heightened surface functionality while dispersants, latexes and rheology modifiers were included to impart paint characteristics.
3.3.1 Materials

Omycarb Extra-KA CACO$_3$ particles (1.4 µm diameter) were acquired from Omya. Octadecanoic acid (FA C$_{18}$) and NaOH were acquired from Sigma-Aldrich. Laboratory grade solvents were supplied by Fisher Scientific. TiO$_2$ particles (250 nm diameter), dispersants, latexes and rheology modifying materials were provided by Akznobel. All chemicals were of analytical standard and used as received.

3.3.2 Hydrophobic Model Paint Generation Using CaCO$_3$ Particles with/without Dopant

Water was heated to 75 °C prior to the addition, with magnetic stirring, of octadecanoic acid (FA C$_{18}$). NaOH (2.00 mol dm$^{-3}$) was then added dropwise until the suspension reached pH 8. To aid particle incorporation, Orotan CA2500 (hydrophobic copolymer dispersant) was magnetically stirred into the formulation (x0.02 wt% of CaCO$_3$ particles). CaCO$_3$ particles were then added in small amounts and magnetically stirred for a further 30 min, FA C$_{18}$-particle ratios or polymer/mineral (P/M) ratios of 0.67 were held constant. The appropriate amount of slurry was mixed with Akzonobel’s 1052 acrylic latex component using a 400 rpm overhead stirrer for 30 min. Texanol was subsequently added (x0.05 wt% of 1052 latex) and left to stir for a further 10 min. Model paint formulations were applied to glass substrates using a draw down bar (304.8 µm clearance or wet film thickness of 6 mL) and left to dry overnight at room temperature and pressure.

The use of TiO$_2$ particles dopants were also explored to assess their impact on CaCO$_3$ particles with FA C$_{18}$ containing paints. TiO$_2$ particles (250 nm diameter), in 5 wt%, 10 wt%, 25 wt% or 50 wt% dopant level amounts, were added to the described formulation process at the point of general particle addition. Doped model paints were similarly applied to glass substrates using a draw down bar and left to dry overnight at room temperature and pressure. Formulation components have been comprehensively outlined in Table 3.1.
Table 3.1. CaCO$_3$ based model paints with and without a TiO$_2$ particle dopant. CaCO$_3$ particles with various wt% of a TiO$_2$ (250 nm diameter) particle dopant were embedded in FA C$_{18}$ and a 1052 latex mixture before being drawn down on glass substrates (wet film thickness of 6 mL) and then dried. Orotan CA2500 was the dispersant used to generate mixtures with a 0.67 P/M ratio.

<table>
<thead>
<tr>
<th>P/M ratio</th>
<th>FA C$_{18}$</th>
<th>Particles wt%</th>
<th>Water wt%</th>
<th>Orotan CA2500 wt%</th>
<th>1052 Latex wt%</th>
<th>Texanol wt%</th>
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<td>3.86</td>
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<td>85.22</td>
<td>1.60</td>
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<td>5.79</td>
<td>85.22</td>
<td>1.60</td>
<td>3.35</td>
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3.3.3 Hydrophobic Model Paint Generation Using CaO₃ Particles with Rheology Modifiers

Formulation coatings produced in Chapter 3 have incorporated a complete set of desired model paint components: water, additives (pH modifiers or dispersants), extenders (functionalising reagents), pigments (coloured particles) and polymer binders or latex. The use of rheology additives and hydrophobic paint agents were subsequently explored to improve aesthetics while still preserving or enhancing paint functionality. Natrosol (hydroxyethylcellulose) was added prior to latex incorporation in line with the formulation process outlined in Part 3.3.2. This nonionic cellulose polymer derivative afforded paint thickening features and worked to strengthen the resulting coating. Finally, an aminofunctional siloxane was trialled as an additional hydrophobising agent to further improve the surface wetting properties of paint coatings. Table 3.2 displays the formulation changes required to incorporate further paint additive use.

As described functional paint coatings were drawn down (304.8 µm clearance or wet film thickness of 6 mL) as top coats on Akzonobel’s commercially available Diamond Matt paint coated substrates for functional property comparison purposes.
Table 3.2. CaCO$_3$ based model paints with a TiO$_2$ particle dopant component and further rheology modifying or hydrophobising paint additives. CaCO$_3$ particles with various wt% of a TiO$_2$ (250 nm diameter) particle dopant were embedded in FA C$_{18}$ and a 1052 latex mixture containing a Natrosol (hydroxyethylcellulose) rheology modifier and/or an aminofunctional siloxane hydrophobising agent. Model paints were then drawn down on glass substrates (wet film thickness of 6 mL) and then dried. Orotan CA2500 was the dispersant used to generate mixtures with a 0.67 P/M ratio.

<table>
<thead>
<tr>
<th>P/M ratio</th>
<th>FA C$_{18}$</th>
<th>Particles/wt%</th>
<th>Water/wt%</th>
<th>Orotan CA2500/wt%</th>
<th>1052 Latex/wt%</th>
<th>Texanol/wt%</th>
<th>Natrosol/wt%</th>
<th>Siloxane/wt%</th>
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<td>1.60</td>
<td>3.35</td>
<td>0.18</td>
<td>0.25</td>
</tr>
</tbody>
</table>
3.3.4 Material Characterisation Techniques

X-ray photoelectron spectroscopy (XPS) was carried out using a Thermo Scientific X-ray photoelectron spectrometer with a monochromated Al-K$_\alpha$ X-ray source (8.3381 Å). Peaks were modelled using CasaXPS software and binding energies were adjusted for adventitious carbon (284.5 eV). X-ray diffraction (XRD) patterns were obtained using a Bruker D8 Discover diffractometer with monochromated Cu-K$_\alpha$ radiation (1.5406 Å). Fourier transform infrared (FT-IR) spectroscopy was carried out using Bruker alpha platinum ATR equipment between 400 and 4000 cm$^{-2}$. Raman spectra were recorded between 100 and 3000 cm$^{-2}$ on a Reinshaw 1000 spectrometer equipped with a 514.5 nm laser. Surface topographies were investigated using a JEOL JSM-6301F scanning electron microscope (SEM) with an acceleration voltage of 5 or 10 kV; films were gold coated prior to SEM analysis to negate charging effects. Finally, profilometry mapping was achieved by Dr Suraj Pawar at Akzonobel (Slough) on a Keyence VHX-5000 digital microscope with a 1 µm tolerance, 500x500 µm coating areas were measured.

3.3.5 Functionality and Performance Testing Techniques

Three water contact angles were measured per coating at ambient temperature via the sessile-drop method using a FTA 100 optical contact angle meter (13.00 µg water droplet). An average value and associated error were calculated for each sample stored in ambient conditions at 0, 3 and 6 month intervals where appropriate. The tilting angle, defined as the angle at which a water droplet readily slides off a slanted surface (fixed droplet weight of 0.5000 g), was recorded using a digital angle finder. Averages and standard deviations were again calculated for each sample stored in ambient conditions at timed intervals where appropriate.

Paint self-cleaning properties were explored in the following ways: dried formulation covered substrates were tilted by 40°, for visual ease, and then covered in glitter, which acted as a dust/dirt alternative. When placed under water flow, glitter collecting spherical water droplets rolled down the substrate and removed a degree of unwanted foreign material. Additional staining tests were utilised to determine the self-cleaning or stain repellency capabilities of the novel model paint systems. Firstly, dried paint panels were slanted by 80° and red wine, tea (tea bag brewed for 1 min in hot water (100 mL)) and coffee (freeze dried coffee (1 g) in hot water (200 ml)) were used to stain the panels. A pipette decanted the staining liquids (1 mL) in such a way that they flowed from top to bottom down the coated substrate. For analysis purposes a stain bead ranking was
given per sample stain: a rank of 0 indicated no stain, 1 corresponded to well spaced rounded stain beads, rank 2 was representative of elongated stain beads, 3 depicted a broken thin stain stream, 4 was visualised as a thin unbroken stain stream with 5 represented by a thicker unbroken stain stream. Alternatively, the staining liquids (0.5 mL, in separate 1 cm x 5 cm strips) were applied to painted substrates that were laid flat. After 20 min of staining, cotton wool was used to absorb any residue. Images were recorded after all testing procedures to document paint degradation for visual comparison purposes.

3.4 Results and Discussion

Building on Chapter 2’s findings, a switch to the CaCO$_3$ mineral afforded a new category of interior decorative wall paints. The coming results document various trials towards formulating further optimised functional self-cleaning model paints with additional rheology and hydrophobising modifiers. In a bid to achieve superhydrophobic Cassie-Baxter regimes, the use of TiO$_2$ particle dopants and top coat formulations were key areas of inquiry. Correlations were drawn between both chemical and physical surface properties and the functional testing data which included self-cleaning and stain removal characterisation.

3.4.1 Material Characterisation

In order to understand the functional properties of the water repellent coatings generated according to Part 3.3, thorough surface characterisation was carried out as follows. X-ray photoelectron spectroscopy (XPS) data was collected to identify material composition, preferred oxidation states, chemical environments and elemental abundances. C1s and Ca2p XPS data for model paint system comprising CaCO$_3$ particles in octadecanoic acid (FA C$_{18}$) with a 1052 latex and an Orotan CA2500 dispersant have been represented in Figures 3.1 and 3.2 respectively. Paint formulation specifics are outlined in Table 3.1.

Peaks at 284.4 eV, 286.0 eV and 288.3 eV in the C1s scan were artefacts of surface carbon contaminant species coupled with the long FA C$_{18}$ hydrocarbon backbone, the C-O(OR) ester environment and the C-O(OH) acid environment respectively. The C-O(OR) region confirmed the presence of CaCO$_3$-FA C$_{18}$ ester linkages. Deconvoluted regions identified at 347.7 eV and 351.5 eV in the Ca2p scan were attributed to CaCO$_3$2p$^{1/2}$ and CaCO$_3$2p$^{3/2}$ environments and confirmed the presence of CaCO$_3$ roughening surface particles.
Figure 3.1. XPS C1s scan of the model paint containing CaCO₃ particles dispersed in a FA C₁₈ aqueous slurry containing a 1052 latex and an Orotan CA2500 dispersant. The ratio of fatty acid to H-SiO₂ particles was equal to 0.67.

Figure 3.2. XPS Ca2p scan of the model paint containing CaCO₃ particles dispersed in a FA C₁₈ aqueous slurry containing a 1052 latex and an Orotan CA2500 dispersant. The ratio of fatty acid to H-SiO₂ particles was equal to 0.67.

The model paint system formulation was then adapted to incorporate TiO₂ particles as part of a dopant trial. Comparable C1s and Ca2p regions were identified in all new doped paint coatings, as expected, due to reagent consistency. Further peaks visualised at appropriate Ti2p binding energies were associated with the TiO₂2p₃/₂ and TiO₂2p₁/₂ environments respectively; associated values of 458.7 eV and 464.5 eV were in keeping with literature findings, Figure 3.3. Furthermore, the O1s scan contained a notable peak at 519.9 eV which corresponded to the presence of TiO₂ hierarchical surface roughening material.
Figure 3.3. XPS Ti2p scan of the model paint containing CaCO₃ particles dispersed in a FA C₁₈ aqueous slurry containing a 1052 latex and an Orotan CA2500 dispersant. The ratio of fatty acid to H-SiO₂ particles was equal to 0.67.

The use of rheology additives and hydrophobic paint agents were subsequently explored to improve the visual properties desired of commercial paints. CaCO₃ based formulations with a TiO₂ particle dopant component and further Natrosol (hydroxyethylcellulose) and/or an aminofunctional siloxane rheology modifying or hydrophobising paint additives were XPS tested. Where appropriate, both Natrosol (0.25 wt%) and siloxane (1.00 wt%) were added in very small quantities so their presence was not detectable in the C1s scan. The hydrocarbon chains in both components perhaps contributed to the peak at 284.7 eV, which was characteristic of long chain alkyl groups. No other notable variations in the survey scan were visualised, again attributed to low additive concentrations.

X-ray diffraction (XRD) patterns for the model paint samples comprising CaCO₃ particles with various degrees of TiO₂ particle doping, 5 and 50 wt% are recorded in Figure 3.4. Particles were dispersed in a FA C₁₈ aqueous mixture that contained a 1052 acrylic latex and Orotan CA2500 component, formulations were as described in Table 3.1. In accordance with the inorganic crystal structure database, the highest intensity FA C₁₈ crystalline peaks were seen at 20°, 22°, 23° and 24°. Calcite peaks were noted at 23°, 29°, 48° and 49° while the anatase phase of TiO₂ was identified as present from characteristic peaks at 27°, 36°, 39°, 41°, 43°, 54° and 57°.

Figure 3.5 shows Fourier transform infrared (FT-IR) spectra of key formulation precursors and the drawn down model paint system comprising CaCO₃ particles doped with TiO₂ mineral (50 wt%), as described in Table 3.1. CaCO₃ particles generated a spectrum with peaks at 714 cm⁻¹, 873
Figure 3.4. XRD patterns of samples comprising CaCO$_3$ particles with various degrees of TiO$_2$ mineral doping. FA C$_{18}$, a 1052 acrylic latex and an Orotan CA2500 dispersant were also present in the drawn down paint. Peaks consistent with FA C$_{18}$, calcite and anatase phases have been referenced accordingly.

cm$^{-1}$, 1090 cm$^{-1}$, 1397 cm$^{-1}$ and 1797 cm$^{-1}$. These were indicative of symmetric CO$_3$, asymmetric CO$_3$, symmetric CO$_3$, asymmetric CO$_3$ and symmetric CO$_3$ vibrations respectively. TiO$_2$ particles separately afforded bands at 492 cm$^{-1}$, 1646 cm$^{-1}$ and 3347 cm$^{-1}$ that are characterised as a Ti-O stretching band and surface water O-H bending and O-H stretching vibrations respectively.

The final reagent spectrum of FA C$_{18}$ produced peaks at 2846 cm$^{-1}$, 2870 cm$^{-1}$, 2911 cm$^{-1}$ and 2954 cm$^{-1}$. In order of documented peak position, CH$_2$ symmetric, CH$_3$ symmetric, CH$_2$ asymmetric and asymmetric CH$_3$ C-H stretching vibrations were visualised. C-H bending vibrations were noted at 720 cm$^{-1}$ and again at 1472 cm$^{-1}$. The 939 cm$^{-1}$ and 1296 cm$^{-1}$ bands were associated with C-O carboxylic acid bending and stretching respectively. A C=O carboxylic acid stretch at 1701 cm$^{-1}$ was characteristic of the FA C$_{18}$ reagent but the lack of a broad O-H stretch at 3000 cm$^{-1}$ confirmed acid dimerisation in the condensed state. The spectrum for the paint sample comprising CaCO$_3$ particles doped with TiO$_2$ mineral (50 wt%) dispersed in FA C$_{18}$ slurries containing 1052 acrylic latex and an Orotan CA2500 dispersant showed comparable peak positions to those associated with their subsstituents’ individual chemical bond vibrations. Identical peaks were visualised in the doped sample that contained further aesthetic additives. Natrosol (hydroxyethylcellulose) (0.25 wt%) and/or an aminofunctional siloxane (1.00 wt%) were incorporated in such small amounts that there was no deviation from the base formulation spectrum.

The surface structure of model paint samples comprising an aqueous FA C$_{18}$ component with
a CaCO$_3$ particle roughening system was assessed using scanning electron microscopy (SEM), formulations are detailed in Table 3.1. Areas of mixed scale surface protrusions were formed through combination of nano and micron sized particle deposits and agglomerates; a requirement for hydrophobic functionality. The paint surface generated with 5 wt% of the TiO$_2$ dopant mineral displayed clear evidence of CaCO$_3$ non-uniform micro clusters (>1.4 µm) with near spherical TiO$_2$ particles (250 nm diameter) sparingly distributed between the bulkier calcite surface structure components. This model paint’s surface hierarchy contributed to an average water contact angle of 148±1°, as shown in Figure 3.10 from Part 3.4.2. Furthermore, the 50 wt% addition of TiO$_2$ particle dopant afforded a superhydrophobic average water contact angle of 154±5°. This highly doped paint surface was characteristic of the Cassie-Baxter wetting regime as water droplets freely rolled on the coated sample. SEM image analysis highlighted the small morphological tweaks that were likely responsible for the more favourable surface functionalities. Micro roughening CaCO$_3$ particles were again visualised across the sample surface, however, there was a clear increase in TiO$_2$ particles that filled structural voids. This resulted in a more consistently textured sample and consequently improved lubricating air layer retention for Cassie-Baxter type wetting.  

These same model paints doped with TiO$_2$ particles were modified, first with the rheology altering Natrosol (hydroxyethylcellulose) (0.25 wt%) and then with Natrosol (0.25 wt%) and a hydrophobic aminofunctional siloxane (1.00 wt%). SEM images seen in Figure 3.7 depict the surface structural changes with each additive step in this trial. As explained in Part 3.4.2, CaCO$_3$ systems
doped with TiO\textsubscript{2} particles (25 wt\%) produced an average water contact angle of 133±6°. The hydrophobic functionality was partially explained by the nano and micron sized particle deposits and agglomerates. Larger non-spherical features were indicative of the CaCO\textsubscript{3} mineral (>1.4 µm) while a much smaller proportion of spherical TiO\textsubscript{2} particles (250 nm diameter) were evenly distributed across the dried sample. On addition of Natrosol, a hydrophilic surface was produced and was a consequence of the hydrogen bonding that arose between hydroxyethylcellulose and surface water, see Part 3.4.2 for further details. SEM images also highlighted the increase of TiO\textsubscript{2} particles at the paint surface, which eluded to the fact that TiO\textsubscript{2}-Natrosol binding interactions drew the less dense particles to the solid-gas interface. When the hydrophobic aminofunctional siloxane agent was incorporated, the previously negative wetting interactions were reversed and the surface benefited from an extremely structured morphology. Water contact angles reached a maximum value of 145° on the described model paint and more importantly, the Cassie-Baxter regime was achieved.

Figure 3.8 shows the surface profilometry mapping of systems consisting CaCO\textsubscript{3} particles...
Figure 3.7. SEM images of CaCO$_3$ particle based model paint system doped with TiO$_2$ particles (25 wt%). FA C$_{18}$, a 1052 acrylic latex and an Orotan CA2500 dispersant were also present in the drawn down paint (wet film thickness of 6 mL). Further modifications included the rheology altering Natrosol (hydroxyethylcellulose) (0.25 wt%) and then with Natrosol (0.25 wt%) and a hydrophobic aminofunctional siloxane (1.00 wt%).

doped with TiO$_2$ mineral (25 wt%), as formulated in Table 3.2. Of the coatings applied to glass substrates, the basic or non additive system displayed few large micro sized CaCO$_3$/TiO$_2$ clumps (2000 µm diameter). The coating protrusion height was recorded as 318.70 µm and an average contact angle of 133±6° was calculated with water droplet adhesion. The average water contact angle was comparable when Natrosol and siloxane were added to this formulation mixture but the switch to a Cassie-Baxter wetting regime was a suspected consequence of changing surface morphology. Many smaller scale micro clusters were observed and a smaller protrusion height value was measured, 258.39 µm. This was possibly due to the TiO$_2$-Natrosol binding interactions, which drew the less dense TiO$_2$ particles to the solid-gas interface. Bulkier CaCO$_3$ particles therefore arranged at the bottom of the paint coating and formed the profilometer’s base zero value. When the non additive system was applied as a top coat on Dulux Trade Diamond Matt paint covered plaster board, considerable quantities of small micron sized particle clumps were visualised. A
sample protrusion height value of 292.05 µm was measured and was expected to have contributed to the mixed Cassie-Baxter/Wenzel wetting regime. When Natrosol and siloxane were included in this top coat, the protrusion height increased to a value of 299.37 µm. It was thought that the Diamond Matt covered substrate had a residual surface water layer that was not present on the previously mentioned solvent washed glass substrates. It was this adsorbed layer that afforded hydrogen bonding with Natrosol coated TiO$_2$ particles, thus drawing the smaller TiO$_2$ particles to the bottom of the top coat paint layer and allowing larger CaCO$_3$ to reside closer to the solid-gas interface. The small step changes in surface protrusion height, and therefore roughness, were not large enough to generate significant changes in water contact angles. Tilting angles, however, tended towards lower values at reduced sample protrusion heights.
Figure 3.8. Profilometry mapping of CaCO$_3$ particle based model paint system doped with TiO$_2$ particles (25 wt%). FA C$_{18}$, a 1052 acrylic latex and an Orotan CA2500 dispersant were also present in the drawn down paint (wet film thickness of 6 mL). Other modifications were subsequently explored by way of rheology altering Natrosol (hydroxyethylcellulose) (0.25 wt%) and hydrophobic aminofunctional siloxane (1.00 wt%) incorporation. Described coatings were also trialled as top coats; a draw down was applied to plaster board covered Diamond Matt coated paint.
Figure 3.9 goes on to display the surface profilometry mapping of systems consisting CaCO$_3$ particles doped with TiO$_2$ mineral (50 wt%), as formulated in Table 3.2. On solvent cleaned glass substrates, the basic or non additive system displayed many small micro sized TiO$_2$ clumps (200 µm diameter). The coating protrusion height was recorded as 394.44 µm and an average contact angle of 154±5° was calculated with Cassie-Baxter surface characteristics. The average water contact angle was significantly lower when Natrosol and siloxane were added to this formulation mixture and the switch to a Wenzel wetting model was a suspected consequence of changing surface morphology. Fewer small scale micro clusters were observed and the reduced protrusion height trend was upheld, 217.89 µm. This was again described through TiO$_2$-Natrosol binding interactions, which drew the less dense TiO$_2$ particles to the solid-gas interface. Bulkier CaCO$_3$ particles therefore arranged at the bottom of the paint coating and formed the profilometer’s base zero value, as seen in the 25 wt% dopant analysis. When the non additive system was applied as a top coat, few larger micron sized particle clumps (2000 µm diameter) were visualised. A sample protrusion height value of 219.87 µm was measured and was expected to have contributed to the mixed Cassie-Baxter/Wenzel wetting regime, water tilting angle of 90±8°. When Natrosol and siloxane were in the sample’s top coat, the protrusion height increased to a value of 261.81 µm. The same Diamond Matt surface water layer presence was again assumed and consequently effected Natrosol coated TiO$_2$-water hydrogen bonding. Smaller TiO$_2$ particles were therefore more concentrated towards the base of the top coat paint layer, such that larger CaCO$_3$ particles resided closer to the solid-gas interface. The profilometry data collected for the 50 wt% doped formulations with identical additive components, indicated that higher quantities of smaller micron sized protrusions generated higher average water contact angles and lower average water tilting angles.
Figure 3.9. Profilometry mapping of CaCO₃ particle based model paint system doped with TiO₂ particles (50 wt%). FA C₁₈₈, a 1052 acrylic latex and an Orotan CA2500 dispersant were also present in the drawn down paint (wet film thickness of 6 mL). Other modifications were subsequently explored by way of rheology altering Natrosol (hydroxyethylcellulose) (0.25 wt%) and hydrophobic aminofunctional siloxane (1.00 wt%) incorporation. Described coatings were also trialled as top coats; a draw down was applied to plaster board covered Diamond Matt coated paint.
Characterisation techniques that explored surface morphology were of most use during the 
CaCO$_3$ mineral study. Formulations that incorporated a combination of nano and micro sized 
particle deposits had a tendency to display more hydrophobic functionalities. Further addition 
of rheology modifying and paint hydrophobising agents saw a decrease and subsequent increase 
in sample water repellency respectively. The most promising final paint sample for use in self-
cleaning applications was identified as containing a 1:3 TiO$_2$ to CaCO$_3$ mineral ratio with FA C$_{18}$, 
a 1052 acrylic latex and an Orotan CA2500 dispersant. Natrosol (0.25 wt%) and a hydrophobic 
amino functional siloxane (1.00 wt%) were the final paint additives, with the latter causing a shift 
from the Wenzel wetting regime to the Cassie-Baxter model.

3.4.2 Functional Properties and Performance Testing

The model paint formulation processes described in Chapter 2 have been carried forward with a 
shift towards CaCO$_3$ mineral inclusion. A slurry containing CaCO$_3$ particles and octadecanoic 
acid (FA C$_{18}$) was created with a 1052 acrylic latex and Orotan CA2500 component. All incor-
porations and weight ratios, FA C$_{18}$-particle ratios or polymer/mineral (P/M) ratios of 0.67, were 
chosen in light of the successes noted in the previous SiO$_2$ systems. An average water contact angle 
of 83±18° and complete droplet adhesion were noted on the CaCO$_3$ based paint surface. Figure 
3.10 subsequently displays the effect of TiO$_2$ particle (250 nm diameter) doping on CaCO$_3$ paint’s 
hydrophobicity. Sample water repellency increased to 148±1° at 5 wt% dopant levels, after which 
trends linking TiO$_2$ wt% to hydrophobicity were not determinable. With that said, 154±5° was cal-
culated on the 50 wt% doped paint at and a Cassie-Baxter/Wenzel wetting regime was supported 
by the average water tilting angle of 67±6°. This water repellency value was significantly higher 
than 135±9°, which was achieved on the 50 wt% doped H-SiO$_2$ formulation from Chapter 2. The 
shift to superhydrophobicity was attributed to the stark contrast in base mineral/dopant particle 
size and the strong tendency towards Ca$_{2+}$-acid attachment. Microscale CaCO$_3$ particles (1.4 μm) 
complemented the nano TiO$_2$ mineral extender to build a dual-scale surface scaffold; one molecule 
of FA C$_{18}$ reacted with each Ca$_{2+}$ cation on the calcite surface to produce calcium stearate bicar-
bonate. Long alkyl chains vertically oriented to the surface and therefore resulted in the observed 
superhydrophobic interactions with incoming water droplets. The production of these CaCO$_3$ 
superhydrophobic aqueous model paints were found to outperform any comparable literature stand-
ards. In some cases, even those that required abrasive multistep physical processes post surface 
coating did not afford maximum water contact angle values of 159°. Extremely favourable
average water tilting angles were also calculated on these TiO$_2$ doped draw down coatings. With both minerals present, droplet rolling was readily achieved when the painted substrates were tilted $<3^\circ$ - a result indicative of surface fully conforming to the Cassie-Baxter model. A lubricant air layer had formed within surface structure asperities and worked to minimise the solid-liquid surface area interface, which consequently drove down tilting angle values. The functional data collected provided strong evidence to suggest these formulations were potentially ideal candidates for self-cleaning applications.

![Average water contact angles of model paints. CaCO$_3$ particles and various wt% of a TiO$_2$ dopant (250 nm diameter) were embedded in FA C$_{18}$ and 1052 latex mixtures before being draw down on glass substrates (wet film thickness of 6 mL) and then dried. Orotan CA2500 was the dispersant used to generate mixtures with a 0.67 P/M ratio.](image)

Paint systems in Chapter 3 contained all required model paint components, such as water, additives, extenders, pigments and polymer binders or latex. The use of rheology additives and hydrophobic paint agents were subsequently explored to improve paint aesthetics for commercial use. To the TiO$_2$ doped CaCO$_3$ system generation process, Natrosol (hydroxyethylcellulose) was added before latex incorporation in accordance with Part 3.3.2. The non ionic cellulose polymer derivative was required for paint thickening and strengthening. Table 3.3 shows the average water contact and tilting angle results achieved on the rheology modified model paint surfaces. Previous TiO$_2$ particle doped CaCO$_3$ systems with particle ratios of 3:1 and 1:1 produced average water contact angles of $133\pm6^\circ$ and $154\pm5^\circ$ respectively. The addition of industrially required hydroxyethylcellulose introduced ether functionality and therefore allowed for hydrogen bonding to surface water species. Average water contact angles reflected this interaction and were considerably low-
ered to $93\pm9^\circ$ and $81\pm12^\circ$ respectively. Both paint covered glass substrates were categorised as having Wenzel wetting characteristics as droplets were pinned to both surfaces on inversion. An aminofunctional siloxane agent was subsequently added as an additional industrially common hydrophobising agent to restore the surface wetting properties of paint coatings. The silicon-oxygen backbone surrounded by hydrophobic alkyl and amino chains imparted water repellent properties designed to counteract the action of the natrosol rheology modifier. Corresponding average water contact angle results for TiO$_2$ particle dopant loadings of 25 wt% and 50 wt% were $138\pm6^\circ$ and $102\pm8^\circ$ respectively. In both dopant cases the final addition of siloxane improved hydrophobicity by $>20^\circ$ with the Cassie-Baxter wetting state achieved on the 25 wt% doped draw down. It was apparent that higher TiO$_2$ loading levels created less favourable coatings on industrial additive incorporation. This was likely due to exacerbations in unwanted liquid-solid chemical interactions in combination as the physical changes that were noted in scanning electron microscopy (SEM) images were consistent for all dopant levels at this stage of the Natrosol/siloxane trial, Part 3.4.1. Therefore, it was assumed that TiO$_2$ particle presence strongly accentuated Natrosol-water binding; a suspected consequence of smaller and less dense Natrosol bound TiO$_2$ particles gravitating to the film surface on drying.
Table 3.3. Average water contact and tilting angle results for CaCO$_3$ based model paints with a TiO$_2$ particle dopant component and further rheology modifying or hydrophobising paint additives. CaCO$_3$ particles with various wt% of a TiO$_2$ (250 nm diameter) particle dopant were embedded in FA C$_{18}$ and a 1052 latex mixture containing a Natrosol (hydroxyethylcellulose) rheology modifier and/or an aminofunctional siloxane hydrophobising agent. Model paints were then drawn down on glass substrates (wet film thickness of 6 mL) and then dried. Orotan CA2500 was the dispersant used to generate mixtures with a 0.67 P/M ratio. Full formulation descriptions are displayed in Table 3.2.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Water contact angle°</th>
<th>Water tilting angle°</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Average</td>
<td>Error</td>
</tr>
<tr>
<td>CaCO$_3$ (75 wt%) and TiO$_2$ particle (25 wt%) based paint</td>
<td>133</td>
<td>6</td>
</tr>
<tr>
<td>CaCO$_3$ (50 wt%) and TiO$_2$ particle (50 wt%) based paint</td>
<td>154</td>
<td>5</td>
</tr>
<tr>
<td>CaCO$_3$ (75 wt%) and TiO$_2$ particle (25 wt%) based paint with Natrosol</td>
<td>93</td>
<td>9</td>
</tr>
<tr>
<td>CaCO$_3$ (50 wt%) and TiO$_2$ particle (50 wt%) based paint with Natrosol</td>
<td>81</td>
<td>12</td>
</tr>
<tr>
<td>CaCO$_3$ (75 wt%) and TiO$_2$ particle (25 wt%) based paint with Natrosol and siloxane</td>
<td>138</td>
<td>6</td>
</tr>
<tr>
<td>CaCO$_3$ (50 wt%) and TiO$_2$ particle (50 wt%) based paint with Natrosol and siloxane</td>
<td>102</td>
<td>8</td>
</tr>
</tbody>
</table>
Figure 3.11 displays the self-cleaning ability of the CaCO$_3$ based model paint with TiO$_2$ particle dopants (50 wt%) and further Akzonobel required rheology modifying, Natrosol, and hydrophobising, siloxane, paint additives. This particular sample had an average tilting angle of 3±3° so was a Cassie-Baxter type surface. The paint covered substrate was held at 40°, for visual ease, and was then covered in glitter, which acted a dust/dirt alternative. When placed in a water flow path, glitter collecting spherical water droplets rolled down the substrate and consequently removed all traces of the unwanted foreign material. As internal decorative wall paints are commonly applied to vertical substrates, this test more than accounts for the self-cleaning capabilities of this formulation.

Figure 3.11. Self-cleaning ability of the CaCO$_3$ based model paint with TiO$_2$ particle dopants (50 wt%) and further rheology modifying, Natrosol (0.25 wt%), and hydrophobising, siloxane (1.00 wt%), paint additives. The formulation was drawn down on a glass substrate (wet film thickness of 6 mL), dried and then covered in glitter. Water flow was used to display the self-cleaning functionality, through which the foreign material was removed.

To this point, model paint coatings have been utilised and tested as single coat basic systems. These optimum formulations were subsequently explored as top coats. A uniform coating of Dulux Trade Diamond Matt white paint was applied to a plaster board panel before draw downs of 25 wt% and 50 wt% TiO$_2$ particle doped CaCO$_3$ systems without rheology modifying Natrosol and hydrophobic siloxane, with Natrosol and finally with Natrosol and siloxane were functionally tested, Table 3.4. The average water contact angle on the 25 wt% doped top coat was similar, within experimental error, to the equivalent single coat data in Table 3.3. However, the top coat of the TiO$_2$ doped (50 wt%) formulation saw a drop in average contact angle of 15° and a shift from the Cassie-Baxter to Wenzel wetting system. Results for top coat samples with the rheology modifier and the rheology modifier plus hydrophobising agent were statistically similar to the original single coatings with the exception of the 50 wt% TiO$_2$ dopant level sample with both Natrosol and siloxane present. This surface saw an average water contact angle increase of 33°. While some formulations generated slightly higher average contact angle values, thought to be due to the innate roughness of the underlying Diamond Matt paint, Figure 3.9, the top coats were only able to effect the desired self-cleaning abilities at high tilting angles. Unfortunately, data contrasting
was not easily possible due to the lack of literature in this area. Wu’s research group produced the only similar formulation through the use of CaCO$_3$ nano fillers, hydrophobised with octadecanoic acid, in a pre-existing commercial paint emulsion. Water contact angles were not quoted in Wu’s work, but a result much lower than the hydrophobic values achieved in this chapter’s studies was assumed, based on published droplet imaging.\textsuperscript{196}
Table 3.4. Average water contact and tilting angle results for top coats of CaCO₃ based model paints with a TiO₂ particle dopant component and further rheology modifying or hydrophobising paint additives. CaCO₃ particles with various wt% of a TiO₂ (250 nm diameter) particle dopant were embedded in FA C₁₈ and a 1052 latex mixture containing a Natrosol (hydroxyethylcellulose) rheology modifier and/or an aminofunctional siloxane hydrophobising agent. Model paints were then drawn down on glass substrates (wet film thickness of 6 mL) and then dried. Orotan CA2500 was the dispersant used to generate mixtures with a 0.67 P/M ratio. Full formulation descriptions are displayed in Table 3.2 and the top coats were applied onto plaster board covered Dulux Trade Diamond Matt white paint.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Water contact angle°</th>
<th>Water tilting angle°</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Average</td>
<td>Error</td>
</tr>
<tr>
<td>CaCO₃ (75 wt%) and TiO₂ particle (25 wt%) based top coat</td>
<td>132</td>
<td>6</td>
</tr>
<tr>
<td>CaCO₃ (50 wt%) and TiO₂ particle (50 wt%) based top coat</td>
<td>139</td>
<td>2</td>
</tr>
<tr>
<td>CaCO₃ (75 wt%) and TiO₂ particle (25 wt%) based top coat with Natrosol</td>
<td>103</td>
<td>13</td>
</tr>
<tr>
<td>CaCO₂ (50 wt%) and TiO₂ particle (50 wt%) based top coat with Natrosol</td>
<td>91</td>
<td>14</td>
</tr>
<tr>
<td>CaCO₃ (75 wt%) and TiO₂ particle (25 wt%) based top coat with Natrosol and siloxane</td>
<td>131</td>
<td>7</td>
</tr>
<tr>
<td>CaCO₃ (50 wt%) and TiO₂ particle (50 wt%) based top coat with Natrosol and siloxane</td>
<td>135</td>
<td>9</td>
</tr>
</tbody>
</table>
Top coat samples were then tested for their self-cleaning or stain resistance capabilities, Figure 3.12. Dried draw downs of the 25 wt% and 50 wt% TiO$_2$ doped CaCO$_3$ particle containing systems, detailed in Table 3.2, were applied as a top coat to Diamond Matt coated plaster board and tested accordingly. Paint panels were slanted by 80° and red wine, tea and coffee were used for staining due to their common place as household staining agents. The coloured liquids were pipetted down the samples and the degree of staining was monitored. For analysis purposes a stain bead ranking was given per sample stain: a rank of 0 indicated no stain, 1 corresponded to well spaced rounded stain beads, rank 2 was representative of elongated stain beads, 3 depicted a broken thin stain stream, 4 was visualised as a thin unbroken stain stream with 5 represented by a thicker unbroken stain stream. From the beading results shown in Table 3.5, it was clear that the 50 wt% doped top coat containing Natrosol and siloxane was most effective at retarding stains, it had a combined stain bead ranking of 0. This sample was closely followed by the 25 wt% system, again containing both Natrosol and siloxane additives, which had a summed rank of 2. Formulations that excluded rheology or hydrophobising agents caused most sample staining. The stain bead ranking for 25 wt% and 50 wt% TiO$_2$ dopant loadings were 3 and 6 respectively. These scores were correlated to the corresponding tilting angle values of Table 3.4. Samples with the lowest average tilting angles produced the least amount of staining and therefore demonstrated the greatest self-cleaning capability.
Figure 3.12. Self-cleaning data for commercially available Diamond Matt paint, CaCO₃ particle based model paint systems doped with TiO₂ particles (25 wt% or 50 wt%). FA C₁₈, a 1052 acrylic latex and an Orotan CA2500 dispersant were also present in the drawn down paint (wet film thickness of 6 mL). Other modifications were subsequently explored by way of rheology altering Natrosol (hydroxyethylcellulose) (0.25 wt%) or Natrosol and hydrophobic aminofunctional siloxane (1.00 wt%) incorporation. All coatings were applied to plaster board panels covered Diamond Matt paint. The top coat samples were held at a 80° and red wine, tea and coffee (0.5 mL) were used to stain the panels. Images recorded staining after the testing process for comparison.
Table 3.5. Stain bead ranking for top coats of CaCO₃ based model paints with a TiO₂ particle dopant component and further rheology modifying or hydrophobising paint additives. CaCO₃ particles with various wt% of a TiO₂ (250 nm diameter) particle dopant were embedded in FA C₁₈ and a 1052 latex mixture containing a Natrosol (hydroxyethylcellulose) rheology modifier and/or an aminofunctional siloxane hydrophobising agent. Full formulation descriptions are displayed in Table 3.2 and the top coats were applied onto plaster board covered Dulux Trade Diamond Matt white paint. After flowing red wine, tea or coffee down tilted samples, a stain ranking of 0 was used to indicate no stain, 1 corresponded to well spaced rounded stain beads, rank 2 was representative of elongated stain beads, 3 depicted a broken thin stain stream, 4 was visualised as a thin unbroken stain stream with 5 represented by a thicker unbroken stain stream.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Stain bead ranking</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Red wine</td>
</tr>
<tr>
<td>CaCO₃ (75 wt%) and TiO₂ particle (25 wt%) based top coat</td>
<td>2</td>
</tr>
<tr>
<td>CaCO₃ (50 wt%) and TiO₂ particle (50 wt%) based top coat</td>
<td>3</td>
</tr>
<tr>
<td>CaCO₃ (75 wt%) and TiO₂ particle (25 wt%) based top coat with Natrosol</td>
<td>2</td>
</tr>
<tr>
<td>CaCO₃ (50 wt%) and TiO₂ particle (50 wt%) based top coat with Natrosol</td>
<td>2</td>
</tr>
<tr>
<td>CaCO₃ (75 wt%) and TiO₂ particle (25 wt%) based top coat with Natrosol and siloxane</td>
<td>1</td>
</tr>
<tr>
<td>CaCO₃ (50 wt%) and TiO₂ particle (50 wt%) based top coat with Natrosol and siloxane</td>
<td>0</td>
</tr>
</tbody>
</table>
Alternatively, the staining liquids were applied to identical top coat painted substrates that were laid flat. After 20 min of staining, cotton wool was used to absorb liquid residue. The images recorded in Figure 3.13 were recorded to document paint degradation. Again, there was a clear correlation between the average tilting angle recorded and stained area. The base coat of Diamond Matt paint produced the largest stained area as the Wenzel wetting state was realised. Samples that displayed beading resulted in the least staining liquid-surface contact and therefore afforded a cleaner surface when the coloured liquids were removed with cotton wool. It was noted that average tilting angle was most closely correlated with resulting stained area. The most stain retardant top coat paints had the lowest average tilting angles, supported by the 50 wt% doped formulation containing Natrosol and siloxane's average tilting angle of $25\pm4^\circ$. It was also noted that the presence of the siloxane hydrophobising agent resulted in a red wine repellent effect. The $-\text{Si-O-Si-}$ siloxane backbone, surrounded by amino functional side groups, was able to effect red wine surface beading due to higher energy surface-alcohol interactions than alcohol-gas interactions.
Figure 3.13. Self-cleaning data for commercially available Diamond Matt paint, CaCO$_3$ particle based model paint systems doped with TiO$_2$ particles (25 wt% or 50 wt%). FA C$_{18}$, a 1052 acrylic latex and an Orotan CA2500 dispersant were also present in the drawn down paint (wet film thickness of 6 mL). Other modifications were subsequently explored by way of rheology altering Natrosol (hydroxyethylcellulose) (0.25 wt%) or Natrosol and hydrophobic aminofunctional siloxane (1.00 wt%) incorporation. All coatings were applied to plaster board panels covered Diamond Matt paint. The top coat samples were laid flat and red wine, tea and coffee (0.5 mL, in separate 1 cm x 5 cm strips) were used to stain the panels, as seen in the top row images. After 20 min of staining, cotton wool was used to absorb the staining liquids, as represented in the bottom row images.
Functional testing and performance data presented throughout this chapter have led to the conclusion that TiO\textsubscript{2} (25 wt%) doped CaCO\textsubscript{3} systems with octadecanoic acid (FA C\textsubscript{18}), a 1052 acrylic latex, an Orotan CA2500 dispersant, Natrosol and an aminofunctional siloxane produced the optimum basic single coat paint formulation while the 50 wt% doped equivalent afforded the most stain resistant top coat paint. A considerable step change from a leading market Dulux Trade paint had been realised and as both systems contained all components required of commercial paints, a considerable self-cleaning field advancement had been achieved.

3.5 Summary

Superhydrophobic, Cassie-Baxter wetting regime model paints were achieved using low toxicity and low cost CaCO\textsubscript{3} particles with octadecanoic acid (FA C\textsubscript{18}) containing aqueous systems. A range of TiO\textsubscript{2} dopant particle loadings were introduced into the formulation and the 50 wt% dopant level produced the most superhydrophobic drawn down paint, average water contact angle of 154° ± 5°.

The incorporation of rheology additives and hydrophobic paint agents were explored to effect a desired commercial paint aesthetic and hydrophobic corrective properties respectively. The sole use of paint thickening Natrosol (hydroxyethylcellulose) was found to drastically reduce sample water repellency and the Wenzel wetting state was always observed. On further hydrophobic aminofunctional siloxane formulation incorporation, the TiO\textsubscript{2} particle (25 wt%) dopant containing draw down had the most increased average water contact angle of 138° ± 6°. Water droplets freely rolled on this Cassie-Baxter type sample and self-cleaning properties were clearly observed.

Identical formulations were carried forward for top coat trials. Studies were performed on Dulux Trade Diamond Matt white paint coated plaster boards. The TiO\textsubscript{2} particle (25 wt%) dopant containing sample free from rheology modifiers or siloxane hydrophobic additives was similar, within experimental error, to its basic one coat system counterpart. The 50 wt% dopant level top coat alternative saw a 15° drop in average water contact angle and a switch from the Cassie-Baxter to Wenzel surface model was realised. Following these results, samples with the rheology modifier and the rheology modifier plus hydrophobising agent were found to be statistically similar to their corresponding original base coat samples. That is, with the exception of the 50 wt% TiO\textsubscript{2} dopant formulation, which showed the greatest promotion in surface roughening due to the underlying Diamond Matt paint and consequently displayed favourable self-cleaning functionality.
Stain resistance testing identified a strong correlation between the samples with the lowest average tilting angle/tendency towards the Cassie-Baxter wetting regime and resistance to red wine, tea and coffee staining. Stain bead rankings identified the most successful self-cleaning decorative wall paint as the CaCO$_3$ particle system doped with TiO$_2$ particles (50 wt%). The top coat paint also comprised FA C$_{18}$, a 1052 acrylic latex, an Orotan CA2500 dispersant, Natrosol and an aminofunctional siloxane.

This chapter concludes the body of work that focused on generating smart paints with exceptional wettabilites. Chapter 4 goes on to explore the benefits of other special wettability films and coatings for a range of different applications. Despite the use of new fabrication methods, many reagent materials remain consistent. This demonstrating the versatility and suitability of the roughening and surface energy lowering components chosen for this project.
Chapter 4

Slippery Liquid Infused Porous TiO$_2$/SnO$_2$ Thin Film Composites Generated via AACVD for Anti-icing and Anti-fogging Applications

4.1 Background

As seen throughout Chapters 2 and 3 the successful production of fit for purpose special wettability materials is key to modern civilisation advancement. Water repellent ‘smart’ materials, which display extreme liquid-surface interactions, are heavily researched for their anti-icing and anti-fogging characteristics. Said technology offers a favourable alternative to energy intensive routes utilised to facilitate the efficient working and preservation of commercial devices, infrastructure and alike.

Ice accretion is currently of greatest concern in areas of colder climate whereas fogging is more of an issue in humid atmospheric conditions. A range of commonly employed smooth, textured and slippery material design strategies have been explored in order to overcome both icing and fogging events, many of which have been detailed in Chapter 1. This chapter’s work centres on slippery liquid infused porous surfaces (SLIPS), which have been thought of as ideal ice and fog reduction candidates due to their ability to rapidly shed water or condensate droplets through a liquid sliding motion.
4.1.1 TiO$_2$-SnO$_2$ thin films with SLIPS Technology for Anti-icing and Anti-fogging Applications

Slippery liquid infused porous surfaces (SLIPS) have been found to suppress ice and fog accumulation through nucleation prevention and condensation removal. A continuous and inert slippery top coat is usually embedded within a closed-cell roughened architecture to promote mechanical robustness and stability; surface pores and features additionally provide an optimum lubricant impregnation medium.

Dou et al. worked to identify the effect of ice adhesion strengths on a variety of samples. Structured surfaces with lubricant incorporation fared well and were found to dramatically reduce ice adhesion strengths to within the 10 to 150 kPa range. Many of the samples tested fell within the upper threshold for spontaneous removal of accreted ice through wind or natural vibrations, <20 kPa.$^{10,81}$ Subramanyam et al. indicated that ice accretion was dependent on the level of surface lubrication with increased adhesion linked to lubricant depletion below the maximum height of surface structures. Ice nucleation was therefore substantially halted due to high level lubricant retention held within closely spaced structural voids.$^{79,82}$

Slippery anti-fogging surfaces have been comparably under researched despite the expected translatable advantages to their use in ice retardant applications. Unfortunately, poor longevity made existing highly structured materials an ineffective choice for use in extreme weather conditions and therefore catalysed investigation into highly specific SLIPS. Aqueous top layers on anti-fogging surfaces are expected to solve lifespan issues through lubricant replenishment from natural moisture sources. For this application, innate hydrophilicites are generally favoured as they afford droplet sheeting, and therefore also maintain the desired sample optical properties.

The use of highly textured TiO$_2$-SnO$_2$ nanocomposites have previously been generated for their photocatalytic properties. Chadwick et al. employed combinatorial aerosol assisted chemical vapour deposition (cAACVD) to afford monolithic topographical films of mixed phase. These mechanically robust thin films had many of the required anti-icing and anti-fogging characteristics as the high surface area of nano oxide features provided adequate incentive to explore alternative functional applications.$^{201,202}$

This work presents the used of AACVD to produce mixed morphology TiO$_2$-SnO$_2$ thin films with further slippery modification. Varying solvent systems produced different surface structural features, which affected the way spin coated surface lubricating agents interacted with the films’
However, liquid retardant properties do not guarantee anti-icing or anti-fogging functionalities. The mixed oxide films required an extra SLIPS provision, a modification that is now revolutionising how the potential impacts of harsh environmental conditions are managed.

4.2 Aims

Experiments in this chapter aim to produce special wettability micro and nano scale hierarchical TiO$_2$/SnO$_2$ thin films with a final surface lubricant modification. The use of TiO$_2$ as a morphology generating component follows from the work carried out in Chapters 2 and 3. However, instead of the previously employed draw down paint formulation application method, aerosol assisted chemical vapour deposition (AACVD) was decided upon for thin film production. Variation in solvent type and/or combination was to be explored for deposition morphology optimisation. After spin coating a Krytox lubricant top layer, the anti-icing and fog retardant properties of the slippery liquid infused porous surfaces (SLIPS) should be assessed.

4.3 Experimental

The generation of mixed morphology TiO$_2$ and SnO$_2$ thin films, via aerosol assisted chemical vapour deposition (AACVD), with further slippery liquid infused porous surface (SLIPS) modification have been optimised for anti-icing and anti-fogging applications. These materials were chosen due to their known susceptibility for surface structural changes upon solvent system alterations, which in turn impacts subsequent surface-spin coated lubricant interaction. SLIPS generation goes some way to revolutionising the way harsh environmental conditions are managed using special wettability physical surface features.

4.3.1 Materials

SiO$_2$ coated float-glass was supplied from Pilkingotn NSG, Nitrogen (99.9%) was acquired from BOC and the following solvents were obtained from Fischer Scientific: ethyl acetate (99%), toluene (99%) and dichloromethane (99%). Aerosol assisted chemical vapour deposition (AACVD) titanium isopropoxide (99%) and butyltin trichloride (99%) precursors were purchased from Sigma-Aldrich and Krytox lubricant was sourced from Dow Corning. All chemicals were of analytical standard and used as received.
4.3.2 AACVD of Ti(OCH(CH$_3$)$_2$)$_4$ and Sn(C$_4$H$_9$)$_3$Cl$_3$ Precursors

A range of samples with different surface textures were produced via aerosol assisted chemical vapour deposition (AACVD) of titanium isopropoxide and butyltin trichloride precursors. Thin films were deposited on barrier layer coated float-glass substrates inside a cold wall chemical vapour deposition (CVD) reactor, Figure 4.1.

![AACVD schematic](image)

**Figure 4.1.** AACVD schematic.

The glass substrates (90 mm x 45 mm x 4 mm) underwent isopropanol and acetone washes prior to air drying. A Whatman heating cartridge was contained within a graphite block and used to heat the glass substrate to 450°C; temperature was monitored with a PtRh thermocouple. A PIFCO ultrasonic humidifier vaporised the precursors dissolved in room temperature and pressure solvent systems, according to Table 4.1. The resulting aerosol was transported into the reactor via a stream of nitrogen gas (1.0 lmin$^{-1}$) through a brass baffle to achieve laminar flow. Total deposition times were dependent on precursor and solvent combination but tended to fall within a 25-35 min range. Once completed, the coated glass substrate was cooled under the flow of nitrogen at <100 °C.
Table 4.1. Surface structure generation via AACVD for anti-icing and anti-fogging applications.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Titanium isopropoxide/g</th>
<th>Butyltin trichloride/g</th>
<th>Ethyl acetate/ml</th>
<th>Toluene/ml</th>
<th>Dichloromethane/ml</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.50</td>
<td>0.50</td>
<td>15</td>
<td>15</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>0.50</td>
<td>0.50</td>
<td>0</td>
<td>30</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>0.50</td>
<td>0.50</td>
<td>30</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>0.50</td>
<td>0.50</td>
<td>0</td>
<td>0</td>
<td>30</td>
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<tr>
<td>5</td>
<td>0.50</td>
<td>0.50</td>
<td>0</td>
<td>15</td>
<td>15</td>
</tr>
<tr>
<td>6</td>
<td>0.50</td>
<td>0.50</td>
<td>15</td>
<td>0</td>
<td>15</td>
</tr>
</tbody>
</table>
4.3.3 SLIPS Generation

Thin film coated glass substrates, generated using the precursor solutions in Table 4.1, were cut into small coupons (10 mm x 10 mm x 4 mm) prior to the spin coating of hydrocarbon Krytox lubricant (0.5 ml) at 2000 rpm for 30 s. Resulting samples were carefully stored at room temperature and pressure with care taken to prevent any inadvertent degradation of the anti-icing and anti-fogging dependent surface layers through physical abrasion.

4.3.4 Material Characterisation Techniques

X-ray photoelectron spectroscopy (XPS) was carried out using a Thermo Scientific X-ray photo-electron spectrometer with a monochromated Al-K\(\alpha\) X-ray source (8.3381 Å). Peaks were modelled using CasaXPS software and binding energies were adjusted for adventitious carbon (284.5 eV). X-ray diffraction (XRD) patterns were obtained using a Bruker D8 Discover diffractometer with monochromated Cu-K\(\alpha\) radiation (1.5406 Å). Fourier transform infrared (FT-IR) spectroscopy was carried out using Bruker alpha platinum ATR equipment between 400 and 4000 cm\(^{-2}\). Raman spectra were recorded between 100 and 3000 cm\(^{-2}\) on a Reinshaw 1000 spectrometer equipped with a 514.5 nm laser. Surface topographies were investigated using a JEOL JSM-6301F scanning electron microscope (SEM) with an acceleration voltage of 5 or 10 kV; films were gold coated prior to SEM analysis to negate charging effects. Atomic force microscopy (AFM) was completed on a Bruker Dimension Icon instrument to 3D map sample surfaces and finally, ultraviolet-visible (UV-Vis) spectroscopy was carried out on a Shimadzu UV-2700 spectrophotometer in transmission mode between the wavelengths of 250 and 900 nm.

4.3.5 Functionality and Performance Testing Techniques

Three water contact angles were measured per coating at ambient temperature via the sessile-drop method using a FTA 100 optical contact angle meter (13.00 µg water droplet). An average value and associated error were calculated for each sample stored in ambient conditions. The tilting angle, defined as the angle at which a water droplet readily slides off a slanted surface (fixed droplet weight of 0.5000 g), was recorded using a digital angle finder. Averages and standard deviations were again calculated for each sample stored in ambient conditions at timed intervals where appropriate.

Anti-icing performance testing was carried out using the set-up displayed in Figure 4.2. Functional samples (10 mm x 10 mm x 4 mm) were placed in a sealed cooling chamber (10 cm x 10
cm x 5 cm) held at -10 °C. The chamber temperature was achieved via a through flow of cold ethylene glycol and monitored with a PtRh thermocouple. Samples placed in the chamber were immediately coupled with a surface water droplet (0.0088 g) and the time to droplet freezing was recorded. Average freezing times and standard deviations were achieved based on three repeat results per sample. Qualitative anti-frosting functionality was then assessed using a cryogenic fluid - liquid nitrogen. After 1 min of submergence, samples were removed from the -200 °C fluid and left to reacclimatise at room temperature and humidity for a further minute. Sample transparency was promptly assessed using images for comparison. Anti-fogging ability was subsequently determined by holding identical sample coupons 10 cm over 80 °C water for 1 min. Comparison images and ultraviolet-visible (UV-Vis) spectra were recorded after samples were held at room temperature and pressure for 1 min.

**Figure 4.2.** Anti-icing performance monitoring set-up. Functional samples were placed into the -10 °C icing chamber and time taken for water droplet (0.008 g) freezing was recorded.

**4.4 Results and Discussion**

Highly functional slippery liquid infused porous surfaces (SLIPS) for anti-icing and anti-fogging applications were fabricated using micro and nano scale topographies combined with a surface lubricant top layer.

A range of surface structure generating composite TiO$_2$-SnO$_2$ thin films were initially synthesised on glass substrates via aerosol assisted chemical vapour deposition (AACVD). TiO$_2$ was chosen due to its success as a special wettability surface, as described in the studies of Chapters 2 and 3, whereas the SnO$_2$ combination was selected based on literature findings.\cite{201,202} Film synthesis involved deposition of molar equivalents of titanium isopropoxide and butyltin trichloride at 450 °C with ethyl acetate and/or toluene and/or dichloromethane acting as both the oxygen source
and/or the transport medium. The rough, pale yellow, translucent films were highly adhesive and well suited for the addition of a spin coated Krytox lubricant top layer. Resulting slippery surfaces were highly effective ice- and fog-phobic devices that were fully characterised and performance tested.

4.4.0.1 Material Characterisation

In order to understand the functional properties of the composite thin films, full characterisation was completed as follows.

X-ray photoelectron spectroscopy (XPS) was the technique used to identify the Ti and Sn oxidation states and elemental abundances present in the TiO$_2$-SnO$_2$ thin films, Figures 4.3 and 4.4. Film sample 6 produced a Ti2p scan representative of the Ti$^{4+}$ oxidation state; this was supported by the Ti2p$^{3/2}$ binding energy of 458.9 eV. From the Sn3d scan, Sn was also found to be in the 4+ oxidation state as a Sn3d$^{5/2}$ peak with a binding energy of 486.9 eV was identified. Elemental abundance was calculated at the film surface as well as in the bulk by contrasting the peak area of the relevant depth argon beam etching scans, Table 4.2. It was found that the thin film’s surface was 2.6 times richer in Sn than Ti, while the bulk was 6.2 times richer in Ti than Sn. This film growth pattern was consistent across all trials described in this chapter and the higher Ti abundance was characteristic of similar depositions documented in the literature.

Figure 4.3. XPS data for thin film sample 6’s Ti2p environments. The precursor solution composition is recorded in Table 4.1 and 0s and 500s etch scans are representative of surface and bulk material.

Figure 4.5 depicts the X-ray diffraction (XRD) patterns of thin film samples 1-6, precursors as
Figure 4.4. XPS data for thin film sample 6’s Sn3d environments. The precursor solution composition is recorded in Table 4.1 and 0s and 500s etch scans are representative of surface and bulk material.

Table 4.2. Elemental abundance with etch time for film sample 6. Table 4.1 outlines the precursor solution composition. Results have been derived from XPS.

<table>
<thead>
<tr>
<th>Etch time/s</th>
<th>Elemental abundance/%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
</tr>
<tr>
<td>0</td>
<td>38.3</td>
</tr>
<tr>
<td>500</td>
<td>3.2</td>
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</tbody>
</table>

listed in Table 4.1. Typical TiO$_2$ anatase peaks were identified in the films’ diffraction patterns at 25° (101), 37° (112), 54° (105) and 55° (211). SnO$_2$ was present in its cassiterite phase, as denoted by the 27° (110) and 34° (101) diffraction peaks. Crystal orientation was impacted by the mixed oxide, as opposed to single oxide, systems due to the noted preferential growth in the described planes. This conclusion was solidified when this data was compared with the preferred orientations of the literature/ICSD’s pure TiO$_2$ and SnO$_2$ films.$^{202}$
Figure 4.5. XRD patterns generated from thin film precursor solutions 1-6, Table 4.1. Anatase and cassiterite peaks have been labelled with red and blue vertical dotted lines respectively.

Characteristic TiO$_2$ anatase and SnO$_2$ cassiterite peaks were absent from the Raman spectra of thin film samples 1-5, which was a suspected outcome of film thinness and/or surface contaminants. However, Figure 4.6 displays the Raman spectrum for sample 6 in which peaks were assigned to TiO$_2$ anatase tetragonal symmetry. The peak at 145 cm$^{-1}$ $E_g$ was indicative of a pure TiO$_2$ material. This suggested that there was little impact on unit cell size on composite film formation.$^{202}$

Figure 4.6. Raman spectrum of thin film sample 6, precursor solution composition outlined in Table 4.1. Anatase peaks have been labelled.

The effects of varying precursor solvent composition has been highlighted in the scanning electron microscope (SEM) images of thin film samples 1-6, Figure 4.7. Film 1 was prepared from an
ethyl acetate/toluene solvent system and had non-uniform surface features with no clearly identifiable shape; most particle clusters were >1 \( \mu \)m in diameter. Planar flower structures, around 100 nm in diameter, were attributed to film 2’s toluene solvent system while film 3’s hybrid needle/sphere morphology was created from an ethyl acetate solvent system. Dichloromethane produced film 4’s well-defined and uniform 200 nm needle structure inclusive surface, whereas film 5 consisted of almost spherical particle protrusions which were uniformly distributed in consequence of the toluene/dichloromethane solvent combination. Finally, film 6’s risen flower structure was a product of an ethyl acetate and dichloromethane solvent precursor mixture. This film displayed intricately textured nanoparticles, 150 nm in diameter, that had 90% surface coverage.

It was determined that solvent variation and combination was solely responsible for topography changes as all films were generated using equal molar quantities of Ti and Sn based precursors. This was a key finding as surface morphology was closely correlated to the anti-icing and anti-fogging performance of this chapter’s trialled samples. Solvent dielectric constant, viscosity and volatility are properties thought to have the most profound effect on surface topography. As seen from Table 4.3, the good miscibility between toluene, ethyl acetate and dichloromethane was supported by the relatively small difference in dielectric constants. Solvent viscosities are of the same order of magnitude so were also not predicted to significantly influence film growth rate or surface feature dimensions. Volatility was therefore most likely responsible for the variation in film uniformity and size of surface features; high volatility was linked to enhanced rate of precursor delivery to the substrate surface. Of the solvent boiling points, dichloromethane had the lowest boiling point, 40 °C, and toluene the largest, 111 °C. Consequently, the films with the largest, most uniform and close packed surface features that protruded furthest from the substrate plane were made using dichloromethane; the reverse was true of films produced using toluene. Samples 3, 4 and 6 were made from precursor solutions that did not include toluene. The resulting slippery films resisted surface water droplet freezing for the greatest time period and were therefore more functional, as described in Part 4.4.0.2.
Figure 4.7. SEM images a-f of thin film samples 1-6, precursor solution compositions have been documented in Table 4.1. Samples were gold coated prior to analysis to reduce charging effects.

Table 4.3. Common solvent dielectric constants, viscosities and boiling points.³

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Dielectric constant</th>
<th>Viscosity x10⁻³/Pa.s</th>
<th>Boiling point °C</th>
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</thead>
<tbody>
<tr>
<td>Toluene</td>
<td>2.38</td>
<td>0.552</td>
<td>111</td>
</tr>
<tr>
<td>Ethyl acetate</td>
<td>6.02</td>
<td>0.426</td>
<td>77</td>
</tr>
<tr>
<td>Dichloromethane</td>
<td>8.93</td>
<td>0.830</td>
<td>40</td>
</tr>
</tbody>
</table>

Atomic force microscopy (AFM) was another technique implemented to give insight into the
film’s surface structures. In addition, 3D surface features and average roughness values were visualised and calculated respectively, Figure 4.8. Ti/Sn containing precursor solutions with either toluene, ethyl acetate or dichloromethane correspond to samples 2-4. The toluene solvent system saw film protrusions, averaging 30.7 nm, in the vertical plane. Smaller structures, 11.0 nm, were a product of the ethyl acetate solvent system with morphological features protruding from the surface by 26.0 nm was characteristic of dichloromethane solvent systems. Unfortunately, the more extreme micro roughness of samples 1 and 6 made it impossible to get useful AFM data.

![AFM images](image)

**Figure 4.8.** AFM images a-c correspond to thin film samples 2-4, precursor solution composition described in Table 4.1. Average roughness \( R_a \) and maximum roughness \( R_{\text{max}} \) factors have been quoted.

As with Chapters 2 and 3, the most insightful characterisation techniques were those centred around surface morphology. It was found that multiscale structure on structure had the greatest effect on the thin films’ surface area. Higher densities of jagged topographical features and film pores ultimately resulted in the most substantial delay in ice nucleation.
4.4.0.2 Functional Properties and Performance Testing

Film coating samples characterised in Part 4.4.0.1 were spin coated in the Krytox lubricant to afford anti-icing and anti-fogging slippery liquid infused porous surfaces (SLIPS). Sample functionality and performance included evaluation of the average water contact and tilting angles, time to surface water droplet freezing in sub-zero conditions, degree of surface frosting after immersion in liquid nitrogen and degree of fogging after sample suspension above a 80 °C water bath.

Average water contact angles were recorded on blank glass, Krytox coated on blank glass, non-SLIPS thin film sample 1 and SLIPS thin film samples 1-6. Results have been displayed in Figure 4.9 and precursor solutions for all aerosol assisted chemical vapour depositions (AACVD) were outlined in Table 4.1. Average water contact angles of 25±6° and 34±8° were recorded on blank glass and Krytox coated glass samples respectively. The surface structured non-slippery thin film sample 1 had an increased average contact angle value of 78±8°. SLIPS modified samples 1-6 showed no further hydrophobicity increase, which indicated that water contact angle was most crucially impacted by thin film surface topography. Average water tilting angles displayed the reverse trend. Complete droplet adhesion was realised on blank glass and non-SLIPS thin film sample 1, whereas water tilting angles were <5° on all lubricant coated surfaces.

Figure 4.9. Average water contact angle data for blank glass, Krytox on glass, non-SLIPS thin film sample and SLIPS thin film samples 1-6. Precursor solutions are outlined in Table 4.1.

Within a -10° chamber, water droplets were placed on standards and thin film slippery samples 1 through 6. Anti-icing capability was measured as a function of time taken for water droplets to freeze on a given testing surface, Figure 4.10. Water droplets froze within a 3±1 min time period on blank glass and the non-SLIPS textured thin film sample. Freezing was delayed for 5±4 min on...
the Krytox coated glass standard, which indicated the potential benefits of slippery modifications for anti-icing applications. SLIPS thin film samples 1-6 were consequently tested using the same procedure. Ice formation was delayed by 9±1 min on sample 1, proving that highly structured surfaces in combination with a top layer lubricant beneficially affected icing results. Samples 2-5 had enhanced icephobicities as a result of varying surface morphologies. Sample 4’s dichloromethane solvent system generated a hydrophobic film with nano needle topography, which, unlike sample 1, protruded a greater distance out of the film’s horizontal plane, $R_{\text{max}}=551.0$ nm. Ice formation was consequently retarded for the longer duration of 13±1 min. Sample 6 was found to comprise hybrid nano sphere/flower topographies in consequence of an ethyl acetate/dichloromethane solvent system. As a result, this sample outperformed all other trialled surfaces with the most favourable ice accretion prevention time of >30 min. Functional testing results supported the theory that a combination of surface roughness and lubrication provided unique ice prevention benefits that neither physical characteristic alone could facilitate. Furthermore, sample 6 was able to delay ice freezing for >25 min longer than the independent lubricant or corresponding thin film sample standards.

Film durability was confirmed after running a scalpel up and down the length of all slippery samples ten times. Scalpel markings were initially visualised in the top coat Krytox lubricant but were spontaneously refilled with surrounding lubricant material after 3 s; this lubrication layer regeneration resulted in unchanged functionality within the original experimental error. Functionality was also preserved, again within experimental error, on leaving samples open to the atmosphere for 50 days provided that the lubricant wasn’t abraded through other physical means. The final durability test was carried out using sample 6. Said sample was initially placed in -10° conditions and the time period for a surface water droplet (0.0088 g) to freeze was monitored. After which, it was immediately exposed to room temperature and pressure until the translucent solid droplet melted. A further identical set of 24 freeze-thaw cycles saw no change in the >30 min droplet freezing period and supported previous film stability findings. Due to the absence of standardised ice accretion testing methods, literature comparison was a non-trivial undertaking. Alizadeh et al. produced superhydrophobic nanostructured silicon substrates capable of delaying freezing of a 4 µl droplet by 60 s when subjected to -20 °C conditions. Other published works cite samples’ ice adhesion strength but neglect to assess droplet freezing temperatures or time to freezing. Dou et al. has recorded ice adhesion strengths of 25 kPa at -53 °C temperatures after 30 freeze-thaw cycles on comparable SLIPS samples.

Anti-frosting characteristics were then explored on identical standards and slippery samples.
Firstly, they were submerged in liquid nitrogen for 1 min and then left to acclimatise at room temperature and humidity for a further minute. Frost accumulation was visually monitored via a transparency assessment, Figure 4.11. Separately, anti-fogging properties were tested by holding sample coupons 10 cm above 80 °C water for 1 min. The degree of fogging/visual obstruction was recorded after another minute of acclimatisation to room temperature and humidity, Figure 4.11. Blank glass standards performed poorly in both the frosting and fogging tests as the visual performance was entirely and partially compromised in the frosting and fogging experiments respectively. The Krytox top coat on a glass substrate resulted in significant quantities of ice adhesion but successfully repelled condensed water vapour, the non-SLIPS thin films saw excessive frost and fog build up and the SLIPS thin film samples were found to be most effective frost and fog retardant materials. Figure 4.12 displays the ultraviolet-visible (UV-Vis) spectra of sample 6 prior to and after the fogging test, as described above. The blank glass standard had between 95% and 100% transmittance in the visible region, which reduced to 60% on functionalisation via thin film deposition and a spin coated lubricant top coat. Fogging tests were quantitatively found to only slightly reduce the sample’s transparency, 50% transparency was recorded, which supported the qualitative evidence that visual performance was not greatly compromised. It was hypothesised that surface structure and lubricant combination significantly retarded foreign material adhesion. The slippery top coat was thought to fully saturate thin film pores and therefore reduced the number of ice nucleation sites - promoting condensate sheeting. After considering the ambiguities associated with functional testing, coatings generated in this chapter prevented frost and/or fog accumulation to a
similar degree to samples documented in the literature.\textsuperscript{9,36,38,68,76,77,207}

![Figure 4.11. Qualitative frosting and fogging test images for blank glass, Krytox on glass, non-SLIPS thin film sample and SLIPS thin film sample 6. Precursor solutions have been outlined in 4.1. Frosting experiments were carried out by submerging sample coupons in liquid nitrogen, 1 min, while fogging tests were performed above a 80 °C water bath for 1 min. Images were collected 1 min after samples were returned to room temperature and pressure.](image)

![Figure 4.12. Quantitative UV-Vis spectra of sample 6 prior to and after the fogging test. Precursor solution has been outlined in 4.1 and a blank glass standard was analysed for comparison.](image)

TiO$_2$ based thin film structures were generated in response to the previously known advantageous chemical and physical properties imparted that prevent liquid wetting, discussed throughout Chapters 2 and 3. Literature research proved that intricate surface morphologies were produced during TiO$_2$-SnO$_2$ growth with scope to explore the effect of solvent on these films’ morphologies.\textsuperscript{202} The resulting textured films fell just short of hydrophobic so a slippery lubricant spin coated top coat afforded SLIPS samples. Ice, frost and fog were retarded from the lubricated surface with
both qualitative and quantitative proof that SLIPS benefited from the rough surface generated from an ethyl acetate/dichloromethane solvent system in which the slippery medium could penetrate.

4.5 Summary

TiO$_2$-SnO$_2$ thin film composites were produced using aerosol assisted chemical vapour deposition (AACVD) and then spin coated with a Krytox lubricant. Resulting slippery liquid infused porous surfaces (SLIPS) had underlying intricate nano and micro protrusions, which contributed to the samples’ exceptional anti-icing and anti-fogging properties.

Titanium isopropoxide and butyltin trichloride precursors were dissolved in an ethyl acetate/dichloromethane solvent system in preparation for AACVD. A uniform thin film with hybrid sphere and flower features on the nanoscale was consequently produced. After a final lubricant spin coat modification, ice accretion was halted for $>30$ min in $-10^\circ$C conditions and reasonable levels of optical transparency was maintained after frosting and fogging testing analysis. These nano sized flower structures were found to outperform other surface features produced in this study, such as spheres and needles. It was concluded that AACVD afforded optimised surface morphologies, which reduced ice nucleation sites with little variation in production conditions. Water sheeting was simultaneously maximised due to the well dispersed network of highly textured nano sized protrusions in which the lubricant could fully saturate - fogging was retarded in result.

Chapter 5 goes on to explore AACVD thin film morphology and the resulting special wettability functionality on samples produced using a combination of the materials and/or the methods documented in all previous chapters. Extreme superhydrophobic wettabilities have therefore been realised on depositions generated from SiO$_2$ nanoparticle/fluorinated and non-fluorinated polymer solvent systems.
Chapter 5

Transparent SiO$_2$-based Thin Films Generated via AACVD with Superhydrophobic and Self-cleaning Functionalities

5.1 Background

Aerosol assisted chemical vapour deposition (AACVD), previously used throughout Chapter 4, has generated a range of highly functional thin films that yielded superhydrophobic, self-cleaning and transparent physical surface characteristics. Research and development into the advancement of transparent Cassie-Baxter superhydrophobic surfaces is crucial for applications such as architectural glazing, coatings for solar panels and protective layers on electronic devices. Unfortunately, the literature describes specific difficulties surrounding the generation of thin films rough enough to satisfy superhydrophobic requirements while still retaining sample transparency. This is a result of their competing natures: as films become more rough, water repellency is heightened but increased light scattering leads to a loss of visible light transmittance.

The main advantage to the use of AACVD for this functional outcome, as opposed to conventional superhydrophobic generating sol-gel, etching, electrospinning, spray coating or dip coating processes, is the ability to study a wider range of precursors. This is due to the solution based reagent requirement. Within reason, any precursor dissolved in a chosen solvent could provide a uniform thin film output on controlling the main deposition parameters. Optimising reagent composition, carrier gas flow rate, deposition time and deposition temperature have afforded many exceptional superhydrophobic thin films, which greatly vary from one another.
### 5.1.1 SiO$_2$-based Thin Films Generated via AACVD

Production of water repellent polymer films via aerosol chemical vapour deposition (AACVD) has marked a key advancement in superhydrophobic material generation. Zhuang et al. published a study explaining the use of polytetrafluoroethylene (PTFE) in fabricating hierarchical micro and nano structured thin films with water contact angles of 168° and visible light transmittance >90%. This research saw the production of films comprising nano PTFE particles arranged in micro clusters, separated by 1 µm, on deposition of an aqueous polymer dispersion for 15 min at 450 °C. The high light transmittance was justified by way of 70% of the substrate remaining unobstructed by particles. Li et al. made use of polydimethylsiloxane (PDMS) in combination with a SiO$_2$ precursor, tetraethyl orthosilicate (TEOS), to achieve a raspberry-like surface morphology. The Cassie-Baxter films afforded contact angles in excess of 160° and also demonstrated self-cleaning abilities as coal ashes and dye powders were spontaneously removed from the film surface after continuously rolling water droplets down the contaminant interface. Transparent films were subsequently generated by Tombesi et al. A first layer of 3-methacryloxypropyltrimethoxysilane was deposited for 5 min at 450 °C, followed by TEOS for 5 min at 350 °C and finally 1H,1H,2H,2H-perfluorooctyltriethoxysilane (FAS $\text{C}_8$) at 270 °C for 5 min. Water contact angles of up to 168°, visible light transmittance exceeding 90% and self-cleaning abilities were observed on said aggregated nanoparticle containing multilayer thin films.

Crick et al. have also conducted several studies citing the production of superhydrophobic AACVD thin films using a suspended nanoparticle precursor mixture. More specifically, TiO$_2$ nanoparticles were coated in oleic acid, functionalised with PDMS and dispersed in chloroform prior to undergoing a one-pot 390 °C AACVD process. Scanning electron microscopy (SEM) images highlighted the preservation of nano sized particle dimensions along with additional multiscale protrusions that were associated with polymer incorporation. Average water contact angles of 162° were measured and water tilting angles indicated potential self-cleaning abilities. Inspiration was taken from these particle based depositions, in combination with Bravo et al.’s layer-by-layer dip coating process that incorporated SiO$_2$ nanoparticles with FAS $\text{C}_8$, to fashion nanoparticle/FAS $\text{C}_8$/PDMS containing AACVD precursor suspensions for extreme functionality thin film production.
5.2 Aims

On completion of superhydrophobic and self-cleaning paint studies in Chapters 2 and 3 and the investigation into highly functional and transparent aerosol assisted chemical vapour depositions (AACVD) in Chapter 4, the following experiments explore AACVD of TiO$_2$ or SiO$_2$ particles in combination with superhydrophobic fluorinated and non-fluorinated polymers. Extreme water repellency, self-cleaning ability and transparency are to be optimised via the adjustment of material combinations, loadings and deposition temperatures.

5.3 Experimental

Transparent and superhydrophobic thin films were produced via aerosol assisted chemical vapour deposition (AACVD) of TiO$_2$ or SiO$_2$ particle precursors and fluorinated and non-fluorinated functional and adhesive polymers. Thin films were deposited on barrier layer coated float-glass substrates inside a cold wall chemical vapour deposition (CVD) reactor with the heating block situated above the deposition substrate due to thermophoresis, Figure 5.1. In order to maximise thin film functionality, particle and polymer loading studies were completed in conjunction with temperature trials.

![Figure 5.1. AACVD apparatus.](image-url)
5.3.1 Materials

SiO$_2$ coated float-glass was supplied from Pilkington NSG, Nitrogen (99.9%) was acquired from BOC and the ethyl acetate solvent (99%) was obtained from Fischer Scientific. Aerosol assisted chemical vapour deposition (AACVD) precursors included TiO$_2$ (21 nm diameter) particles, Aerosil OX50 fumed SiO$_2$ (45 nm diameter) particles, 1H,1H,2H,2H-perfluorooctyltriethoxysilane (FAS C$_8$) and polydimethylsiloxane precursors were purchased from Sigma-Aldrich, Envonik, Sigma-Aldrich and Dow Corning respectively. All chemicals were of analytical standard and used as received.

5.3.2 Particle and Polymer Loading Studies: AACVD of TiO$_2$ or SiO$_2$ Particles with FAS C$_8$ and PDMS Polymer Species

Prior to the generation of TiO$_2$ or SiO$_2$ particle-1H,1H,2H,2H-perfluorooctyltriethoxysilane (FAS C$_8$) and polydimethylsiloxane (PDMS) polymer thin films, each glass substrate (90 mm x 45 mm x 4 mm) underwent isopropanol/acetone washes and was subsequently air dried. The Whatman heating cartridge, contained in the graphite block, was used to heat the glass substrate to 400 °C. Deposition temperatures were monitored with a PtRh thermocouple. A PIFCO ultrasonic humidifier vaporised the superhydrophobic precursor components that were dispersed in room temperature and pressure ethyl acetate, according to the particle loading Table 5.1 and the polymer loading Table 5.2. The resulting particle containing aerosol was transported into the reactor via a stream of nitrogen gas (1.0 lmin$^{-1}$) through a brass baffle to achieve laminar flow. Total deposition times were dependent on precursor and solvent combination but tended to fall within a 25-35 min range. Once completed, the coated glass substrate was cooled under the flow of nitrogen at <100 °C.
Table 5.1. TiO$_2$ (21 nm diameter) or SiO$_2$ (45 nm diameter) particle loading study with FAS C$_8$ and PDMS polymer additives. Thin films were generated via AACVD at 400 °C.

<table>
<thead>
<tr>
<th>Sample</th>
<th>TiO$_2$ particles/g</th>
<th>SiO$_2$ particles/g</th>
<th>FAS C$_8$/g</th>
<th>PDMS/g</th>
<th>Ethyl acetate/ml</th>
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<tr>
<td>1</td>
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Table 5.2. FAS C₈ and PDMS polymer loading study with SiO₂ (45 nm diameter) particle additives. Thin films were generated via AACVD at 400 °C.

<table>
<thead>
<tr>
<th>Sample</th>
<th>SiO₂ particles/g</th>
<th>FAS C₈/g</th>
<th>PDMS/g</th>
<th>Ethyl acetate/ml</th>
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</table>
5.3.3 Temperature Study: AACVD of SiO$_2$ Particles with FAS C$_8$ and PDMS Polymer Species

According to the experimental outline in section 5.3.2, the following aerosol assisted chemical vapour deposition (AACVD) temperature study required initial glass substrate solvent washes and a deposition rig set-up as displayed in Figure 5.1. Optimised reagent loadings and combinations were carried forward based on the data collected from previous depositions. Table 5.3 details the conditions needed to generate films 21-25.
Table 5.3. Temperature study of SiO$_2$ (45 nm diameter) particles with FAS C$_8$ and PDMS polymer additives. Thin films were generated via AACVD.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Temperature/°C</th>
<th>SiO$_2$ particles/g</th>
<th>FAS C$_8$/g</th>
<th>PDMS/g</th>
<th>Ethyl acetate/ml</th>
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5.3.4 Material Characterisation Techniques

X-ray photoelectron spectroscopy (XPS) was carried out using a Thermo Scientific X-ray photo-electron spectrometer with a monochromated Al-K$_\alpha$ X-ray source (8.3381 Å). Peaks were modelled using CasaXPS software and binding energies were adjusted for adventitious carbon (284.5 eV). X-ray diffraction (XRD) patterns were obtained using a Bruker D8 Discover diffractometer with monochromated Cu-K$_\alpha$ radiation (1.5406 Å). Surface topographies were investigated using a JEOL JSM-6301F scanning electron microscope (SEM) with an acceleration voltage of 5 or 10 kV; films were gold coated prior to SEM analysis to negate charging effects. Digital microscopy was achieved by Dr Suraj Pawar at Akzonobel (Slough) on a Keyence VHX-5000 digital microscope and finally, ultraviolet-visible (UV-Vis) spectroscopy was carried out on a Shimadzu UV-2700 spectrophotometer in transmission mode between the wavelengths of 250 and 900 nm.

5.3.5 Functionality and Performance Testing Techniques

Three water contact angles were measured per coating at ambient temperature via the sessile-drop method using a FTA 100 optical contact angle meter (13.00 µg water droplet). An average value and associated error were calculated for each sample stored in ambient conditions. The tilting angle, defined as the angle at which a water droplet readily slides off a slanted surface (fixed droplet weight of 0.5000 g), was recorded using a digital angle finder. Averages and standard deviations were again calculated for each sample stored in ambient conditions. Self-cleaning properties were explored in the following way: thin film samples were tilted by 40°, for visual ease, and then covered in glitter, which acted as a dust/dirt alternative. When placed under water flow, glitter collecting spherical water droplets rolled down the substrate and removed a degree of unwanted foreign material.

5.4 Results and Discussion

This chapter presents transparent, superhydrophobic and self-cleaning thin films produced via aerosol assisted chemical vapour deposition (AACVD). TiO$_2$ and SiO$_2$ (21 nm and 45 nm diameter respectively) particles in a fluorinated and non-fluorinated polymer mixture were deposited on glass substrates to effect highly functional films. The minerals and polymers selected in this chapter were chosen on merit and remained in keeping with previous chapter material themes, Chapters 2, 3 and 4. The resulting transparent films showed excellent mechanical stability and scratch resistance after durability testing.
5.4.1 Material Characterisation

Firstly, TiO$_2$ (21 nm diameter) particles were suspended in a 1H,1H,2H,2H-perfluorooctyltriethoxysilane (FAS C$_8$) and polydimethylsiloxane (PDMS) polymer-ethyl acetate mixture, according to Table 5.1, and deposited on float glass in a 400 °C reactor. TiO$_2$ particle loadings were subsequently optimised through trial and error according to functionality testing data.

X-ray photoelectron spectroscopy (XPS) was the technique utilised to confirm the chemical environments and elemental abundances present in the TiO$_2$ containing thin film samples. Thin film sample 1 generated the C1s, Si2p, O1s, F1s and Ti2p spectra visualised in Figures 5.2, 5.3, 5.4, 5.5 and 5.6 respectively. The peak at 284.8 eV and 286.3 eV corresponded to artefacts of surface carbon contaminant species and the C-OR ether environment respectively. The deconvoluted Si2p peaks at 102.3 eV and 103.9 eV were subsequently identified as -Si(CH$_3$)$_2$-O$_2$- chains, found in the PDMS polymer, and surface roughening SiO$_2$ particles. The O1s data also highlighted the presence of SiO$_2$ particles, binding energy of 532.7 eV, and FAS C$_8$’s -COR environment, binding energy of 534.2 eV. A single peak in the F1s region at 689.7 eV was indicative of -CF$_2$-CF$_2$- chains in FAS C$_8$. The Ti2p scan identified Ti$^{4+}$ oxidation state presence and was attributed to TiO$_2$ structural particles, supported by the Ti2p$^{3/2}$ binding energy of 458.8 eV.

Figure 5.2. XPS 0s etch data for thin film sample 1’s C1s environments. The precursor mixture composition is recorded in Table 5.1.

Thin film sample 1’s elemental abundance was measured at the film surface, a point between the surface and the bulk and in the sample bulk, Figure 5.7. The surface was found to be rich in carbon due to its associated 39.1% elemental abundance, a 29.3% oxygen presence made it the second most
plentiful surface element and smaller contributions from silicon, fluorine and titanium were realised based on the 27.7%, 3.4% and 0.4% abundance values respectively. After sample etching for 200s, the percentage of oxygen detected dramatically increased while carbon and silicon displayed the reverse trend. The associated values were 69.0%, 12.6% and 18.2% respectively. This mid point between the surface and the bulk also saw an elevated 1.3% titanium abundance but fluorine was no longer detected. Furthermore, the sample bulk was exposed after a 400s etch. Oxygen was again determined most abundant while fluorine remained undetected. A slight increase in carbon and silicon was measured with values of 19.4% and 33.2% respectively.
Figure 5.5. XPS 0s etch data for thin film sample 1’s F1s environment. The precursor solution composition is recorded in Table 5.1.

Abundance data therefore indicated that the FAS C₈ and PDMS reagents were predominantly found at the sample surface. This was assumed based on the knowledge that the polymer species were the sole contributors of the high relative proportion of carbon and fluorine elements in the 0s etch experiment. The increase in oxygen abundance at 200s, followed by a decrease at 400s, led to the understanding that metal oxide particles were positioned just below the polymer surface layer and extended into the bulk. The described decrease after a 400s etch may have been an artefact of the depletion of oxygen containing polymers. A fact further supported by the gradual increase in titanium’s elemental abundance with sample depth, refer to Figure 5.7.
Figure 5.7. XPS elemental abundance data for thin film sample 1. The precursor solution composition is recorded in Table 5.1 and 0s, 200s and 400s etch scans are representative of the surface, mid point between the surface and bulk and bulk material respectively.

Figure 5.8. XPS elemental abundance data for thin film sample 6. The precursor solution composition is recorded in table 5.1 and 0s, 200s, 400s and 600s etch scans are representative of data points moving from the surface to bulk material.

Based on the poor sample transparency and hydrophobic nature of the TiO₂ particle containing thin films, Figures 5.20 and 5.21, depositions focused on varying the loading of SiO₂ particles were produced, Table 5.1. Figures 5.8, 5.9, 5.10, 5.11 and 5.12 display the elemental abundances for carbon, silicon, oxygen and fluorine in 0s, 200s, 400s and 800s etch experiments. It was determined that carbon’s elemental abundance decreased for all SiO₂ particle loading quantities moving from the sample surface towards the bulk. This was a likely result of water repellent FAS C₈ and PDMS polymers residing at a film’s surface and was supported by sample 6 and 8’s 18.4% and 18.2%
carbon reduction respectively. Conversely, silicon and oxygen experienced a percentage increase with etch duration. Sample 7 had 6.9% more silicon and 9.5% more oxygen in the film bulk than surface due to an arrangement of SiO$_2$ particles below the top polymer layer. While fluorine did not follow a distinctive abundance trend, it was found that higher percentages in the 0s and 200s etch regions were associated with elevated average water contact angles; further supporting the argument that the fluorinated polymer species migrated to the film surface. Sample 9 had a fluorine abundance of 4.1% at a 200s etched point and the highest associated average water contact angle of

Figure 5.9. XPS elemental abundance data for thin film sample 7. The precursor solution composition is recorded in Table 5.1 and 0s, 200s, 400s and 600s etch scans are representative of data points moving from the surface to bulk material.

Figure 5.10. XPS elemental abundance data for thin film sample 8. The precursor solution composition is recorded in Table 5.1 and 0s, 200s, 400s and 600s etch scans are representative of data points moving from the surface to bulk material.
Figure 5.11. XPS elemental abundance data for thin film sample 9. The precursor solution composition is recorded in Table 5.1 and 0s, 200s, 400s and 600s etch scans are representative of data points moving from the surface to bulk material.

Figure 5.12. XPS elemental abundance data for thin film sample 10. The precursor solution composition is recorded in Table 5.1 and 0s, 200s, 400s and 600s etch scans are representative of data points moving from the surface to bulk material.

167±2°. Additional fluctuations were realised across all samples for a given etch duration, which could explain the reasoning behind only slight changes in water retardant functional properties.

Figures 5.13, 5.14, 5.15 and 5.16 represent the XPS data of thin film sample 9, also corresponds to identical films 13, 17 and 24 from other loading and temperature studies. As with previous data, the C1s scan was deconvoluted into a major peak at 284.9 eV and a less pronounced side peak at 286.8 eV. These regions were indicative of surface carbon contaminants, including hydrocarbons, and C-O(OR) ester environments respectively. The Si2p scan contained an -CF₂-CF₂- environ-
Figure 5.13. XPS Os etch data for thin film sample 9/13/17/24’s C1s environments. The precursor mixture composition is recorded in Table 5.1.

ment, 102.5 eV, and a peak associated with SiO$_2$ particles, 104.3 eV. SiO$_2$ particle presence was also confirmed in O1s XPS data due to the 532.7 eV peak. A small O1s 535.3 eV environment supported the presence of -COR components that were representative of the polymer functional groups.\textsuperscript{217,218} Finally, the F1s scan contained -CF$_2$-CF$_2$- chains, as expected, in consequence of the FAS C$_{8}$ component at a binding energy of 689.7 eV.\textsuperscript{203}

Due to the amorphous nature of both the fluorinated and non fluorinated polymer species and SiO$_2$ particles, the X-ray diffraction (XRD) patterns of thin film samples 6-25 showed no distinguishable peaks. The presence of crystalline TiO$_2$ particles in samples 1-5, reagents detailed in
Figure 5.15. XPS O1s etch data for thin film sample 9/13/17/24's O1s environments. The precursor solution composition is recorded in Table 5.1.

Table 5.1, gave some weakly resolved peaks in their respective patterns. Figure 5.17 displays the extremely noisy XRD pattern of thin film sample 1, an anatase (101) peak at 25° was the only conclusively identifiable crystalline artefact and was thought to be a result of the 3 to 1 ratio of anatase to rutile phases in the TiO₂ reagent. This was a consistent finding across all TiO₂ containing films and the inorganic crystal structure database supported the peak position.

Variations in particle loading and polymer compositions were explored using scanning electron microscopy (SEM). Images of thin film samples 5, 9 (synonymous with 13/17/24) and 20 have been presented in Figure 5.18. Sample 5 consisted of many spherical and non agglomerated >50
nm TiO$_2$ particles along with few larger 5 µm clusters. The lack of uniformity and abundance of non textured nanoparticles resulted in a relatively low average water contact angle of 101±1°. Conversely, the highest average water contact angle of 167±2° was recorded on the SiO$_2$ particle containing thin film sample 9. This film comprised few non spherical nanoparticles and many textured >1 µm SiO$_2$ particle clusters; thought to have enhanced film functionality. Thin film sample 20 had a lower average water contact angle of 127±9° despite its identical SiO$_2$ particle and fluorinated polymer loading. The increased PDMS content was determined to be responsible for the visually apparent thick surface coating that resulted in smoothed SiO$_2$ agglomerates. This physical property was expected to have muted the water repellent surface roughening effect previously achieved on films with textured >1 µm particle clusters.

Digital microscopy was then employed to visualise surface structural components over a larger area, Figure 5.19. Thin film sample 9, also labelled as 13/17/24, was deposited at 400 °C and afforded the extremely high water contact angle of 167±2°. SEM had previously identified that this film had large clusters of SiO$_2$ particles but digital microscopy highlighted that said clusters were components of a much larger agglomeration network with dimensions in excess of 100 µm. These textured protrusions were interchanged with few smaller nanoscale features creating a multiscale interface on which water droplets would interact. Thin film sample 21 had the same precursor composition, Table 5.3, but was deposited at 250 °C. A lower water contact angle of 133±7° was the product of many non agglomerated spherical particles in combination with fewer small SiO$_2$ clusters, <100 µm. Film 25 was then deposited at 450 °C and produced a high density of uniform
Figure 5.18. SEM images of a-b, thin film sample 5, c-d, thin film sample 9/13/17/24 and e-f, thin film sample 20. The precursor solution compositions have been recorded in Tables 5.1, 5.2 and 5.3. Samples were gold coated prior to analysis to reduce charging effects.

nanoparticle protrusions. The lack of particle clustering and an absence of multiscale texture was attributed to the associated low average water contact angle, $114\pm11^\circ$. It was conclusively determined that a deposition temperature of 400 °C resulted in the most superhydrophobic sample surface and therefore marked the completion of variable optimisation.

Ultraviolet-visible (UV-Vis) transparency testing was finally performed on the characterised
Figure 5.19. Digital microscopy images of a-b, thin film sample 9/13/17/24, c-d, thin film sample 21, and e-f, thin film sample 25. The precursor solution compositions have been recorded in Tables 5.1, 5.2 and 5.3.

samples. Figure 5.20 displays the UV-Vis spectra of a standard and numerous thin film samples, reagent compositions outlined in Tables 5.1, 5.2 and 5.3. The blank glass standard was found to have >95% transmittance in the visible region, whereas thin film 1 had poor sample transparency of between 24% and 29% owing to the appearance of white opaque TiO₂ particles. Sample 20 displayed between 15% and 20% visible light transmittance. This was caused by the thicker surface PDMS polymer layer that produced a white haze across the substrate surface. Thin film 9, also labelled as 13/17/24, had the most transparent functional surface. Values of 79% to 91% were were
most likely achieved due to the presence of regions that remained unpopulated by SiO$_2$ particles. In this example, low surface energy polymer coated and textured agglomerates were substantial enough to repel water droplets but distinctly separated so that light could be transmitted through the sample. This result was in line with some of the best results found in the literature. For example, light transmittance of above 90% was achieved on Zhuang et al.’s polytetrafluoroethylene (PTFE) thin films$^{100}$ and by Tombesi et al., who made use of tetraethyl orthosilicate (TEOS) and FAS C$_8$ to generate transparent surface morphologies.$^{103}$

![Figure 5.20](image.png)

**Figure 5.20.** Quantitative UV-Vis spectra of a blank glass standard, thin film samples 1, 9/13/17/24 and 20. Precursor solution has been outlined in Table 5.1.

As seen in Chapter 4, multiscale textured surface roughness characterisation techniques were of most use when understanding functional variations. SEM and digital microscopy made it possible to determine that highly textured non spherical SiO$_2$ clusters were most likely to generate extreme superhydrophobic properties that were optimised to allow visible light transmission of up to 91%. XPS was another useful technique in understanding polymer and particle sample depth positioning. When thin coatings of surface energy lowering polymer resided at the film interface, roughening particles were able to maintain the desired morphology without becoming lost to the bulk. Therefore, the two characteristic superhydrophobic components were realised: a waxy surface and hierarchical topographies.
5.4.2 Functional Properties and Performance Testing

The water repellency and self-cleaning abilities were subsequently measured for the aerosol-assisted chemical vapour deposition (AACVD) thin film samples generated with either TiO$_2$ or SiO$_2$ particles, 1H,1H,2H,2H-perfluorooctyltriethoxysilane (FAS C$_8$) and polydimethylsiloxane (PDMS). The impact of particle type and loading, polymer loading and deposition temperature, according to Tables 5.1, 5.2 and 5.3, were assessed by way of water contact angle measurements, high speed camera analysis and qualitative self-cleaning tests. All performance testing methods have been described in Part 5.3.5.

Figure 5.21 displays the average contact angle results for thin film samples deposited at 400 °C. The FAS C$_8$ and polydimethylsiloxane precursor total content was consistent, 0.60 g of each, while the TiO$_2$ nanoparticle loading was altered. In this study, the highest average water contact angle was recorded on a 0.10 g particle loading deposition, 148±8°. A clear reduction in hydrophobicity with increasing particle loading was then realised; the film with a 0.30 g TiO$_2$ particle input had a 101±1° average water contact angle. A similar study was then carried out with SiO$_2$ particles. The thin films produced average water contact angles between 146° and 153°. This increased functionality was a consequence of the larger SiO$_2$ nanoparticles forming highly textured clusters, as opposed to less favourable uniform bed of spherical TiO$_2$ nanoparticles that were observed in the first deposition set. Scanning electron microscope (SEM) images from Part 5.4.1 highlighted these physical differences.

Further trials focused on refining FAS C$_8$ and PDMS precursor masses while keeping the optimised SiO$_2$ particle loading constant, 0.25 g. The highest average water contact angle was associated with the sample generated using a 0.60 g of both polymer species, Figure 5.22. Sample 9, which is synonymous with 13, 17, 24 and 20, see Tables 5.1, 5.2 and 5.3, resulted in an average water contact angle of 167±2°. The optimisation of each polymer species loading, while the other was held constant, resulted in a functionality trend whereby values decreased either side of the 0.60 g loading peak. This was clearly visible in the case of PDMS. The lowest average water contact angle value, 106±1°, was noted for a loading of 0.50 g and values of 153, 135 and 127 were recorded for 0.70 g, 0.80 g and 0.90 g loadings respectively. Said finding was likely the result of insufficient polymer coverage below loadings of 0.60 g. At these values, surface energy may not have been adequately lowered and therefore regions of uncoated roughening particles could have made contact with surface water droplets - decreasing the average water contact angle result.
A clearly detrimental physical impact on surface morphology was visualised on larger loadings, see SEM images in Part 5.4.1. Thick layers of viscous PDMS compromised the multiscale surface roughness and produced an undesirable smoothed surface on which water droplets resided.

Temperature was the final deposition variable explored. Figure 5.23 highlights the functional changes experienced on the optimised precursor loading mixture, 9, also labelled as 13, 17, 24 and
There was a loose trend to suggest an increase in water repellency with temperature, which resulted in a peak at 400 °C. Beyond this point there was a sharp decrease in functionality as the average water contact angle fell from 167±2° to 114±11° between 400 °C and 450 °C. Digital microscopy images proved that with increasing temperature there was a tendency towards a more uniform arrangement of non clustered near spherical particles that displayed less variation in texture across the film surface. Substrate temperature impacts the solvent evaporation rate and therefore how quickly the polymer reagents enter the gaseous state. At increased temperatures the polymer more rapidly entered said state and was thought to form a more even surface layer on a SiO₂ particle bed. As multiscale roughness was required, an element of delayed evaporation was needed so that polymer/particle binding could occur in order to form a mixture of nano and micro scale surface protrusions. The maximum water contact angle achieved in this chapter’s work performed extremely well in comparison with similar literature studies. Maximum values attained on depositions that made use of identical or near identical polymers were between 160° and 168°; therefore validating the extremely favourable functionalities realised in the SiO₂ particle studies.

The ability of a water droplet to bounce on a surface has recently been defined as a measure of superhydrophobicity. Figure 5.24 displays a time lapse of a water droplet bouncing on the optimised precursor solution deposited at 400 °C to produce sample 9/13/17/24/20. The repre-
sented bouncing property provides further evidence to support the extremely high average water contact angle recorded for said surface. According to Crick et al., the number of bounces can also be attributed to the contact angle value. Their testing indicates that for a contact angle of $167^\circ$, 8-10 bounces would be observed on film 9/13/17/24/20. Due to slight deviations in experimental set ups, the high speed camera was only able to record between 3-5 bounces on different sample regions.

All superhydrophobic samples described in this chapter had tilting angle values characteristic of the Cassie-Baxter wetting regime, values of less than 5°. As explained in great detail throughout Chapters 2, 3 and 4, low tilting angle values were indicative of a sample's self-cleaning ability. Figure 5.25 displays the self-cleaning action of the optimised thin film sample 9/13/17/24/20. The functionalised substrate was held at 40°, for visual ease, and was then covered in glitter, which acted a dust/dirt alternative. When placed in a water flow path, glitter collecting spherical water droplets rolled down the substrate and consequently removed all traces of the unwanted foreign material.

**Figure 5.24.** Water droplet bouncing on thin film sample 9/13/17/24. Precursor solution has been outlined in Table 5.3.

**Figure 5.25.** Water flow was used to display the self-cleaning functionality of glitter covered thin film sample 9/13/17/24. Precursor solution has been outlined in Table 5.3.

In conclusion, SiO$_2$ particle and fluorinated and non fluorinated polymer containing thin film samples were generated via AACVD in response to the favourable properties achieved through the use of similar or identical reagents used in previous chapter studies. The resulting thin film with an optimised morphology fell firmly within the superhydrophobic wetting category, had transparent optical properties and afforded self-cleaning testing results.
5.5 Summary

Aerosol assisted chemical vapour deposition (AACVD) was employed to generate a range of thin films with superhydrophobic, transparent and self cleaning properties. TiO$_2$ (21 nm diameter) particles were initially deposited at 400 °C with 1H,1H,2H,2H-perfluorooctyltriethoxysilane (FAS C$_8$) and polydimethylsiloxane (PDMS) polymers. Ethyl acetate was the solvent of choice. This study’s maximum average water contact angle, $148 \pm 8^\circ$, was achieved on a system loaded with 0.10 g of TiO$_2$ particles. Scanning electron microscopy (SEM) images highlighted the presence of many spherical and non agglomerated surfaces particles integrated with few larger 5 µm clusters. A lack of topographical uniformity and the abundance of non textured nanoparticles were expected to have the greatest impact on the film’s suboptimal functionality. Sample transparency was also compromised, again due to the uniform arrangement of white opaque TiO$_2$ particles, as visible light transmittance was between 24% and 29%. Furthermore, the sample was not superhydrophobic in nature and therefore did not satisfy Cassie-Baxter regime requirements - the desired self-cleaning properties were not observed.

The negative results associated with the use of TiO$_2$ particles, inspired the switch to SiO$_2$ (45 nm diameter) particles. Particle loading was initially refined, such that few non spherical nanoparticles and many textured >1 µm SiO$_2$ particle clusters formed superhydrophobic film surfaces. FAS C$_8$ and PDMS polymer loadings were later adjusted. An increase in PDMS, beyond 0.60 g, was linked to muted surface roughening as the viscous polymer resulted in surface agglomerate smoothing. SiO$_2$ particles, 0.25 g, FAS C$_8$, 0.60 g, and PDMS, 0.60 g, precursor solutions underwent final temperature refinements in order to identify the most favourable thin film deposit. At 400 °C, an average water contact angle of $167 \pm 2^\circ$ was measured on a Cassie-Baxter self-cleaning surface. Water droplets were proven to bounce on said film, which was also able to transmit up to 91% of visible light.
Conclusion

Experiments completed as part of this doctorate have centred around four different streams of research: SiO$_2$ particle inclusive self-cleaning paints, CaCO$_3$ particle inclusive superhydrophobic self-cleaning paints, TiO$_2$-SnO$_2$ composite thin films with slippery liquid infused porous surface (SLIPS) modification for anti-icing and anti-fogging applications and superhydrophobic self-cleaning SiO$_2$ particle containing thin films with high level transparency.

Chapter 2 investigated the use of low toxicity and low cost surface roughening SiO$_2$ particles with aqueous low surface energy octadecanoic acid (FA C$_{18}$) formulations that contained commercial paint latex. Water contact angles fell slightly short, 130±8°, of the desired superhydrophobic requirement and the mixed Cassie-Baxter/Wenzel wetting regime prevented self-cleaning droplet rolling characteristics. The use of CaCO$_3$ particles in chapter 3’s studies produced a superhydrophobic paint, water contact angle of 154±5°, with self-cleaning Cassie-Baxter wetting properties. Rheology modifiers were incorporated to achieve commercially required properties and TiO$_2$ particle doping was explored for functionality enhancement. Top coat formulations that comprised CaCO$_2$ and TiO$_2$ particles in equal measure, FA C$_{18}$, an acrylic latex and rheology modifiers were applied to Dulux Trade Diamond Matt paint. The samples were water repellent in nature and showed a good degree of resistance to red wine, tea and coffee staining. The superhydrophobic, self-cleaning, inexpensive and commercially compatible decorative paint brief had been achieved and future work should be focussed on both scale up procedures and other niche aesthetic requirements. The key advancements to the existing field have centered on the ability to produce an aqueous paint of commercial grade, as opposed to many of the generic coatings that have previously been documented as paints. Said examples have all lacked key components, such as extenders, modifiers, binders and latex.

Beyond the special wettability paint, chapter 4 focused on fabricating thin film composites for anti-icing anti-fogging applications via aerosol assisted chemical vapour deposition (AACVD). Titanium isopropoxide and butyltin trichloride precursors were deposited using a variety of differ-
ent solvent combinations, which provided more opportunity for insight compared with the previously explored single solvent systems. A nano sized surface flower topography was the product of an ethyl acetate/ dichloromethane solvent system. Subsequent lubricant modification fulfilled the SLIPS requirement, which prevented unwanted light scattering on icing and fogging testing. Surface lubricants are known to suffer from durability issues; additional methods for lubricant anchoring would be an area to develop.

Finally, chapter 5 continued the AACVD theme to synthesise thin films with superhydrophobic, transparent and self cleaning functionalities. SiO\(_2\) nanoparticles were dispersed in 1H,1H,2H,2H-perfluorooctyltriethoxysilane (FAS C\(_8\)) and polydimethylsiloxane (PDMS) polymers prior to deposition on glass substrates. Particle and polymer loadings, dopants and temperature studies were carried out to afford an optimised film with an average water contact angle of 167±2°. Self-cleaning properties were also realised due to the extremely low water tilting angle, <5°, and transparency was confirmed by way of visible light transmission measurements. This work is currently the only known example of SiO\(_2\) particles in combination with both fluorinated and non-fluorinated polymers to produce morphological control over AACVD thin films.

Future work should include investigation into the physical and/or chemical limits associated with the realisation of Wenzel, Wenzel/Cassie-Baxter and Cassie-Baxter wetting regimes. The use of different metal oxides, such as ZnO or SiO\(_2\), thin films for further SLIPS modification in anti-icing, anti-frosting and anti-fogging research. Final developments should incorporate AACVD studies that examine the worth of SiO\(_2\) nanoparticles/stearic acid precursor mixtures for transparent, non-toxic and low cost superhydrophobic thin films.
Publications


References


