Robust superhydrophobic nanocomposite coatings

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I, ZHUYANG CHEN, confirm that the work presented in this thesis is my own. Where information has been derived from other sources, I confirm that this has been indicated in the thesis.
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Abstract

A solid surface is described as superhydrophobic when it possesses a large water contact angle ($\theta_w \geq 150^\circ$) and a small contact angle hysteresis ($\Delta \theta \leq 10^\circ$). These surfaces have many applications, such as microfluidic channels, anti-icing, self-cleaning and anti-bacterial surfaces. Superhydrophobic surfaces have been achieved through the control of chemical composition of the surface, to acquire low surface energy and suitable roughness.

Applying nanocomposite coatings by wet chemical spraying is one of the most facile, low cost and scalable ways to create superhydrophobic surfaces. The nanocomposite can be simply prepared by dispersing nanosized particles such as SiO$_2$, carbon black, or/and metallic oxide particles (such as ZnO, TiO$_2$, Al$_2$O$_3$, etc.) in a hydrophobic polymer matrix such as polystyrene (PS), polyethylene (PE) and polyurethane (PU), where the nanoparticles provide the necessary roughness and the polymer reduces the overall surface energy.

Durability of superhydrophobic nanocomposite coatings is an important issue. The micro/nanostructure that is formed by particles with some of the non-flexible polymers is easily damaged under mechanical shears/stresses and liquid impact. Research has shown that the hydrophobicity of certain nanocomposite coatings would degrade after UV/sunlight or strong chemical exposure. The damage of the particles or polymer would lead to an increase in the liquid/solid contact area and a change of the composition associated with the surface chemistry, resulting in a loss of hydrophobicity.

In this thesis, the fundamental/theoretical aspects of the surface wetting property were briefly introduced and explained. This was followed by a thorough literature review which covered more than 50 literature published in the past decade related to the fabrication of mostly nanocomposite based superhydrophobic surfaces, also showing their material selection and durability testing methods/results. It is clear that development/applications of superhydrophobic surfaces are still facing many challenges such as achieving mechanically and chemically stable surfaces.

In experimental work, the material selection and fabrication process of two types of superhydrophobic nanocomposite coatings: water-based oxide nanocomposite and PKFE (Polytetrafluoroethylene particle mixed with Kytex oil and Fluoropolymer-grafted epoxy resin) were demonstrated, followed by the descriptions of different durability and multifunctional tests that were relevant to superhydrophobic coatings.
The durability test performance of the superhydrophobic nanocomposite coatings were then presented and discussed accordingly. All the nanocomposite coatings are scalable and facile as they are produced via off-the-shelf material and wet chemical spraying. The coated surfaces demonstrated good mechanical (remained superhydrophobic after at multiple cycles of tape peeling, abrasion and sand abrasion tests), chemical (remained superhydrophobic after immersing in strong acid/alkane solution for at least 2 hours) and environmentally stable (remained superhydrophobic under UV exposure up to 2 weeks) properties.

Furthermore, an excellent droplet impalement resistance was noted, with PKFE superhydrophobic surfaces withstanding impact by a water jet travelling at maximum speed of 32.5 m/s, without losing its anti-wetting property. The extreme liquid impalement resistance could be attributed to the flexible nature of the epoxy which was used in the coatings, and it also provided the mechanical/chemical stability.

Water-based oxide superhydrophobic nanocomposite possesses transparent and others unique optical properties. The 1-2 µm thick coated sample was found to have an optical transmittance of over 90%. However, transparency decreased due to the Mie scattering of light from the increase of surface roughness. Mie scattering on nanocomposite superhydrophobic coatings has rarely been experimentally studied previously. Therefore, in my work, ASTM standard Haze and Clarity measurements were used to evaluate wide (scattering angle larger than 2.5) and narrow angle light scattering. Experimental results indicated that the increase of coating thickness and the use of larger particle size (particle agglomeration) would lead to a poorer Haze and Clarity performance. In practice, low clarity would result in the transmitted image to blur more as the observation distance is increased and a low Haze would result in the transmitted image being unclear.
Impact Statement

The superhydrophobic nanocomposite coatings, both the water-based oxide nanocomposite and PKFE developed in this research were found to demonstrate excellent durability and scalability. Most of the performance tests were carried out by following the industrial standard, suggesting that these coatings can be potentially commercialised for industrial and everyday anti-wetting applications.

More importantly, PKFE superhydrophobic coatings demonstrated the ability to withstand the impact of a water jet travelling up to a speed of 35 m/s, without losing its anti-wetting property. Such liquid impalement resistance has not been achieved by any other superhydrophobic coatings in the past and the results of this work were published in Nature Material. This work provided meaningful insights into the study of high pressure liquid-solid interaction or the development of robust superhydrophobic surfaces.

The optical properties of the water-based oxide nanocomposite were carefully studied. ASTM standard Haze and Clarity measurements were employed to experimentally examine how different factors such as material refractive index affect the light scattering within the nanocomposite coatings. Other researchers should be able to benefit from the output of this work as how to control the transmittance of nanocomposite coatings.
# Nomenclature

<table>
<thead>
<tr>
<th>Symbols</th>
<th>Abbreviations &amp; Subscripts</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A$ : Area (m$^2$)</td>
<td>ASTM: American Society for Testing and Material</td>
</tr>
<tr>
<td>$b$ : Width (m)</td>
<td>APTES: γ-aminopropyltriethoxysilane</td>
</tr>
<tr>
<td>$c$: Speed of sound (m/s)</td>
<td>ATH: Alumina tri-hydrate</td>
</tr>
<tr>
<td>$D$ (d): Diameter (m)</td>
<td>CB: Carbon black</td>
</tr>
<tr>
<td>$E$: Energy (J)</td>
<td>CNF: Carbon nanofibre</td>
</tr>
<tr>
<td>$F$: Force (N)</td>
<td>CNT: Carbon nanotube</td>
</tr>
<tr>
<td>$F_{hel}$: Total Helmholtz free energy (J)</td>
<td>CTAB: Hexadecyltrimethylammonium bromide</td>
</tr>
<tr>
<td>$f_{a or s}$ : Air (solid) area fractions</td>
<td>CR: Critical</td>
</tr>
<tr>
<td>$g$: Standard gravity (m/s$^2$)</td>
<td>DSTM: Dopamine-silica trimethylsilyl modified</td>
</tr>
<tr>
<td>$h$: Height (m)</td>
<td>FTIR: Fourier-transform infrared spectroscopy (FTIR)</td>
</tr>
<tr>
<td>$I$: Intensity of light (J/m$^2$)</td>
<td>LbL: Layer by layer</td>
</tr>
<tr>
<td>$k_{WH}$: Water hammer coefficient</td>
<td>la: Liquid-air interface</td>
</tr>
<tr>
<td>$K$: Mie scattering coefficient</td>
<td>Is: Liquid-solid interface</td>
</tr>
<tr>
<td>$m$: Mass (kg)</td>
<td>Max: Maximum</td>
</tr>
<tr>
<td>$P_{CD}$ or $P_{WH}$: Capillary (Dynamic, or Water hammer) pressure (Pa)</td>
<td>Min: Minimum</td>
</tr>
<tr>
<td>$R$: Diameter (m)</td>
<td>MTES: Methyltriethoxysilane</td>
</tr>
<tr>
<td>$r$: Roughness factor</td>
<td>NP: Nanoparticle</td>
</tr>
<tr>
<td>$s$: Spreading parameter</td>
<td>NW: Nanowire</td>
</tr>
<tr>
<td>$s$: Moving distance (m)</td>
<td>SEM: Scanning electron microscope</td>
</tr>
<tr>
<td>$T$: Temperature (°C)</td>
<td>PA: Alkylphosphonic acid</td>
</tr>
<tr>
<td>$T_{X \rightarrow Y}$: Transmittance intensity of light at an angle (between a range). (J/m$^2$)</td>
<td>PAA: Poly acrylic acid</td>
</tr>
<tr>
<td>$V$: Velocity (m/s)</td>
<td>PAH: Polyallylamine hydrochloride</td>
</tr>
<tr>
<td>$W$: Work done (J)</td>
<td>PDMS: Polydimethylsiloxane</td>
</tr>
<tr>
<td>$Z$: Acoustic impedances (rayl/m$^2$)</td>
<td>PE: Polyethylene</td>
</tr>
<tr>
<td>$\alpha$: Inclined angle (°)</td>
<td>PET: pentaerythritol tetra (3-mercaptopropionate)</td>
</tr>
<tr>
<td>$\gamma$: Surface energy density (J/m$^2$)</td>
<td>PFDT: Perfluorodecyltrichlorosilane</td>
</tr>
<tr>
<td>$\varepsilon$: Gas compressibility</td>
<td>PFSA: [N-methyl-perfluoro hexane-1-sulfonamide] ethyl acrylate</td>
</tr>
<tr>
<td>$\theta$ (or $\theta_w$): Water contact angle (°)</td>
<td>PFOS: Proper fluoroalkyl silane</td>
</tr>
<tr>
<td>$\lambda$: Wavelength (nm)</td>
<td>PKFE:</td>
</tr>
<tr>
<td>$\mu$: Kinematic viscosity (m$^2$/s)</td>
<td>PMC: Poly (perfluoroalkyl methacrylic) copolymer</td>
</tr>
<tr>
<td>$\rho$: Density (kg/m$^3$)</td>
<td>PMMA: Poly (methyl methacrylate)</td>
</tr>
<tr>
<td>$\delta$: Solid fraction</td>
<td>PP: Polypropylene</td>
</tr>
<tr>
<td>$\phi$: Solid fraction</td>
<td>PS: Polystyrene</td>
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<tr>
<td>Acronym</td>
<td>Description</td>
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<tr>
<td>---------</td>
<td>--------------------------------------------------</td>
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<tr>
<td>PKFE</td>
<td>Polytetrafluoroethylene particle mixed with Kytox oil and Fluoropolymer-grafted epoxy resin</td>
</tr>
<tr>
<td>PTFE</td>
<td>Polytetrafluoroethylene</td>
</tr>
<tr>
<td>PU</td>
<td>Polyurethane</td>
</tr>
<tr>
<td>PVC</td>
<td>Poly (vinyl chloride)</td>
</tr>
<tr>
<td>sa</td>
<td>Solid-air interface</td>
</tr>
<tr>
<td>SPS</td>
<td>Polysodium 4-styrenesulfonate</td>
</tr>
<tr>
<td>St</td>
<td>Stoke number</td>
</tr>
<tr>
<td>RTV</td>
<td>Room temperature vulcanizing</td>
</tr>
<tr>
<td>TEOS</td>
<td>Tetraethylorthosilicate</td>
</tr>
<tr>
<td>TNB</td>
<td>Titanite nanobelt</td>
</tr>
<tr>
<td>UV</td>
<td>Ultraviolet</td>
</tr>
<tr>
<td>WCA</td>
<td>Water contact angle</td>
</tr>
<tr>
<td>We</td>
<td>Weber number</td>
</tr>
<tr>
<td>WH</td>
<td>Water hammer</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray photoelectron spectroscopy</td>
</tr>
</tbody>
</table>
## Figures index

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Figure 1</td>
<td>Schematic illustration of surface tension (energy)</td>
<td>6</td>
</tr>
<tr>
<td>Figure 2</td>
<td>Schematic illustration of wetting and contact angle hysteresis</td>
<td>8</td>
</tr>
<tr>
<td>Figure 3</td>
<td>Johnson and Dettre experiment: relation of surface roughness and contact angle</td>
<td>10</td>
</tr>
<tr>
<td>Figure 4</td>
<td>Wenzel and Cassie-Baxter wetting state modes</td>
<td>13</td>
</tr>
<tr>
<td>Figure 5</td>
<td>Wetting state transition caused by evaporation</td>
<td>15</td>
</tr>
<tr>
<td>Figure 6</td>
<td>Wetting state transition caused by droplet impact</td>
<td>19</td>
</tr>
<tr>
<td>Figure 7</td>
<td>Bottom-up approach: Layer by layer</td>
<td>26</td>
</tr>
<tr>
<td>Figure 8</td>
<td>Bottom-up approach: Chemical Vapor Deposing</td>
<td>30</td>
</tr>
<tr>
<td>Figure 9</td>
<td>Metallic oxide-based nanocomposite coating</td>
<td>37</td>
</tr>
<tr>
<td>Figure 10</td>
<td>Polymers selection for superhydrophobic nanocomposite coating</td>
<td>43</td>
</tr>
<tr>
<td>Figure 11</td>
<td>Mechanical durability tests</td>
<td>49</td>
</tr>
<tr>
<td>Figure 12</td>
<td>Liquid impalement tests</td>
<td>53</td>
</tr>
<tr>
<td>Figure 13</td>
<td>PKFE and oxide/PMC-base nanocomposite coatings fabrication process</td>
<td>70</td>
</tr>
<tr>
<td>Figure 14</td>
<td>Wettability measurement experimental set-up</td>
<td>74-75</td>
</tr>
<tr>
<td>Figure 15</td>
<td>Wettability measurement and SEM image of surface morphology for PKFE and oxide/PMC-base nanocomposite</td>
<td>80</td>
</tr>
<tr>
<td>Figure 16</td>
<td>FTIR measurement shows chemical composition of PKFE and oxide/PMC-base nanocomposite.</td>
<td>85</td>
</tr>
<tr>
<td>Figure 17</td>
<td>Particle concentration and coating thickness affect wettability.</td>
<td>88</td>
</tr>
<tr>
<td>Figure 18</td>
<td>Substrate adhesion (peeling) test results</td>
<td>90</td>
</tr>
<tr>
<td>Figure 19</td>
<td>Abrasion resistance (Taber) test results</td>
<td>93</td>
</tr>
<tr>
<td>Figure 20</td>
<td>Solid impact resistance (sand) test results</td>
<td>96</td>
</tr>
<tr>
<td>Figure 21</td>
<td>Coating lost superhydrophobicity due to damage of surface morphology</td>
<td>98</td>
</tr>
<tr>
<td>Figure 22</td>
<td>Environmental durability (UV-chamber) test results</td>
<td>101</td>
</tr>
<tr>
<td>Figure 23.</td>
<td>Chemical (corrosion) resistance test results</td>
<td>104</td>
</tr>
<tr>
<td>Figure 24.</td>
<td>Photogeneration phenomenon mechanism for oxide-based nanocomposite</td>
<td>106</td>
</tr>
<tr>
<td>Figure 25.</td>
<td>Mechanism of fluorinated amine curing agent synthesis and hardening (PKFE coating)</td>
<td>111</td>
</tr>
<tr>
<td>Figure 26.</td>
<td>Liquid impalement resistance (droplet impact) test results</td>
<td>115</td>
</tr>
<tr>
<td>Figure 27.</td>
<td>Liquid impalement resistance (Jet impact) test results</td>
<td>118-119</td>
</tr>
<tr>
<td>Figure 28.</td>
<td>Liquid impalement resistance (restitution coefficient) test results</td>
<td>123</td>
</tr>
<tr>
<td>Figure 29.</td>
<td>Liquid impalement resistance is affected by coating softness</td>
<td>124</td>
</tr>
<tr>
<td>Figure 30.</td>
<td>The PKFE and oxide based coatings were used to compare with several commercial available sprayable superhydrophobic coatings</td>
<td>126</td>
</tr>
<tr>
<td>Figure 31.</td>
<td>Transparency test results for oxide-based nanocomposites</td>
<td>129</td>
</tr>
<tr>
<td>Figure 32.</td>
<td>Schematic of haze and clarity measurement</td>
<td>131</td>
</tr>
<tr>
<td>Figure 33.</td>
<td>Optical properties measurement for different types (thickness) of oxide-based nanocomposites</td>
<td>133</td>
</tr>
<tr>
<td>Figure 34.</td>
<td>Theoretical analysis for Mie (Rayleigh) scattering</td>
<td>136</td>
</tr>
</tbody>
</table>
Content

Acknowledgement ......................................................................................................................... II
Abstract ........................................................................................................................................... III
Impact Statement ............................................................................................................................ V
Nomenclature ................................................................................................................................. VI
Figures index .................................................................................................................................... VIII

1. Introduction .................................................................................................................................. 1
   1.1. Fundamental Theories ........................................................................................................... 3
       1.1.1. Surface Tension (Energy) and wetting .............................................................................. 4
       1.1.2. Surface roughness (Structure) and wetting ....................................................................... 9

2. Literature Review ......................................................................................................................... 22
   2.1. Fabrication and material selection of artificial superhydrophobic surfaces ......................... 22
       2.1.1. Top-down approaches ........................................................................................................ 23
       2.1.2. Bottom-up approaches ..................................................................................................... 24
       2.1.3. Material selection for superhydrophobic coating ............................................................... 32
   2.2. Durability tests for nanocomposite superhydrophobic coating .............................................. 46
       2.2.1. Mechanical durability test ................................................................................................. 46
       2.2.2. Chemical corrosion durability test .................................................................................... 51
       2.2.3. Liquid impact resistance tests ............................................................................................ 52
       2.2.4. Environmental durability tests ........................................................................................... 54
   2.3. Applications ............................................................................................................................. 61
   2.4. Literature review conclusion .................................................................................................. 63

3. Experiment .................................................................................................................................... 66
   3.1. Material and equipment .......................................................................................................... 66
   3.2. Coating Fabrication ................................................................................................................ 68
       3.2.1. PTFE/Epoxy resin based nanocomposite (PKFE) coating .................................................. 68
       3.2.2. Oxide/PMC-based nanocomposite coating ...................................................................... 71
       3.2.3. Spraying polymer nanocomposite coating ......................................................................... 72
   3.3. Surface characteristics and robustness tests ............................................................................ 72
       3.3.1. Surface characteristics ....................................................................................................... 72
       3.3.2. Wettability test .................................................................................................................. 72
       3.3.3. Mechanical durability tests ............................................................................................... 73
       3.3.4. Chemical corrosion durability tests ................................................................................... 74
       3.3.5. Liquid impalement resistance tests .................................................................................... 75
       3.3.6. Environmental / UV resistance ........................................................................................ 76
3.3.7. Optical characteristics tests: ................................................................. 76

4. Experimental results and discussion ................................................................. 78

4.1. Surface wettability and characteristics ......................................................... 79
   4.1.1. Surface wettability and morphology ....................................................... 79
   4.1.2. Surface chemical composition ................................................................. 82
   4.1.3. Nanoparticle concentration ..................................................................... 86

4.2. Durability test results and discussion ............................................................ 89
   4.2.1. Mechanical durability ............................................................................... 89
   4.2.2. Environmental and Chemical (corrosion) durability ................................. 100
   4.2.3. Liquid impalement resistance ................................................................... 114

4.3. Comparison with commercial sprayable superhydrophobic coating ............... 125

4.4. Optical properties of the oxide nanocomposite coatings ............................... 128

5. Conclusion and future work ............................................................................. 138

6. Bibliography ....................................................................................................... 143

7. Publications and Conferences record ............................................................... 173
1. Introduction

The idea of nanotechnology first came from the famous American physicist Richard Feynman who described a process by which the ability to manipulate individual atoms and molecules might be developed in 1959 [1]. He noted things would behave differently and have unusual physical and chemical characteristics under nanometre scale, due to surface tension and Van der Waals attraction become more significant compare to gravity and also because things are subjected to quantum effects [2].

The term of “Nano-technology was firstly used in a conference by Noiro Taniguchi who was from Tokyo University of Science. In his definition of nanotechnology mainly consists of separation, consolidation and deformation of material by one atom or one molecule [3]. Later on, the definition was renewed by National Nanotechnology Initiative in 2000, defining nanotechnology as the manipulation of a with at least one dimension sized from 1 to 100 nanometres. This new definition reflects the fact that quantum mechanical effects are important at this particular scale, and therefore the definition change from a particular technological goal to a research category including all types of research that investigate the special properties of matter which occur below the size threshold [4]. Since the beginning of the 21st century, nanotechnology has been developing very rapidly in research fields ranging from traditional industry and agriculture to military [5–10].

Meanwhile, the characteristics of bio-inspired superhydrophobic (anti-wetting) surfaces have attracted worldwide attention during the past decade due to their peculiar properties and potential applications [11–13]. It is particularly worth mentioning here that more than 6000 articles related to “superhydrophobic surfaces” have been published and this topic was ranked 7th in the top 20 research fronts in materials science from 2006 to 2010 on the Essential Science Indicators Database [14]. With the rapid development of material science, a series of artificial superhydrophobic surfaces can now be achieved via facile one-step process such as spraying nanocomposite coatings [15–17].

The methods used for achieving superhydrophobic surfaces vary. However, approaches which are using direct surface modification on substrates (also referred to as “Top-down approaches”) such as lithography and etching are substrate dependent and also require expensive equipment. Therefore, coating (also referred to as “Bottom-up approaches”) is considered a better way to change solid surface properties to create superhydrophobic surfaces for large-scale applications.
Different from many “Top-down approaches”, the coating approach is considered as an indirect modification method through chemical or physical processes to fabricate a new layer of substances with protective or/and multifunction properties [12,16,18–20].

Superhydrophobic nanocomposite coatings are coatings that include at least one nanoscaled raw material that plays a crucial role in the coating’s properties. The keys of forming a superhydrophobic surface is not only evolving around nanoscale morphology, but also relates to the low surface energy of the material. Therefore many polymers which have such characteristics were chosen to mix with the nanoscaled material to form superhydrophobic nanocomposites [13,21,22].

The unique way in which a superhydrophobic surface interacts with liquids makes them a promising platform for many applications such as self-cleaning [23,24], drag reduction [25,26], anti-icing [22,27,28], corrosion resistance [21,29,30] and so on [19,20,31]. Since researchers are developing superhydrophobic nanocomposite coatings for practical applications, additional factors, such as the mechanical/chemical durability and environmental stability should be evaluated as well [32–35].

In this thesis, the fundamental/theoretical aspects of the surface wetting property were briefly introduced and explained. It was followed by a literature review that examines recent publications covering the materials, fabrications, durability testing methods and applications of superhydrophobic nanocomposite coatings. In experimental work, the material selection and fabrication process of two types of superhydrophobic nanocomposite coatings: water-based oxide nanocomposite and PKFE nanocomposite (Polytetrafluoroethylene particle mixed with Kytox oil and Fluoropolymer-grafted epoxy resin) were demonstrated, followed by presenting different durability and multifunctional tests that were relevant to superhydrophobic coatings. The test performance of the superhydrophobic nanocomposite coatings were discussed accordingly. Water-based oxide superhydrophobic nanocomposite has an easily accessible material choice and a simple fabrication process, the coating solution is environmental friendly and final coating has reasonable durability, possessing transparent and others unique optical properties. On the other hand, PKFE superhydrophobic nanocomposite coatings were found to demonstrate extreme durability performance at many aspects; particularly it could withstand impact by a water jet travelling at a maximum speed of 35 m/s and without losing its anti-wetting property. The extreme
liquid impalement resistance could be attributed to the flexible nature of the epoxy which was used in the coatings, and it also provided the mechanical/chemical stability.

1.1. Fundamental Theories

Surface wetting behaviour can be divided into 4 different regimes according to the water contact angle (θ, which is the angle often measured through the liquid, where liquid-air interface meets a solid surface). The hydrophilic and hydrophobic regimes are defined as when the θ falls into the range of $10^\circ < \theta < 90^\circ$ and $90^\circ < \theta < 150^\circ$, respectively, are the most typical regimes. Superhydrophilic and superhydrophobic regimes are more appealing for the extremes of surface wetting behaviour with the θ falls into in the range of $0^\circ < \theta < 10^\circ$ and $150^\circ < \theta < 180^\circ$ respectively [36,37]. Superhydrophobicity has described a state of nearly perfect non-wetting therefore a superhydrophobic surfaces should also exhibit extremely low water contact angle hysteresis ($\Delta \theta$) (<10°) that results in the water droplets can easily roll off from the surface [38].

Nature had a large number of biological surfaces that exhibited superhydrophobicity; these included for examples lotus leaves (Nelumbo Nucifera) [39,40], Taro leaf (Colocasia)[41], gecko feet [42] and water strider [19]. The mechanism behind this phenomenon was resolved by the introduction of the scanning electron microscopy (SEM) after a few decades. Lotus leaves were examined under SEM, scientists found that the surfaces of the lotus leaves was consisted with protruding nubs, 20–40 µm apart, and each nub was covered with a smaller scale roughness of epicuticular wax crystalloids. The nanoscale morphology trapped a large fraction of air to form air-cushions that prevent water from the surface which is the first example of nanostructure-based superhydrophobicity [39,40]. In fact, for rough surfaces, seeking to understand the relationship between surface roughness and superhydrophobicity, two wetting models : Wenzel’s and Cassie’s models [43,44] were established and applied a long time ago. These two models describe different wetting states and supply theoretical guidance for researchers. Low surface energy materials which contains such as –CF₃ groups, silyl compounds, or fluorocarbons, are other requirement for preparing superhydrophobic surfaces inspired by the epicuticular wax crystalloids of the lotus leaf [19].
1.1.1. Surface Tension (Energy) and wetting

Surface tension ($\sigma_{la}$) can be defined as the total cohesive forces among molecules at the interfacial boundary [45]. Inside of a phase (gas, solid or liquid), the cohesive forces on a molecule calibrate each other. However, at the interface forces from outside are missing (or significantly weaker), which results in a net force pointing toward of centre (Figure 1a).

In many research, surface tension is also referred as surface energy ($\gamma_{la}$) [46], which is defined as the free interfacial energy at the boundary. The surface energy of the liquid-air interface can be experimentally measured by stretching a liquid membrane. Inside an inverted U-shaped wire frame with a movable hoop at the open end, a thin liquid film is spanned (Figure 1b). The surface force of the film equals the pulling force $F_A$ exerted by the hoop. To displace the hoop by a distance of $\Delta s$, there is a corresponding increase of the surface area by $\Delta A = 2b\Delta s$. The surface energy (tension) is defined as: $\gamma_{la} = \sigma_{la} = \frac{F}{2b}$, with units of N m$^{-1}$. The work done ($W_{int}$) required to increase the surface area is $W_{int} = F_A \cdot \Delta s = \gamma_{la} \cdot \Delta s \cdot 2b$ [45].

The surface energy of the solid-air interface can be experimentally measured by using another method at high temperature. At high temperature, the solid creeps and even though the surface area changes, the volume remains approximately constant. If $\gamma_{sa}$ is the solid/gas interface surface energy for a cylindrical rod of radius $r$ and length $l$ at high temperature under a constant uniaxial tension $P$, and at equilibrium, the variation of the total Helmholtz free energy, $F_{Hel}$, can be neglected [47]. Then

$$\delta F_{Hel} = -P\delta l + \gamma_{sa}\delta A = 0,$$  
and  
$$\gamma_{sa} = P \frac{\delta l}{\delta A}$$

where $A$ is the surface area of the rod.

$$A = 2\pi r^2 + 2\pi rl,$$  
and  
$$\delta A = 4\pi r \delta r + 2\pi rl \delta r + 2\pi r \delta l$$
Since the volume is assumed constant, therefore the variation of the volume is zero.

\[
\text{Volume} = \pi r^2 l = \text{constant}, \quad \text{Change of volume} = 2\pi r l \delta r + \pi r^2 \delta l = 0,
\]

\[
\text{and} \quad \delta r = -\frac{r}{2l} \delta l
\]

The surface energy of a solid-air interface can be written as

\[
\gamma_{sa} = \frac{Pl}{\pi r (l - 2r)}
\]

and \(\gamma_{sa}\) can be obtained by measuring \(P, r \text{ and } l\) at equilibrium.

This method is valid under the assumption that the solid is isotropic, meaning the surface energy is the same for all crystallographic orientations. Glass as an amorphous solid is a good example of an isotropic solid. For those polygranular solid (most metal) or solid made by powder sintering, this method can only get a good approximation of \(\gamma_{sa}\) [48]. Adamson and Gast (1997) [49] described some others techniques for measuring surface energy of solid-liquid interface such as Wilhelmy’s method, in which one dips a thin solid plate on a selected liquid and measures the capillary force acting on the plate.
Figure 1. Schematic illustration of surface tension (energy) (a) Inside of a phase (gas, solid or liquid), the cohesive forces on a molecule calibrate each other. However, at the interface forces from outside are missing. (b) Schematic illustration of measuring liquid/air surface tension. (c) and (d) tension forces for the liquid-air interface \( F_{la} \), the liquid-solid interface \( F_{ls} \), the solid–air interface \( F_{sa} \) and adhesive force \( F_a \) at a situation when a selected liquid is in a glass tube.

Let’s look at a situation when a selected liquid is in a glass tube (Figures 1c and d). Besides the liquid/air interface and solid/air interface at the top surface, there is also an interface between the liquid and the glass wall. The surface tension between the liquid and air is usually different (greater than) to the surface tension between the liquid and the glass wall. When two surfaces meet, the intersection angle (commonly known as the Contact Angle, \( \theta \)) between the liquid-solid interface and the liquid-vapour interface must form in a way to keep all tension forces balanced.

Figures 1c and d show various tension forces for the liquid-air interface \( F_{la} \), the liquid-solid interface \( F_{ls} \), the solid–air interface \( F_{sa} \) and adhesive force \( F_a \). At equilibrium state, both the
vertical and horizontal forces must be cancelling out at individual contact points. The horizontal component of $F_{ta}$ is cancelled by the adhesive force, $F_A = F_{ta} \sin \theta$. The vertical component of $F_{ta}$ plus $F_{sa}$ must exactly cancel out the force, $F_{ts}$, i.e. $F_{ts} - F_{sa} = F_{ta} \cos \theta$, and accordingly:

$$\gamma_{ts} - \gamma_{sa} = -\gamma_{ta} \cos \theta.$$ 

The contact angle can be expressed as, $\theta = \arccos \frac{\gamma_{sa} - \gamma_{st}}{\gamma_{ta}}$. A concave meniscus has a contact angle less than 90° (Figure 1c) and a convex meniscus has a contact angle greater than 90° (Figure 1d). The equation is named the Static/Young contact angle equation, (Law of Young-Dupre), first published by in 1805 [50].

Static/Young contact angle equation is closely linked to a parameter that describes the wetting of a solid surface, and this parameter is called spreading parameter, $S$ [45]. This parameter measures the difference between the surface energy of the solid when dry and wet:

$$S = [E_{substrate}]_{dry} - [E_{substrate}]_{wet} = \gamma_{sa} - (\gamma_{ts} + \gamma_{ta})$$

and

$$S = \gamma_{ta} (\cos \theta - 1)$$

If the parameter $S$ is zero ($\theta = 0$) the liquid spreads completely on the the solid surface forming a thin film (Total Wetting, Figure 2a). Under the condition when $S$ is negative ($S < 0$) the liquid droplet forms a spherical cap at equilibrium and rest on the solid surface with the static/Young contact angle, $\theta$. (Partial Wetting, Figure 2b) [45].

However, when a droplet is under metastable state [51] or moving on a solid surface, the measurement of the Young static contact angle is no longer sufficient to characterize the wetting behaviour fully. A “dynamic” contact angle measurement is needed and accordingly a concept of “Contact Angle Hysteresis” ($\Delta \theta$) is introduced [52].

Imagine when a small enough amount of liquid is added to a droplet, the droplet volume will increase. The liquid/solid interface contact line is initially pinned and the contact angle will increase. This increased contact angle is referred to as advancing contact angle ($\theta_A$). On the other hand, a receding contact angle ($\theta_R$) is measured while the droplet volume is reducing due to the withdrawal
of a small enough quantity of liquid from the droplet, as illustrated in (Figure 2c). Both of these angles have a range, and the static contact angle is somewhere between the minimum $\theta_A$ and the maximum $\theta_R$, and the difference between maximum $\theta_A$ and minimum $\theta_R$ is the $\Delta\theta$ of the surface.

![Figure 2. Schematic illustration of wetting and contact angle hysteresis (a) and (b) Schematic illustration of a solid surface is totally or partially wetted by a liquid. (c) Contact angle hysteresis ($\Delta\theta$) is obtained by calculating the difference between the advancing angle($\theta_A$) and receding angle($\theta_R$). (d) Measuring the sliding angle.](image)

An alternative way to measure the $\Delta\theta$ is shown in Figure 2d; the droplet will slide down when the substrate is tilted to a certain angle. In this case, the substrate is wetted by the advancing liquid front and de-wetted at the receding back, with the corresponding $\theta_A$ and $\theta_R$; the difference between them is termed the sliding angle and it theoretically will be the same as $\Delta\theta$ in Figure 2c [53]. Superhydrophobic surface should have a water $\Delta\theta$ smaller than 10° and a static contact angle of more than 150° ensuring water-solid contact area is minimum and water droplet is not sticking onto the surface [37].

Static/Young contact angle equation assumes liquid and solid suace are under stable conditions (constant temperature, pressure and no chemical reaction at the interfaces), and also the solid surface is smooth and chemically homogeneous. Under these conditions, a liquid which has a low
surface energy ($\gamma_{ta}$) such as Isopropanol and silicon oil (Table 1) can wet most solid surfaces. However, this study is only focusing on surfaces interacting with water; therefore to maximize the surface hydrophobicity the surface energy ($\gamma_{sa}$) should be as low as possible.

<table>
<thead>
<tr>
<th>Material</th>
<th>Surface energy (mJ/m$^2$)</th>
<th>Material</th>
<th>Surface energy (mJ/m$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copper</td>
<td>~1650</td>
<td>Acetone</td>
<td>~25</td>
</tr>
<tr>
<td>Steel</td>
<td>~1000</td>
<td>Epoxy</td>
<td>~23</td>
</tr>
<tr>
<td>Aluminium</td>
<td>~840</td>
<td>Paraffin Wax</td>
<td>~26</td>
</tr>
<tr>
<td>Zinc</td>
<td>~750</td>
<td>Polystyrene</td>
<td>~36</td>
</tr>
<tr>
<td>Glass</td>
<td>~310</td>
<td>Polyethylene</td>
<td>~31</td>
</tr>
<tr>
<td>Water</td>
<td>~75</td>
<td>Polypropylene</td>
<td>~29</td>
</tr>
<tr>
<td>Isopropanol</td>
<td>~23</td>
<td>PTFE</td>
<td>~19</td>
</tr>
</tbody>
</table>

Table 1: A list surface energy for some common material [54][55].

Of the lowest surface energy solids, such as waxes, PTFE and fluorinated material, static contact angles in the order of 120° with water are reported [56], Table 1; they are still quite far from being described as superhydrophobic ($\theta > 150^\circ$). In order to increase the non-wetting limit, an appropriate surface structure is essential. In the next session, how roughness plays an important role in wettability will be addressed.

### 1.1.2. Surface roughness (Structure) and wetting

The Young relation is developed based on a perfectly smooth, rigid and homogeneous solid surface. In practice, solids are typically both rough and heterogeneous. In 1964, Johnson and Dettre ran a set of experiments to show how the wetting properties of a substrate changed by altering its surface roughness. A thin layer of wax was sprayed on a flat glass slide and the roughness of the slide was varied by heat treatment; that is the surface became smoother after each bake. The roughness scale was only qualitative, but microphotographs of the sample surfaces showed more and more diluted clusters of sizes between 10 and 100 $\mu$m as the samples were gradually heat treated. Water drops were deposited on the samples, and both the advancing and
receding angles, $\theta_A$ and $\theta_R$, were measured as a function of the roughness, as shown in Figure 3 [57].

**Figure 3.** Johnson and Dettre experiment: relation of surface roughness and contact angle. Experiment results [57] demonstrated contact angle vary with the surface roughness level. (Left-hand side graph is reprinted from [58]).

The smoothest surface is the ideal condition in which the Young relation can be applied, and the static contact angle on this surface was found to be around 105° (i.e. between $\theta_A$ and $\theta_R$), and the contact angle hysteresis was around 15°.

The surface roughness was observed to have a considerable influence on both the contact angles and the hysteresis. At a low roughness, the advancing angle increased with roughness, whereas the receding angle decreased, resulting in an increase in the hysteresis. Beyond a specific value of roughness, both angles increased rather sharply, and at the same time, the hysteresis dropped to a very small value. At a higher roughness, the angles appeared to be rather insensitive to the increase of roughness. These behaviours could be explained by two standard wetting models: Wenzel model and Cassie-Baxter model. Wax being a low surface energy material, superhydrophobicity can only be achieved if it has the right roughness.
**Wenzel Model:**

Wenzel (1936) [43] tried to determine the water contact angle $\theta^*_wz$ on a rough but chemically homogenous surface, assuming the roughness scale to be very much smaller than the size of the water drop. The key parameter is the roughness factor ($r$), defined by Wenzel as the ratio of the actual contact surface area over its apparent one between the water and solid surfaces.

Figure 4a shows water droplet penetrates into the roughness texture, therefore making the actual contact surface area larger than the apparent one. Imagine the edge of the droplet moves across a rough surface by a small displacement $x$. Considering a small movement $dx$ of the line of contact in a direction parallel to the solid surface, the change of energy $dE$ can be expressed as the following equation, including the contact angle $\theta^*_wz$:

$$dE = r(\gamma_{ls} - \gamma_{sa})dx + \gamma_{la}\cos \theta^*_wz dx$$

For a smooth surface, $r = 1$, Young’s relation is recovered and $\theta^*_wz = \theta$, work done by moving the line of contact by a distance $dx$ become:

$$\delta W = (\gamma_{sa} - \gamma_{ls})dx - \gamma_{la}\cos \theta dx$$

Then when $r > 1$, the equilibrium condition leads to Wenzel’s relation:

$$\cos \theta^*_wz = r\cos \theta \ (\text{when } dE = \delta W)$$

For a given $\cos \theta$, there is a value of $r$ exceeding which the surface becomes superhydrophic, with an associated main assumption that the water follows the roughness contours of the solid surface.

**The Cassie-Baxter Model:**

The Wenzel regime is usually recognised as homogeneous wetting, since the liquid completely penetrates into the roughness texture. While certain circumstances, especially for very rough surfaces, air pockets may be trapped underneath the liquid resulting in a composite interface (Figure 4b). This heterogeneous wetting is often described by the Cassie-Baxter model, which assumed the surface is made of air and solid, each
characterized by its own contact angle $\theta_a$ and $\theta_s$. The Cassie-Baxter contact angle can be given by equation:

$$\cos \theta_{CB} = f_a \cos \theta_a + f_s \cos \theta_s$$

where $f_a$ and $f_s$ are respectively representing the area fractions of the air and solid on the surface [44].

Since $\theta_a = 180^\circ$, which implying that a suspended liquid droplet in the air is a perfect sphere, Cassie-Baxter relation can then be expressed as:

$$\cos \theta_{CB}^* = f_s (\cos \theta_s + 1) - 1$$

From Cassie-Baxter relation, it can be found that droplets will have a higher contact angle if less area is in contact with the solid substrate. It also indicates the contact angle can be increased even when the intrinsic contact angle of a liquid on the originally smooth surface is less than $90^\circ$. However, as in the case of Wenzel, when $\theta$ is less than $90^\circ$, it is practically impossible to become hydrophobic. Moreover, the two states differ in contact angle hysteresis, which is much lower at Cassie state, due to at Cassie-Baxter has significantly less liquid-solid contact area. Therefore, it is desirable to achieve the Cassie-Baxter condition.

**Transition between two wetting states:**

The experimental results of Johnson and Dettre (Figure 3b) indicated the transition from Wenzel state to Cassie-Baxter happens during increasing surface roughness, which directly affects surface wetting properties. At a certain threshold roughness, both $\theta_A$ and $\theta_R$ suddenly increase to a very high value. This transition could be explained by the sudden formation of air pockets at that particular roughness. The contact angle hysteresis, which reflects the degree of heterogeneity of the solid surface, then decreases significantly even though the roughness increases. This observation is understood if one considers that the substrate actually becomes homogenized air pockets (Cassie-Baxter state).

In general, the Cassie-Baxter model is more likely to be followed by very rough surfaces, while less rough surface will continue to obey Wenzel’s model. Essentially, which state will dominate is
determined by the formation of air pockets. Gennes et al. (2004) [45] used droplets’ interaction with different sinusoidal surfaces (Figure 4c) to demonstrate the formation of air pockets is only possible with the rougher surface.

Figure 4. Wenzel and Cassie-Baxter wetting state modes (a) A low amplitude sinusoidal surface on which the liquid is able to follow the surface profile. (b) Beyond a certain amplitude threshold, air pockets can form underneath the liquid. (c) and (d) Apparent contact angle vs surface roughness. There is a discontinuity of the contact angle at the threshold when air begins to get trapped (the graph is reprinted from [45]).

In Figure 4c, each of two sinusoidal surfaces has the same wavelength but different amplitudes, assuming their Young’s angle (θ) is already larger than 90° suggesting that they can be considered as hydrophobic [57]. A critical roughness (r*) for initiating air trapping can be expressed in terms of θ. Taking \( y = a \cos(kx) \) to represent the profile of the solid surface, then the slope at any point can be written as \( \frac{dy}{dx} = \tan(\theta) = -ak \sin(kx) \), and the max slope (ak, absolute) occurs at
\[ x = \lambda/4, 3\lambda/4, \ldots \] The condition for the beginning of air trapping (the establishment of a horizontal liquid/vapor line of contact) when \( \theta \) satisfies the following:

\[ a > \frac{\lambda \tan(\theta)}{2\pi} \]

where the wavelength \( \lambda \) of the surface is equal to \( 2\pi/k \) and \( a \) is the amplitude. For an \( \theta \), at say, 120° and \( \lambda = 2 \, \mu m \), air trapping will be possible once the amplitude is in the order of around half a micron. Furthermore, in the limit of \( |ka| \ll 1 \), the roughness can be given by,

\[ r = 1 + \frac{(ka)^2}{4} \]

Combining two equations above, yields a threshold roughness \( r^* \) for air trapping:

\[ r^* = 1 + \frac{\tan^2 \theta}{4} \]

For \( \theta = 150^\circ \), the formation of air pockets will occur for \( r > r^* = 1.75 \). For a roughness smaller than \( r^* \), the solid/liquid interface conforms to the profile of the solid surface, and the contact angle is given by Wenzel's model. Above the threshold \( r^* \), air pockets are trapped and Cassie-Baxter model must be used to determine \( \theta^* \).

Figure 4d shows the calculated results of solid/liquid contact angle at different \( r \) values. The shape of the curve \( \theta^*(r) \) is qualitatively similar to the data of Johnson and Dettre [57] for the advancing angle (Figure 3). At the beginning, the advancing angle increased monotonically with roughness. It then suddenly jumped at the trapping threshold. Beyond that point, the contact angle continued to increase with roughness, although much more slowly. This observation was giving out a clear message that, air trapping can be predicted by critical roughness estimation.

It is clear from above that how one can achieve certain roughness to change the wetting state of a surface from Wenzel state to Cassie-Baxter state. Once a Cassie-Baxter state surface is acquired, it would be interesting to see how it might switch to Wenzel or knowing how the switch could be prevented, considering that Cassie-Baxter state surface is often metastable. If a water drop impales onto the surface, Cassie-Baxter state could potentially switches back to Wenzel state. The wetting
states transition (Wenzel to Cassie-Baxter wetting state or Cassie-Baxter to Wenzel wetting state) has been studied theoretically and experimentally in recent years [59].

Cassie-Baxter to Wenzel transition can be triggered by vibrations [60], squeezing [61], impact [62,63], application of an electric field [64], or evaporation [62,65–68]. “Water drop evaporation on hydrophobic micropillars” (Figure 5a) is a widely used example for studying how various factors such as surface texture morphology, roughness ratio or size of droplet affect the Cassie-Baxter to Wenzel transition.

**Figure 5.** Wetting state transition caused by evaporation. (a) Lithographic printed hydrophobic micropillars structure (pillar diameter d = 3 µm, height h = 4.8 µm and distance l = 17 µm). (b) Evaporation of a water drop sitting on the hydrophobic surface. The initial radius is 120 µm, and the time interval between two successive photos is 5 s. As the drop radius decreases to 75 µm (fifth snapshot), the state of the drop abruptly changes. (c) Sketch of the liquid/vapour interface below a drop under Cassie-Baxter state. “d” is cylindrical micropillars diameter, “h” is micropillars height and “l” is the mutual distance, and α as the angle between the vertical and the tangent to the interface at the post edge. Images in (a) and (b) are modified and reprinted from Reyssat et al. (2008) work [65].

Reyssat et al. (2008)[65] experimentally showed a droplet is evaporating on hydrophobic micropillars structure, and the Cassie-Baxter to Wenzel transition will happen once the droplet radius is reduced to a critical value. The first 5 snapshots in Figure 5b show a droplet is deposited on hydrophobic micropillars, with a measured value of $\theta_\lambda = 180^\circ$ and $\theta_k = 140^\circ$, indicating that the interaction is Cassie-Baxter state. However, this condition changes when the droplet reduces to a critical radius of $R^* = 75 \mu m$, and the transition, as captured by a high-speed camera, happens
within 1 ms. The $\theta_A$ suddenly gets much smaller by about 80° and keeps on decreasing, which implies a sharp increase in the solid/liquid contact area. Since the droplet is pinned, the $\theta_R$ gradually reduces to zero. This phenomenon could be interpreted as resulting from the impalement of the droplet into the texture, and they also defined that wetting is completed when the liquid touches the bottom of the texture. The critical radius ($R^*$) can be related to two geometric parameters:

$$R^* \approx \frac{t^2}{h} \quad (\text{when } d < l \text{ and } d < h) \quad [65]$$

This relation indicated the ways to achieve an ever-lasting superhydrophobic surface which is able to resist the Cassie-Baxter to Wenzel transition under evaporation, i.e. equivalent to saying a small $R^*$ is needed; this can be done by having a small $l$. There are existence in nature of sub-structures at the nanoscale (hierarchical structure), e.g. the surface of some mosquitos eyes, which seems to remain dry even if exposed to fogs or sprays. Since these surfaces had roughness ($d$ and $l$) less than 100 nm [65]. Alternatively, wetting state transition can be prevented by making the pillar structure taller. Experimental results confirmed that by increasing the height of the pillars, $h$, by a factor of 8 ($d$ and $l$, unchanged), the $R^*$ reduces significantly.

Up to now, it is assumed that the liquid-air interface at the bottom of the droplet remains pinned at the edge of the pillars until the interface reaches the bottom of the substrate. This phenomenon is referred as “sagging mechanism” [37,64,69], and it occurs when the angle $\alpha$ (Figure 5c) is between $\theta$ and $\pi - \theta$. (For a hydrophobic surface, $\theta$ is typically between 100° and 120°) If $\alpha$ is larger than this range, the three-phase contact line will most likely unpin from the pillar edge [67,70], which then slide down along the pillar wall, beginning the transition to fully wetting the substrate. This phenomena is referred as “depinning mechanism”. Depinning happens when the droplet is too small, with a droplet radius less than $\frac{t}{2|\cos\theta|}$ [71]. More details of these mechanisms can be found in previous studies, using dynamic models to analyse the interaction between liquid droplets and solid surface [52,72–74].

Wetting state transition due to droplets impacting the surface have also been extensively studied which also included the influence of surface, droplet or/and surrounding temperature [75,76]. Three main factors have been mostly examined: surface morphology, droplet impact parameters and environmental conditions. Maitra et al. (2013)[75] presented that hierarchical morphology (Microstructure + Nanostructure) not only could create superhydrophobic surfaces but also to
reduce the possibility of transiting from Cassie-Baxter state to Wenzel state caused by impact. A pressure balance analysis can be used to explain the wetting states transition under the dynamic impact. The liquid penetration resistance of a hydrophobic surface can be quantified through its capillary pressure:

\[ P_c = \left( -\frac{4\phi}{d(1-\varphi)} \right) \gamma \cos \theta \]

where "d" is the pillar diameter, "\gamma" is the solid surface tension and "\varphi" is the solid fraction; for a square micro-pillar array, "\varphi" can be expressed as \( \pi d^2 / 4(l + d)^2 \). This resistive capillary pressure must overcome the impact pressure that prevents the surface from meniscus penetration [62].

Impact pressure mainly consists of two parts: the dynamic pressure and water hammer pressure. Dynamic pressure can be simply expressed as:

\[ P_D = 0.5 \rho V^2 \]

where "\rho" is the droplet density and "V" is the impact speed. The water hammer pressure comes from sudden deceleration of the liquid upon encountering solid substrate. It is a manifestation of the liquid compressibility and can be written as:

\[ P_{WH} = k_{WH} \rho C V \]

where "\( k_{WH} \)" is the water hammer pressure coefficient, "C" is the speed of sound in water. If \( P_c \) is smaller than the combined pressures of \( P_D \) and \( P_{WH} \), there will be liquid penetration into the texture [70,77,78].

Recent work [79–81] indicated that on textured hydrophobic surfaces, the water hammer pressure coefficient \( k_{WH} \) should be lower than that on smooth surfaces, and it can be calculated through the balance of capillary pressure \( P_c \) with the sum of dynamic pressure \( P_D \) and water hammer pressure \( P_{WH} \) as:
where “$V_{cr}$” is the critical droplet velocity for transition. Dash et al’s (2012) [79] work concluded a two order of magnitude lower $k_{WH}$ appears on microtextured surface when compared to a flat surface. However, the application of the water hammer pressure concept was questioned in some literatures under the conditions that a droplet has a low “Weber number”, $We$ (less than $\sim10^3$).

Weber number ($We$) is a dimensionless parameter, often used to characterize impacting droplets [82]. It is defined as $\frac{\rho V^2 D_0}{\gamma}$, where the $\rho$ denotes the density of the liquid, $\gamma$ is the liquid surface tension, and the $V$ and $D_0$, respectively, are the impact droplet velocity and diameter. For the impact velocity in range of 1 to 10 m/s, which corresponds to a $We$ number in the range of $\sim10^2 - 10^3$. The compressibility of the air layer between approaching droplet and the substrate should play a more dominant role than the compressibility of liquid which begins to dominate at relatively higher $We$ numbers. The air layer must be exhausted from underneath the droplet in order for the droplet to reach the substrate [83]. During the the compressed air getting drained, the droplet would be slowed down the and defroed, generating a dimple (Figure 6a). The formaion of the dimple generates a maximum pressure rise in a ringlike region near the impact point [75,76].
Figure 6. Wetting state transition caused by droplet impact (a) Mechanism of dimple formation and droplet deformation by draining air. The dimple formation and associated rise in pressure near the impact point explain the meniscus penetration. (b) The corresponding We of transition on different micro-structured and hierarchical substrates as reported in Maitra et al. (2013). “μ_{a0}”, where a_{0} denotes the diameter of the micro-pillar and p is the pitch of the square array, both expressed in micrometers and the nanostructures are designated as N_{x,y}, where x can be s (sparse) or d (dense) and y can be s (short) or t (tall). This graph is reprinted from Maitra et al. (2013) work [76].

Maitra et al. (2013) [75,76] demonstrated the pressure peak during the dimple formation of a droplet on a textured surface, based on the asymptotic self-similar solution for a flat surface can be expressed as,

\[ P_{\text{max}} = \frac{1.4}{\varepsilon h_{\text{min}}^{0.5}} \]

where \( h_{\text{min}} \) is the minimum air film thickness before the surface tension force suppresses any further sharpening of the dimple edge for the flat surface, or the minimum distance between the meniscus and the bottom of the texture groove.
\[ h_{\text{min}} = \frac{2.54 \cdot R \cdot St^{8/9}}{\mu_a^{2/3}} \]

where "\( R \)" is the droplet radius and the "\( St = \mu_g / \rho V R \)" is the Stokes number with "\( \mu_g \)" denoting the air viscosity. "\( Ca = \mu_g V / \gamma \)" is the capillary number with \( \gamma \) represents the liquid surface tension. "\( \varepsilon \)" is a parameter that qualifies whether the gas can be considered compressible or incompressible.

\[ \varepsilon = \frac{P_0}{(R \mu_g^{-1} V^{7/3} \rho^{4/3})^{1/3}} \]

"\( P_0 \)" is the ambient pressure. Combining the three equations above gives:

\[ P_{\text{max}} = 0.88 \left( \frac{R \mu_g^{-1} V^{7/3} \rho^{4/3} \gamma}{P_0 R^{3/2} St^{7/2}} \right) \]

\( P_{\text{max}} \) indeed should be considered as the impalement pressure that causes a local transition from Cassie-Baxter to Wenzel. In order to overcome the \( P_{\text{max}} \), a higher capillary pressure \( P_c \) is needed, by using hierarchical morphology. For such structure, solid fraction \( \phi \) is the product of its values for the micro and nanostructure, that is \( \phi = \phi_\mu \cdot \phi_N \). Combining a micro with a nano structure would lead to a lower hysteresis, \( \Delta \theta \). Capillary pressure \( (P_c) \) for hierarchical morphology would be increased by combining micro capillary pressure and nano capillary pressure. Maitra et al. (2013) demonstrated a set of experimental results, Figure 6b, showed that a surface with hierarchical structure could rebound droplet with higher impact speed (Weber number).

Some other factors such as droplet and substrate temperatures could change significantly the dynamic behaviour of the droplet and the impalement results [84]. In addition to static evaporation and direct droplet impact, wetting state transition could be caused by many other factors. Many models have been developed and experiments performed to study the transition [85–87]. For anti-wetting purpose, Cassie-Baxter state to Wenzel state should be carefully avoided [75,76].

In this study, the focus is on the developing durable multi-functional superhydrophobic coatings, therefore understanding the two elements of superhydrophobic surface: low surface energy and
roughness, as well as having the knowledge of the two different wetting state and the state transition are essential. Theoretically speaking, a rough surface which has hierarchical structure combined with a low surface energy material can create a superhydrophobic surface with good impalement resistance. In the next chapter, I am going to review some literature which are related to the experimental development of superhydrophobic surface in the past decade, followed by looking at the stability (durability) of these surfaces in different aspects.
2. Literature Review

The literature review consists of three major sections: (1) fabrication and material selection of artificial superhydrophobic surfaces; (2) testing methods, and durability and wear resistance of superhydrophobic surfaces and (3) multifunctional superhydrophobic surfaces and their potential applications.

Starting with how previous researchers were inspired by nature, both theoretical studies and experimental approaches have been used to develop artificial superhydrophobic surfaces. The limitations of these surfaces were examined together with different types of tests that are used to evaluate their durability. Additional functionalities, such as transparency or conductivity, were incorporated into superhydrophobic surfaces, thus leading such coatings having many potential applications.

2.1. Fabrication and material selection of artificial superhydrophobic surfaces

In this section, common superhydrophobic surface fabrication approaches are divided into two categories: top-down and bottom-up approaches. A general description was given for each of them, followed by their limitations. This literature review focus on the bottom-up approaches which mostly involve applying an (or a number of) extra layer(s) on top the substrate, therefore they are often referred as “coating”.

Most of the bottom-up approaches (coating) have advantages such as without making permanent damage or changing to the substrate. Also the cost of bottom-up approaches (coating) is relatively lower, the fabrication process is relatively more straightforward compared to the top-down approaches [12,15,20]. For example, the micro/nano particle-copolymer composite coatings are the promising material matrix, as the control of roughness and surface could be relatively easy to achieve. A comprehensive literature review of the recent development in the fabrication of nano/micro-copolymer composite coatings and the associated selection of material will be presented here.
Jeevahan et al. (2018) [12], Celia et al. (2013) [19] and Yan et al. (2011) [20] reviewed recently development of artificial superhydrophobic surfaces produced by different approaches, such as lithography, templating, etching, chemical vapor deposition, electrochemical deposition, electrospinning, layer by layer, wet chemical reaction, and so on. These common artificial superhydrophobic surface fabrication approaches could be divided into three categories: top-down, bottom-up and a combination of both.

Assuming the substrate was regarded as the bottom (down), top-down methods were lithography, templating and etching, and bottom-up methods included chemical vapour composition (CVD), wet chemical reaction, layer-by-layer deposition, sol-gel processing and colloidal assembling. Some fabrication processes such as phase separation and electrospinning used a combination of top-down and bottom-up methods [12,19,20,35].

### 2.1.1. Top-down approaches

Lithography [88–96] is a common technique which is used for producing a superhydrophobic surface with micro- and nano-patterns. This technique has very control upon the surface morphology and structure. It allows for the fabrication of different structures like circular and square pillars, with different diameters, height, and spacing. It produces the superhydrophobic surface by duplicating and transferring the pattern of a master template onto a substrate surface allowing a replica in an opposite figure to be formed. Lithography process is usually referred to photolithography in micro/nanotexture fabrication [93], in which a photoactive polymer is irradiated by light, usually ultraviolet rays, through a patterned mask (master template). Either exposed or unexposed polymer is disintegrated upon irradiation, and a positive or negative image is thus formed. X-rays, electron beams, laser beams, etc. can also be used in place of ultraviolet rays. Lithography is considered as a very useful technique for fabricating well-defined morphology and was often used to study interaction phenomenon between solid and liquid [88–90].

Another top-down approach “templating” [97–99] starts with preparing a master template (surface consisting of voids of a particular shape or pattern). Coating material were then used to fill (moulding) the voids so that the following pressing will produce an inverse of the pattern. Subsequent lifting off of the template produced the required rough surface. In general, templating
would create a less precise pattern compared to lithography, but it has advantages of quick fabrication and cost-efficient.

Plasma [100–104] and chemical etchings [105–108] are also considered as cost-effective and accessible top-down approaches. A selected polymer is applied to a surface, followed by plasma, laser or chemical treatment; the polymer then either shrinks randomly or gets selectively removed to produce a rough surface. Etchings are substrate dependent and usually a post-treatment is required [19,20].

Lithography and templating have the advantage of controlling surface morphology and structure, suitable for laboratory application such as fabrication of microfluidic channels with the control of wettability. However, these approaches suffered from scaling limitation; some templates may not be reused due to contamination and often expensive experimental set-up are involved. Therefore, coating can be considered as a better option for changing solid surface properties, since unlike lithography and etching which required “direct surface modification”. Coating is regarded as an indirect modification method through chemical or physical processes to fabricate a layer of new substances with totally different properties on the substrate as a protective or multifunctional layer. Superhydrophobic coatings are mostly applied by those bottom-up approaches.

### 2.1.2. Bottom-up approaches

Chemical vapour composition (CVD), wet chemical reaction, layer-by-layer (LbL) deposition, sol-gel processing and colloidal assembling were all considered as “bottom-top methods” in Celia et al. ’s (2013) [19] review. These methods were also listed under “chemical deposition based surface treatment” category in Yan et al. (2011) ’s [20] review, all sharing some important common features. Most of them involve exposing a selected substrate to a chemical which could deposit on the substrate and form a film or powder layer. One of the essential differences among these methods is how the chemical get applied to the substrate.

LbL deposition [109–118] involved creating a thin multilayer film on the substrate by alternately dipping the substrate into different chemical solutions. The essential principle of the LbL is that the electrical charge of the previous layer would be changed after dipping into a prepared solution, and the new layer will have opposite charges to the next dipping solution. In Cohen and Rubber’s works[111], Polyallylamine hydrochloride (PAH) was used to provide the negative charge and polysodium 4-styrenesulfonate (SPS) was used to provide the positive charge. A glass substrate
was firstly dipped into the PAH solution and the solution would be attached to the substrate and formed a thin negative charged film. The substrate is then dipped into the SPS solution to turn the surface to positively charged creating an adhesion layer, leading to enhanced bonding between polymer and nanoparticle. The body layer consisted of a PAH with a negative charge connected to the adhesion layer and two different sizes of silicon nanoparticles (50 and 20 nm) with positive charge. On the top layer, PAH with negative charge was connected to the positive charge body layer silicon nanoparticle and with additional 20 nm silicon with positive charge bonding with the PAH.

Due to the fact, PAH was a low surface energy material and two different sizes of particles provided the roughness, a superhydrophobic with a water contact angle ($\theta_w$) of 160° and a $\Delta\theta$ of 10° were created. Moreover, due to the fact the oppositely charged bonding is relatively strong, the bonding between each layer is strong (Figure 7a).

In some publications [110,115], superhydrophobic surfaces was fabricated using the similar material PAH and silica particles, but instead of using charged attraction, acid treatment was used to create micro-sized honeycomb structure on the PAH/Polyacrylic acid (PAA) multilayer films. Silica nanoparticles were deposited on top of the honeycomb-like polyelectrolyte multilayer surface to increase the roughness of the structure. At the end, semi-fluorinated silane was coated on the top and a superhydrophobic surface was formed.
Figure 7. Bottom-up approach: Layer by layer (a) LbL approach using PAH, SPS and different size of silicon particle. (b) Schematic illustration of the procedure to prepare rough surfaces (silica) in Cohen and Rubber’s works and optical demonstration of a transparent superhydrophobic silica film with dilution ratio of ethanol: sol of 5:1 spin-cast at 3000 rpm [110,111,115] (photo image is reprinted from [111]).

Sol-gel approach is another commonly used chemical deposition method for creating superhydrophobic surface [119–127]. Sol-gel process is separated into two parts, sol was the chemical deposition acting as a precursor adhered to the substrate and formed a gel-like network, then a material with low surface energy and micro-nano particle filler is added to the network to form superhydrophobicity.

The sol-gel system had good compatibility with glass, due to sol often has self-assemble nature and can be easily adhesive to glass, therefore in many previous publications this approach was used to create superhydrophobic transparent surfaces. Shang et al. (2005) [121] introduced sol-gels
on to glass substrate and carefully tuning the microstructure through controlling hydrolysis and condensation reaction of silica precursors. On the other hand, surface energy is reduced by adding a monolayer through the surface condensation reaction. Despite the fact the coated sample has a $\theta_A$ of 165° and 90% optical transmission, it also has a high $\Delta \theta$ above 50°. Unfortunately, no solution is given to improve this situation in that paper.

Xiu et al. (2009) [127] created a eutectic liquid by combining urea and choline chloride which has very low vapour pressure compared to common sol-gel solvent. Therefore, the eutectic liquid remained in the film under ambient condition which contributed to the control over film thickness and roughness. Porous silica thin films with uneven texture were formed after gelation in the presence of a base catalyst, which was composed of tetraethoxysilane (TEOS), ethanol, HCl and H$_2$O, and subsequent extraction of the eutectic liquid. Proper fluoroalkyl silane (PFOS) treatment imparted the superhydrophobicity with a $\theta_w$ of 170° and a $\Delta \theta$ of 2–3°. They also investigated the trade-off between the transparency and surface thickness (roughness) by diluting the sol with ethanol. By diluting the sol 7 times, optical transmission improves from ~83% to 90% , maintaining a $\theta_w$ of 165° and a $\Delta \theta$ of ~10° (Figure 7b).

Moreover, SHS sol-gel coatings usually have excellent resistance to high temperatures. Ma et al (2012) [119] used an alumina sol which was based on tri-sec-butoxide (Al(O-sec-Bu)$_3$) as raw material. Aluminium particles of ~80 nm were doped into the sol and then spin coated onto a glass substrate, and it was heated up to 400 °C. The alumina nanoparticles form a microstructure on the surface and nanostructure was then introduced by putting the sample into boiling water for 5 mins. The surface showed a $\theta_w$ of ~170 °, and remained hydrophobic stability up to 550 °C.

Electrochemical processes can control both the surface roughness and the surface morphology on small or large substrate. These processes are considerably fast, reproducible and are able to crate many different surface morphologies such as rods, sheets, fibres, ribbons, cones or flower-like structures.[128]. There were four electrochemical processes which were commonly used in the formation of superhydrophobic surfaces, namely, anodization [128–137], electrodeposition of conducting polymers [138–141], electrodeposition of metals and metal oxides [142–146], and electroless galvanic deposition [147–150].

For example, an oxide layer (porous nanostructures) can be created by anodization process at the non-noble metallic surface (substrate) inside an electrochemical cell. Metal ions reacted with water
molecules, and metal oxides are formed on the surface. Jafari et al. (2011) [135] fabricated anodized aluminium alloy with bird’s nest-like structures. After sputtering a thin layer of PTFE on the rough surface, they measured a $\theta_w$ of about 165° with a low $\Delta \theta \sim 3^\circ$. Cho et al. (2012) [137] demonstrated the possibility of modulating the anodizing parameters in order to create pillar-on-pore nanostructures. They controlled the morphology of the pillar structures on a self-ordered porous hexagonal array of the anodized Al by modulating the anodizing voltage. These hybrid structures showed high hydrophilicity, and after coating a hydrophobic monolayer, they became superhydrophobic ($\theta_w \sim 170^\circ$ and $\theta_s \sim 3^\circ$).

In the process of electrodeposition of conducting polymers, a monomer is firstly oxidized in an electrochemical cell to produce the corresponding polymer, and then deposited on the electrode. Various surface morphologies are obtained by controlling deposition time and current. Electrodeposition of conductive polymers is a classic one-step process to create rough low energy surfaces due to there is no hydrophobization post-treatments are required [138–141]. On the other hand, the processes of electrodeposition of metals and metal oxides were electrochemical reduction process where metal ions were reduced into metals and deposited [142–146]. Moreover, in the process of electroless galvanic deposition of metals and metal oxides, a spontaneous deposition of metallic ions occurred when they make contact with a metallic surface (substrate) having a lower oxidation potential. The surface texture of the film is dependent on the electrolyte material [147–150].

Electrospinning is a technique that used electric force to draw charged threads of polymer solutions or polymer melts fibres diameters up to a few nanometres and adhere them on to the substrate [151,152]. The produced filaments/ fibres could be randomly or axially dispersed to form a nonwoven web or uniaxial/biaxial nanofiber assemblies. High degree of surface roughness and low surface energy were achieved. Electrospinning produced fibres of very small diameter (from several nanometers to hundred micrometres) offering a level of surface roughness to the electrospun mats. Post-treatment methods created another level of surface roughness were often needed to help the surface to achieve a larger $\theta_w$ and a lower $\Delta \theta$.

Chemical vapour deposition (CVD) has played a crucial role in the preparation of superhydrophobic coating [153–159]. CVD is a deposition process where gaseous phase chemical precursors are deposited on a flat substrate to form a thin film or on an ordered structure. Shen et al. (2014) [155] demonstrated an oxidative CVD method to prepare nanocomposite coating. The
experiment was set within a chamber, with two electrically heated panels installed, one on the top and the other at the bottom, as it is shown in (Figure 8a). The temperature of the bottom panel produced the decomposition temperature ($T_1$) and the top one produced the oxidative deposition temperature ($T_2$). Both temperatures were controlled independently. Then, the substrate was placed on the support plate and the as-prepared silicone particles were scattered randomly on the bottom heating panel. Then, the mixture gas ($O_2$–$N_2$ was $\sim 1 : 4$) flowed into reactor and then stopped. The values of $T_1$ and $T_2$ were changed with a rising rate of $\sim 30 \, ^\circ C \, min^{-1}$. This process lasted for about 3 hours and a superhydrophobic was formed.

Jung et al. (2009) [157] used catalyst–assisted CVD multi-walled CNT (Carbon Nanotube) composites on microstructured silicon surface with pillars structure which was fabricated by lithography. And the flat epoxy resin was deposited using a spraying method. After spraying the CNTs on the surfaces, the CNT composite structures were then annealed in order to improve the mechanical properties (Figure 8b). After CNT nanostructure deposited on top of the micropatterned Si replica, the hierarchical structure with CNTs showed a $\theta_w$ of 170° and a $\Delta\theta$ of 2°. CVD has limitation of being having strong reliance on the experiment instrumentation and the highly demanding reaction conditions.
Figure 8. Bottom-up approach: Chemical Vapor Depositing (a) Schematic illustration for the CVD experimental setup of the preparation of the coatings [155]. (b) SEM micrographs taken at 45° tilt angle, show three magnifications of nano- and hierarchical structures fabricated with CNTs after 3 h at 120 °C. Images were modified and reprinted from [157]. (c) Schematic illustration showing the electrospraying steps used to synthesize the superhydrophobic micro-nano hierarchical SiO$_2$ layers [160].
Comparing to CVD, liquid-phase fabrication methods (also referred as wet chemical approach) such as spin coating, dip coating or spray have advantages of easy scalability, low overall cost and accessible fabrication [161–164]. A good example is the work of Wu et al. (2008) [164] in which an emulsion solution of \( [\text{CH}_3(\text{CH}_2)_{10}\text{COO}]_2\text{Cu} \) in diluted ethanol was sprayed onto various substrates using pressurised gas (\( \text{N}_2 \)), and the surfaces were allowed to dry at room temperature. Their experimental results showed that a binary micro/nanostructure superhydrophobic coating with a \( \theta_w \) of about 160° and a sliding angle (\( \theta_s \)) of 5° were achieved. However, classic spraying, spinning or dipping coating methods also suffered from non-uniformity [15]. Therefore, electrospraying was introduces to overcome this challenge. Electrospraying process is similar to classic spraying but there are essential differences between them [160,165–169].

Kim et al. (2013) [160] created hierarchical superhydrophobic surface via electrospraying, starting with preparing mixture precursor solution of tetraethylorthosilicate (TEOS, \( \text{Si(OC}_2\text{H}_5)_4 \)) and methyltriethoxysilane (MTES, \( \text{CH}_3\text{Si(OC}_2\text{H}_5)_3 \)), stored within a syringe and applied a microscale-rough \( \text{SiO}_2 \) layer to the substrate. An electrical potential was applied between the syringe needle and a grounded collector, and due to the surface tension, at the tip of the needle the solution formed a droplet slowly. After the electric voltage reached to sufficiently high level, electrostatic repulsion between the charges that collected into the droplets could overcome the surface tension. Leading to the formation of a thin jet and accelerated toward the bottom \( \text{SiO}_2 \) layer. In the second step, in order to apply nanoscale roughness to the microscale-rough \( \text{SiO}_2 \) layers, Au nanoparticles were synthesized on the surface of the \( \text{SiO}_2 \) layers via an ultraviolet (UV)-enhanced chemical reduction process. The micro-nano hierarchical rough surface structure was obtained. Subsequently, the dry samples were heated at 400 °C for 1 h after a fluorination treatment process. Superhydrophobic surface was achieved with \( \theta_w \) of 170°.

Apart from all the approaches which were described above, there are still many other ways to achieve superhydrophobicity. A lot of them are combinations of Top-down and bottom-up approach, such as Jeong and Choi (2012) [170] created porous nanostructures on Al substrate via oxidation process (Top-down approach). The size of pores could be controlled by anodizing parameters (Voltage, temperature, type or concentration of the electrolyte). However, such micro/nanostructure showed high hydrophilicity. Therefore, a layer of hydrophobic monolayer was applied on top of the porous oxide layer via CVD (Bottom-up approach) to turn the surface from hydrophilic to superhydrophobic.
Bottom-up approaches such as spraying or LbL have the benefits of simple fabrication, low costs and scalable. Therefore, they become very adaptable for large-scale industrial applications. However, not every material is suitable for bottom-up approaches or coating; therefore in the next section, a literature review would be given on suitable coating material selection [12,15,18].

2.1.3. Material selection for superhydrophobic coating

The micro/nanoparticle-copolymer composite is considered as one of the most commonly used matrix in the bottom-up approaches (coating) for superhydrophobic surfaces. Since most of the materials used could be easily accessed or purchased [15,19,20,171]. Also the fabrication of the coating solution often does not require sophisticated steps or equipment. Therefore, this part of the review focuses on material selection for the micro/nanoparticle-copolymer composite coatings. The material selection were divided into two categories: micro/nanoparticle and copolymer material.

Micro/nanoparticle material

Silica-based material is the most common choice [172–176]. As a matter of fact, silica-based material is intrinsically hydrophilic due to their porous and amorphous nature, making them easy for further chemical treatment to be applied to obtain superhydrophobicity. Moreover, their excellent optical properties make them a favourable choice for specific optical applications [15].

Seyedmehdi et al. (2012)[174] fabricated a hydrophobic composite via mixing room temperature Vulcanizing (RTV) silicone, hydrophobic fluoric nanoparticles, alumina tri-hydrate (ATH) and solvent. The composite was then applied on a substrate by spraying, dipping or brushing. This coating had an excellent UV durability and remained $\theta_w \approx 140^\circ$ after 1000 hours of UV exposure. However, due to lack of sufficient surface roughness, the $\theta_w$ was considered relatively low.

Xiu et al. (2012) [173] incorporated silica particles (100 nm diameter) into a bisphenol A based epoxy, forming a composite layer, followed by applying an O$_2$ plasma etching treatment to expose the silica particles, thereby generating a sufficiently rough surface. Fluorination was then performed by immersing it in perfluorooctyl trichlorosilane (PFOS), resulting in a surface having
a \( \theta_w \) of 165° and \( \Delta \theta \) of 3°. Their work also showed that the surface structure could be easily damaged by abrasion, leading to the loss of superhydrophobicity.

Xue et al. (2014) [172] sprayed polystyrene/SiO\(_2\) core/shell nanoparticles, as a coating skeleton, and polydimethylsiloxane (PDMS), as the hydrophobic interconnection, and cured at 150 °C, to create a long-lasting and self-healing superhydrophobic coating. The coating exposed new roughening structures during rubbing and abrasion, favouring a return of the superhydrophobic property. Even the surface was damaged by air plasma treatment and lost its superhydrophobic; its anti-wetting property could automatically be restored in 12 hours at room temperature which helped the release of hydrophobic polystyrene.

Li et al. (2014) [175] prepared a superhydrophobic nanocomposite coating which exhibited hierarchical roughness with a \( \theta_w \) of 153°. Interestingly, with an increase in the calcination temperature from 100 °C to 400 °C, the superhydrophobic PDMS/SiO2 coating became transparent with visible light transmittance increasing from 40% to 80%. In addition, when the calcination temperature was raised to above 500 °C, the wetting behaviour of the coating changed from superhydrophobic to superhydrophilic with a \( \theta_w \) of nearly 0°.

Si et al. (2015) [172] designed a novel green approach through a facile reaction, using a trimethyl silyl modified process, to fabricate superhydrophobic nano-coating at room temperature. The coating was found to have good transparency and stability. This coating can be applied to various substrates via simple spraying without the need of using any toxic substances and it has a rapid self-healing property which can be induced by immersing it in organic solvents (e.g. acetone, cyclohexane and 1,2-dichloroethane). The authors proposed a plausible reason of the self-healing mechanism. When immersed in an organic solvent, the wrapped hydrophobic group or hydrophobic bond, such as Si–C, C–C, –C\(_6\)H\(_5\), of the coating migrated to the surface of the DSTM gel nanocoating towards the organic solvent. This phenomenon reduced the surface energy of the DSTM gel nanocoating and re-established the superhydrophobicity of the surface. They therefore claimed their coating satisfied the need of daily life use and can be applied in industry.

Although silica-based superhydrophobic coatings has been studied and developed carefully in the past, their mechanical stability and environmental stability are still the main concerns [175]. Vigil et al. (1994) [177] presented that silica surface underwent slow structural and chemical changes in humid environment, resulted in decrease of dynamic contact angle.
**Carbon-based** material such as carbon nanotube (CNT), carbon black (CB), carbon nanofiber (CNF) and graphene have been a focus in many fields including superhydrophobic coating [178–182]. Carbon-based material are mechanically strong, thermally stable and electrically conductive, but how to achieve nano-roughness in specified dimensions certainly remains challenging.

Lee et al. (2012) [179] achieved a hierarchical structure by mixing a two-dimensional graphene sheet with Nafion. The roughness was controlled by adjusting the composition of the graphene and Nafion to form a nanohybrid film, essentially changing the interpenetrating networked and compactly interlocked structure (surface area 9.65 m$^2$g$^{-1}$) of graphene to the hierarchical petal-like, porous structure (surface area 413.46 m$^2$g$^{-1}$) by adding Nafion. The nanohybrid film shows a $\theta_w$ of 161°.

Zhu et al. (2013) [180] developed a superhydrophobic coating with good reusability and repairability by spraying multi-walled CNTs on to substrates, followed by surface fluoridation, resulting in a surface with a $\theta_w$ of 162° and $\theta_s$ of 3°. Moreover, due to the thermal stability of CNTs, it is possible to recover the decrease of superhydrophobicity caused by oil contamination by heating the surface up to 400 °C to evaporate the oil. Han et al. (2014) [181] exploited the thermal stability of CNTs by creating a multi-walled CNT-silicon composite superhydrophobic coating for anti-frosting applications. The coating could survive over 4000 thermal cycles (-30 °C to room temperature). By applying the coating, the surface exhibit anti-icing properties, showing the frost nucleation temperature was decreased on the surface.

Apart from thermal stability, carbon-based material also opens up the possibilities for creating electrical conductive superhydrophobic surfaces. Lee et al. (2013) [179] introduced a simple routine to obtain a superhydrophobic surface of graphene, thus making the realization of flexible non-wetting electronic devices a possibility.

Asthana et al. (2014) [178] presented an environmentally benign and economical fabrication of highly electrically conductive, polymer-based superhydrophobic coatings, also with an impressive ability to resist dynamic water impalement through droplet impact. In order to impart electrical conductivity, the coatings were prepared by drop casting suspensions of different kinds of carbon nanoparticles in an acidic solution and a fluoropolymer dispersion, on to a substrate. A comprehensive comparison of impalement resistance and electrical conductivity was carried out
on the coatings. Coatings containing CB: GNP: Polymer of 1:1:2 ratio showed both excellent impalement resistance (up to 3.5 m/s with 5 vol % IPA–water mixture drops) and electrical conductivity (∼1000 S/m).

The biggest obstacle of introducing carbon-based material for large-scale preparation is the price of the micro/nanoparticles, and therefore the work seems to be confined to laboratory level.

**Metallic oxide-based**: Different kinds of metallic oxide micro/nanoparticle have been used for fabricating copolymer nanocomposite superhydrophobic coatings. Metallic oxide such as TiO₂, Al₂O₃, ZnO and Fe₃O₄ micro/nanoparticle are known to exhibit hydrophilic characteristics due to their high possibility of synergetic hydrogen-bonding interaction at the solid-water interface [24,183–194]. This also makes them a good selection for chemical treatment that would lead to reducing surface energy.

Macias-Montero et al. (2000) [186] developed a superhydrophobic thin film of TiO₂ by first mixing Titanium acetylacetonate with aluminium acetylacetonate and boehmite in ethanol, followed by spinning coating it on a glass substrate. Calcination of the samples is then performed at 500 °C for 20 seconds; the titanium acetylacetonate (Tiso(C₅H₇O₂)₂) decomposed into TiO₂ and the aluminium acetylacetonate sublimated, resulting in the creation of a thin transparent film of a mixture of TiO₂ and boehmite. The film is subsequently coated with a (fluoroalkyl)silane to form superhydrophobic surface. The film prepared were the first ones reported to satisfy the requirements of transparency, superhydrophobicity and relatively long lifetime simultaneously. However, considerably complicated coating preparation was needed and high-temperature (500 °C) is required for calcination.

Chen et al. (2012) [193] produced a stable suspension of titanite nanobelt (TNB) particles by mixing them with 1H,1H,2H,2H-perfluorooctyltribetuxoyisilane (FAS), creating an intermolecular interaction between the hydroxyl groups of the particles’ surface and FAS’s silanol groups. A one-step electrophoretic deposition was used to apply the suspension on to a conducting glass substrate, resulting in a transparent cross-aligned superhydrophobic TNB/FAS film. By controlling the deposition time, the hydrophobicity could be controlled; a short deposition time would lead to a high θₜ, but also with a high θₜ. Increasing the time would reduce θₜ, thus creating a superhydrophobic surface.
However upon heat treatment at 500 °C, the superhydrophobic state would turn into superhydrophilic, due to the transformation of the hydron titanite to porous TiO$_2$(B) and anatase TiO$_2$. The researchers claimed that various potential applications could be considered such as for anti-forging surface.

Heat treatment can alter the TiO$_2$ particles wettability as shown in the work of Watanabe et al. (2000) [24], Chen et al. (2012) [192] and Wang et al. (1997) [195]. They prepared a thin TiO$_2$ polycrystalline film from anatase sol on a glass surface and demonstrated that it was also possible to transform a TiO$_2$ hydrophobic surface to superhydrophilic surface by irradiating the surface with UV light. A simple model of the transition process was proposed as the UV irradiation could create surface oxygen vacancies at the bridging sites, resulting in the conversion of Ti$^{4+}$ sites to Ti$^{3+}$ sites which were favourable for dissociative water adsorption, forming hydrophilic domains.

Zhu et al. (2010)[194] also achieved wettability transition (superhydrophobic-hydrophilic) on ZnO nanocomposite coated surfaces by applying UV irradiation, and the superhydrophobicity of the coated surface can be recovered by heating the surface at 100 °C for 25 minutes, as shown in Figure 9a. UV exposure generates electron-hole pairs in ZnO and the holes react with lattice oxygen (“electron-hole pairs” is often used in semiconductor study [196]), leading to the creation of surface oxygen vacancies that can combine with water molecules to form hydroxyl groups, thus becoming hydrophilic (Figure 9b). Heat treatment could accelerate the elimination of surface hydroxyl group. Simultaneously, the organic alkyl chains re-aligned with the -CH$_3$ group orientated outside the top surface so as to improve the surface hydrophobicity. In their work, a copper substrate was immersed in ZnCl$_2$ aqueous solution, followed by adding aqueous ammonia (25%). 90 minutes were allowed to have the ZnO nanorods fully developed before the wetted substrate was taken out to dry in the oven for 1.5 h, resulting in an evenly coated ZnO nanorod surface. The rough surface was then dipped into a 5mM ethanol solution of n-octadecanoic acid for 24 hours to obtain superhydrophobic ($\theta_w = 160^\circ$ and $\theta_s = 5^\circ$).
ZnO based composites lose its superhydrophobicity under UV light or sunlight [195] and this limits their outdoor application potential. Wang et.al (2010) [192] coated ZnO nanowire conformally with ultrathin SiO$_2$ shell using layer-by-layer (LbL) deposition to obtain an UV-durable superhydrophobic surface. SiO$_2$ shell was deposited on ZnO by alternately dipping the ZnO nanowire into (react with) polyethyleneimine and silicic acid; the thickness increases incrementally by ~4.17 nm per deposition cycle. The surface energy of ZnO nanowire with SiO$_2$ shell was then reduced by creating a monolayer of octadecyltrimethoxyslane via immersion. The
confinement effect [197] of insulating SiO$_2$ layer on the electron-hole pairs in ZnO significantly improved the UV durability of the superhydrophobic surface, from 180 to 10000 minutes.

(Confinement effect: SiO$_2$ shell has less photosensitivity than ZnO, since the valence and conduction bands of SiO$_2$ lie far lower and higher in energy than the corresponding bands of ZnO, respectively. Under UV irradiation, SiO$_2$ shell protected the core ZnO particle from generating electron-hole pair [192,197])

Siddaramanna et al. (2014) [184] developed a chemical bath deposition to prepare superhydrophobic ZnO surface on aluminium substrate in just one step. Stearic acid was used during the process of surface roughening at relatively low temperature. The ZnO particle size was controlled by the concentration of stearic acid in the deposition process which led to the control of the roughness and wettability of the surface. Li et al. (2018) [191] functionalised ZnO particle with hexadecytrimethoxysilane then mixed it with epoxy resin, following by spraying to create a superhydrophobic surface. The coated surface was used for suppressing biofouling (the attachment of microbial biomass on solid surface), effectively resisting the attachment of bacteria and protein on to the surface. Despite both fabrication processes being simple, there was no work done on evaluating the surface mechanical durability or UV stability.

Manoudis et al. (2008) [190] presented a strategy for the production of superhydrophobic surfaces that included the use of hydrophilic nanoparticles dispersed in a polymer solution. The work mainly focused on dispersing Silica (SiO$_2$) nanoparticles in a solution of poly (methyl methacrylate) (PMMA) and commercial poly(alkyl siloxane) (Rhodorsil 224) and creating the superhydrophobic surface by spraying the silica-based dispersion on to the substrate. They also replaced silica particle by aluminium oxide (Al$_2$O$_3$) nanoparticle, dispersing into the polymer matrix, and despite the size of Al$_2$O$_3$ nanoparticle (45-50 nm) being larger than Silica nanoparticle (7 nm), superhydrophobicity was still achieved. They concluded that the particle size/nature might affect the minimum particle concentration that was necessary to achieve superhydrophobicity. Their work demonstrated the potential of using Al$_2$O$_3$ nanoparticle in nanoparticle-copolymer composite coating due to its easy adaptation of particle functionalization.

Portilla and Halik (2014) [189] presented a simple solution-based procedure for tailoring the surface properties of aluminium oxide nanoparticle by developing a core-shell system. The system started with functionalising Al$_2$O$_3$ nanoparticles with the molecular self-assemble long chained
alkylphosphonic acid (PA). Then a hydrophobic (a partially fluorinated alkyl chain of 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10 heptadeca-fluorodecyl-phosphonic acid [F_{17}C10-PA_{2}]) or a hydrophilic (an oligo glycol structure terminated with a hydroxyl group of (2-{2-[2-Hydroxyethoxy]-ethoxy}-ethyl) phosphonic acid [H-(OC2H4)_{3}-PA_{3}]) chain was attached to the (PA) molecules. Coated surface wettability could be tuned by the amount of hydrophobic/hydrophilic groups, as illustrated in Figure 9c. Al-Shatty et al. (2017) [188] applied a similar functionalising approach to produce Al_{2}O_{3} nanoparticle based hydrophobic/hydrophilic surface but replaced the PA by a hydrocarbon material which could reduce the costs and the associated hazards of the fabrication process.

Li et al. (2014) [183] demonstrated a novel method to fabricate superhydrophobic coating via mixing a few different nanoparticles (ZnO, Al_{2}O_{3} and Fe_{3}O_{4}) and PDMS. The coating was applied to various substrates such as sponge, fabric and paper via the chemical vapour deposition. Figure 9d shows different nanoparticles aggregation forming complex nano/micro-surface structures. However, no further study on the particle interactions and surface durability was performed.

In Azimi et al. (2013) [198] demonstrate a class of ceramic comprising the entire lanthanide oxide series, ranging from ceria to to lutecia, is intrinsically hydrophobic. The hydrophobicity of these Rare-earth oxides (REOs) are attributed by their unique electron structure, which inhibits hydrogen bonding with interfacial H_{2}O molecules. Surface energy mesurement results comfired that polar interaction are minimized at the REOs surface. Furthermore, they showed that ceramic surface which made of REOs promoted dropwise condesation, good droplet impalement and sustained hydrophobicity even after expose to harsh enviroment. Inspired by their discovery, REOs material: Ceria was selected to fromed nanocomposite with poly(perfluoroalkyl methacrylic) copolymer to form nanocomposite

The role of these micro/nanoparticles (silica-based, carbon-based and metallic oxide) provide sufficient roughness and multiple characteristics for superhydrophobic composite coating. On the other hand, polymeric material decides the micro/nanoparticles dispersion quality, applying approaches, coating homogeneity and durability.
Copolymer(polymeric) material

Polymers, such as polyethylene (PE) [199–202], poly(methyl methacrylate) (PMMA) [203–205], polydimethylsiloxane (PDMS) [206–209], polypropylene (PP) [210–212], polystyrene (PS) [213–216], poly(perfluoroalkyl) methacrylate copolymers (PMCs) [217–221] and epoxy resin [173,222–227], have advantages of diverse molecular design, flexibility, good adhesion, low cost, etc. These thus make them good candidates for constructing superhydrophobic coatings [12,15,18].

Low-density PE (density between 0.91 - 0.94 g cm\(^{-3}\)) is a thermoplastic made from the monomer ethylene and has a \(\theta_w\) of 103±1.8° when it is coated on a glass substrate and dried at 120 °C. In order to achieve the \(\theta_w\) to beyond the superhydrophobic benchmark, micro/nano roughness are necessary. Lu et al. (2004) [200] and Yuan et al. (2014) [199] introduced microstructure to the low-density PE (LDPE) and achieved superhydrophobicity by controlling the its crystallization behaviour.

Low-density PE is not reactive at room temperature, however when the solution drying temperature is to rise to within certain temperature range under the atmospheric pressure, it becomes thermodynamically unstable and phase separation happens to form polymer rich and poor phases. The polymer rich phase forms matrix structure around the polymer nuclei whereas the poor phase forms porous structure.

Lu et al. (2004) [200] showed that at 30°C, a \(\theta_w\) of 151.0±1.9° was achieved. The \(\theta_w\) dropped to 117.7±1.8° when the drying temperature was raised to 90°C, (Figure 10a). At these low temperatures, the solvent evaporation rate was relatively low, and thus the phase separation occurred, leading to an increase in nucleation rate and pores formation. Therefore, the inhomogenous and rough surface was formed. However, the phase separation would not be triggered if the drying temperature was too high (e.g. 120 °C) due to the solvent evaporate very quickly. Then lead to a smooth surface with a low \(\theta_w\) (e.g. 103±1.8°).

Despite having a high \(\theta_w\), the water droplet on these surfaces cannot slide off, exhibiting a Wenzel wetting state. Lu et al. (2004) [200] solved this problem by adding in the cyclohexanone, a PE non-solvent, which facilitated the formation of the porous and floral crystal with nanostructures, due to the following. First, the presence of the nonsolvent increased the nucleation rate. Second, the
decrease of polymer solubility in the solvent mixture caused the generation of crystal nuclei at a higher temperature (68 – 74 °C) than that in the xylene (original solvent) alone (52 – 60 °C). In addition, cyclohexanone had a comparatively higher boiling point, 155.7 °C (Xylene boiling point: 136 – 140 °C). Hence, the time to crystallize into more complex surface structure during cooling of the mixture at atmospheric pressure was longer. The resulted three-dimensional imperfect spherulites hierarchical structure had a $\theta_w = 173.0 \pm 1.8^\circ$ and a $\theta_s = 1.9^\circ$, (Figure 10a).

Yuan et al. (2014) [199] added in NH$_4$HCO$_3$, instead of cyclohexanone, since they claimed that the evaporation rate of the cyclohexanone was too slow due to its high boiling point (155.7 °C) and took too long to fabricate the superhydrophobic PE surface. When the NH$_4$HCO$_3$ was added into the Low-density PE solution, the NH$_4$HCO$_3$ was decomposed as NH$_3$, H$_2$O, and CO$_2$ at 50 °C. The decomposed H$_2$O was the nonsolvent for LDPE and would act as a precipitator. The precipitated polymer acted as nuclei, attracting the polymer rich phase to aggregate around them and further promoting the phase separation. At the same time, the volatile NH$_3$ and CO$_2$ helped to prevent the polymer rich phase to aggregate, forming a more porous structure. The combined action of the NH$_3$, CO$_2$, and H$_2$O made the microstructure of the formed LDPE coating surface rougher and more complex, which led to the superhydrophobicity.

PMMA ($C_3O_2H_8$)$_n$, commonly known as acrylic and PDMS as silicones are two good candidates for fabricating superhydrophobic coating, due to being environmental friendly (non-toxic and non-flammable), having good adhesion and low cost [15]. Tserepi and Gogolides’s research group reported (2006) (2007) (2009) [203–205] the use of oxygen plasma treatment for creating micro/nanoroughness on PMMA and PDMS. However, PMMA and PDMS are not naturally hydrophobic and have respectively a $\theta_w$ of 65° and 105°, therefore the increase of roughness would lead to Wenzel wetting state ($\theta_s < 5^\circ$) [55].

After oxygen plasma treatment, the same reactor was used for depositing a thin C$_4$F$_8$ film on top of the rough polymer surface. The reduction of surface energy brought by the fluoro gases led to Cassie-Baxter wetting being achieved with a $\theta_w = 152^\circ$ and a $\theta_s = 8^\circ$, (Figure 10b) [205]. Hurst et al (2012)[206] developed a more economical approach to achieve micro/nanoroughness on PMMA by combining sanding and reactive ion etching treatment (RIE). For each roughen sample, immediately following its RIE treatment, it was coated with a fluorinated silane molecule: (heptadecafluoro-1,1,2,2-tetrahydrodecyl) trichlorosilane ($C_{16}H_{31}Cl_3F_{17}Si$) in a vapour deposition chamber. Superhydrophobicity was achieved with a $\theta_w = 152^\circ$ and lasted for over 90 days.
Xu et al. (2011) [207] prepared an Ag-TiO$_2$-PMMA superhydrophobic copolymer nanocomposite coating with good chemical resistance. The coating benefited from the chemical stability of PMMA and remained superhydrophobic after immersing in (1) acid solution (PH = 1), (2) alkiline solution (PH = 14) or (3) NaCl solution for 2 hours.

Polystyrene (PS) and polypropylene (PP) are both commonly used polymer to fabricate superhydrophobic surfaces, due to their low surface energy (at room temperature, $\gamma_{sl}$ for PP is 30 mN/m, and for PS is 32 mN/m), and therefore they exhibit a relatively high $\theta_w$ even before any roughening treatment (on a flat surface, $\theta_w$ = 95° for PP and $\theta_w$ = 86° for PS) [55]. In Erbil et al’s (2003) early work [211], they introduced a simple surface roughening process to PP that led to superhydrophobicity. A commercially available PP solution was mixed with a suitable solvent such as P-xylene and then a non-solvent, such as Methyl ethyl ketone (MEK), cyclohexanone or isopropanol, was added before cooling. The final solution was coated onto different substrates (glass, stainless steel, Al foil, etc.). The solvent evaporated at 30 °C which resulted in the formation of a spongy aggregates (Figure 10c) with pore diameters between 10-50 um. The roughness of the surface was controlled by the solvents (or non-solvent) selection and the drying temperature. A $\theta_w$ of 160° was achieved by mixing PP with the non-solvent MEK (40%) and solvent P-xylene (60%), followed by drying at 30 °C.

Other surface roughening treatments such as oxygen plasma etching could also be used on these polymers to achieve superhydrophobicity. Mundo et al. (2008) [213] showed that plasma etching processes, fed with CF$_4$/O$_2$, simultaneously roughened and fluorinated a PS surface. Plasma parameters such as CF$_4$:O$_2$ ratio in the feed mixture, power input and treatment time can deeply affect the surface morphology and wettability. The best superhydrophobic performance ($\theta_A$=162°, $\Delta\theta$ = 2°) was obtained at a high input power for a time as short as 5 minutes.

Hejazi et al. (2013) [210] and Qing et al. (2014) [215] respectively mixed ZnO nanoparticles with PS and PP to form superhydrophobic nanocomposite coatings. Their coating fabrication processes were relatively simple, with just mechanical stirring and sonication sufficient enough for creating a stable ZnO particle/polymer dispersion. (Tetrahydrofuran is the solvent for PS and p-xylene is the solvent for PP.) A high content of ZnO nanoparticles was essential (a particle-to-polymer weight ratio of 7:3) for superhydrophobicity because of the need for their migration onto the coating surface to create surface roughness. However, when exposed to UV the presence of
hydrophilic OH group that was residing on the particle surface (Electron-Hole-Pair) would lead to the loss of hydrophobicity.

Hejazi et al. (2013) modified the ZnO nanoparticle by a hydrothermal reaction process with Dodecafluoroheptyl-propyl-trimethoxysilane (DFTMS). The extra hydrophobic groups: CH₃ and CF₂ from DFTMS compensated the hydrophilic OH group and made the surface remain superhydrophobic (θw = 158°) after UV exposure. On the other hand, Qing et al. (2014) used another strategy by pre-calcinating the ZnO particles at 500°C to remove the OH group off the ZnO surface; this was followed by mixing the nanoparticle powder with the polymer and superhydrophobicity was achieved (θw = 162°).

**Figure. 10** Polymers selection for superhydrophobic nanocomposite coating (a) SEM image of LDPE films from a solution (10 mg * mL⁻¹) in xylene when the solvent was evaporated in a vacuum oven at different temperatures: 90°C and 30°C. θw changed according to the evaporated temperature. Graph is reprinted from [200] (b) SEM image of a PDMS elastomer (Sylgard 184) surface after a 6 min SF₆ plasma treatment. 1.45 µm high nanocolumns are shown. As well as, AFM top-view image of the same elastomer surface after a 2 min treatment in SF₆ plasma (roughness was estimated as ~133 nm and periodicity ~240 nm). Graph is reprinted from [205] (c) SEM pictures of i-PP obtained from a solution (20 mg/ml) in p-xylene on glass slides at drying temperatures of 30°C. The i-PP was dissolved in p-xylene at 130°C and the solvent was evaporated in a vacuum oven at the specified temperatures. Then creating a porous structure. As well as, AFM height image of an i-PP coating obtained from a solution (20 mg/ml) in p-xylene on a glass slide.
The peak-to-peak roughness of the porous structure was 3200 nm, and the roughness was 300 nm. Graph is reprinted from [211] (d) Schematic representation of PMC dispersion within the PU network with subsequent solvent evaporation from the coating and polymer crosslinking to form an IPN. As well as, SEM images of surface morphology of the PU/PMC/organoclay nanocomposite coating. Graph is reprinted from [219].

Poly(perfluoroalkyl methacrylic) copolymer (PMC) [217–221] is a relatively new polymer used for fabricating superhydrophobic nanocomposite. Researchers and engineers are attracted by its waterborne and environmental friendly nature, and mechanically robustness. Steele et al. (2012)[228] fabricated a nanocomposite superhydrophobic coating with a PMC modified polyurethane and montmorillonite clay nanofiller (a surface modified by fatty amine/amino-silane). All the polymers and MCN were mixed with ethyl alcohol via vortex mixing, then followed by spraying to form superhydrophobic surface on an Al substrate ($\theta_w = 160^\circ, \Delta\theta = 2^\circ$), Figure 10d. They also reported the surface has a strong adhesion to the Al substrate, and it remained anti-wetting after tape-peeling test. (Tape adhesion 3850 N/m).

The waterborne nature of PMC makes it very suitable for spraying when used in nanocomposite coating. Razavi et al. (2018) [219] firstly sprayed silicon carbide (ethanol solution) on an Al substrate to form a hierarchical micro/nanostructure and followed by spraying PMC solution (2 wt% PMC in water) to form a superhydrophobic surface with ($\theta_w = 158^\circ, \Delta\theta = 8^\circ$). The coated Al substrate was tested for chemical resistance and remained its superhydrophobic after immersion in acidic/alkalinic solution (PH = 2-14) for 10 minutes or salty water for 12 hours. Apart from good chemical resistance, PMC also has a good thermal stability. In another Razavi et al.’s (2018) [220] work, PMC maintained its anti-wetting property after storing in a 200 °C oven for 1 hour. PMC can be applied to various substrates by using different application processes. Tu et al. (2018) [221] applied a TiO$_2$/PMC nanocomposite coating on wood and Nishizawa et al. (2012) [218] applied an TiO$_2$ / PMC nanocomposite coating via layer-by-layer treatment, superhydrophobicity were achieved in both cases.

The last polymeric material to be reviewed is epoxy resin which is considered one of the most mechanical/chemically robust and adhesive polymers for making superhydrophobic nanocomposite matrix. However, it has a relatively high surface energy (39.1 mN/m – 51.6 mN/m) and hence a low $\theta_w$ (38°- 54°). Therefore, extra modification process is required to reduce its surface energy by adding certain hydrophobic functional groups. For instant, Lin et al. (2010)[223]
reported the synthesis and characterization of a novel UV-curable fluorinated epoxy acrylate (FEA) prepared from 1H,1H-perfluorohexan-1-ol (PFHOL), 1,6-hexamethylene diisocyanato (HDI) and epoxy acrylate. The polymer structure incorporated a spacer, which contained a urethane and six-carbon alkyl chain from HDI, to link the side perfluoroalkyl chains to the epoxy acrylate backbone in order to form a superhydrophobic material.

In Xiu et al.’s [173] work, a bis-phenol A based epoxy and silica nanoparticles were used to form a composite layer on substrates. After an O2 plasma treatment of the surface layer, the surface epoxy was etched away and silica nanoparticles exposed on the top, thereby generating a rough surface. A fluoroalkyl saline treatment was followed to create a superhydrophobic surface. Mechanical stability test performed by abrading the coated surface on sandpaper with a 225 g load; the results showed that the surface remained superhydrophobic after abrasion.

Zhu et al. (2018) [227] developed and synthesized a novel branched epoxy named T-FAE; an epoxy group and long-fluorine hydrophobic group were formed into a molecule by base-catalyzed thio-lene Michael Addition reaction of pentaerythritol tetra(3-mercaptopropionate) (PET), glycidyl methacrylate and [N-methyl-perfluoro hexane-1-sulfonamide] ethyl acrylate (PFSA). The T-FAE contained both a long-fluorine chain and epoxy groups, offering low surface energy and low chemical reactivity, respectively. Moreover, the epoxy groups could also form a robust crosslinking network after curing (curing agent: 1-benzyl-2-methyl-1H-imidazole and silicon dioxide) and improved the adhesive strength between the substrate and coating, which increased its mechanical performance. Also during curing, γ-aminopropyltriethoxysilane (APTES) was introduced to further enhance the robustness and adhesion force. The coated sample showed remarkable stability toward abrasion (1000 abrasion cycles under 45 kPa), strong acid exposure (Immersion into PH = 1 solution for 1 hour), UV exposure and thermal treatment (4 hours in the oven under 200 °C without apparently losing its superhydrophobicity.

Most of the polymers which were used in the superhydrophobic nanocomposite matrix have the advantages of good substrate adhesion, strong chemical/mechanical robustness and low cost. However, there are still difficulties researchers have to overcome [15].

Fabrication- and synthesis-wise, for polymers to reach the properties needed for robust coating performance, a very high molecular weight is desirable and this tends to be associated with a high material viscosity, making them difficult to applying via spraying or spin coating techniques.
Maintenance-wise, for some organic polymeric materials, the intrinsic molecular structures make it difficult to overcome durability issues due to their vulnerability to UV exposure. (PP and LDPE have tertiary carbon bonds in their chain structures. UV interacts with these bonds to form free radicals, which then react further with oxygen in the atmosphere, producing carbonyl groups in the main chain. The exposed surface has the risk of cracking, and in extreme cases, complete disintegration can occur [229–231]. For inorganic polymers such as PDMA mixed with inorganic particles, the brittle nature of the materials results in damage to surface micro-and nanostructures when abrasion forces is applied. The flexibility of the nanocomposite coating needs to be carefully controlled in order to maintain adequate durability of the surface [232].

In the next section, different methods or techniques which were used to evaluate the hydrophobic and durability performance will be reviewed and followed by a comparison summary to illustrate the superhydrophobic nanocomposite coating performance from previous research. These tests not only reveal how reliable the nanocomposites coatings are but also give researchers and engineers ideas of what potential applications of their products could be.

### 2.2. Durability tests for nanocomposite superhydrophobic coating

A significant effort has been made to fabricate superhydrophobic surface using various materials and by different fabrication approaches, however very few polymeric superhydrophobic coated surfaces can be considered as durable against different externally applied stresses [233]. Various tests have been introduced to assess their durability before they can be used in real practical applications, and these tests often fall into four main catalogues: mechanical, chemical, drop/jet impact and environmental durability.

#### 2.2.1. Mechanical durability test

Mechanical durability of superhydrophobic surfaces is a critical issue and has become a noticeable concern for co-polymer nanocomposite coating. The micro/nanostructure that are formed by particles, as well as certain non-flexible polymers are found to have high sensitivity to mechanical stresses [32,34,35,233]. The damage of particles or distortion of polymer would lead to an increase in the liquid/solid contact area and a change of the hydrophobic composition associated with the
surface chemistry, resulting in a loss of surface hydrophobicity. The most common strategy for maintaining mechanical durability is to make the surfaces can withstand external forces without affecting the surface roughness as well as the surface morphology and the hydrophobic composition associated with the surface chemistry [234,235].

Three primary characteristics associated with assessing mechanical durability are: adhesive ability to the substrate, the ability to resist tangential abrasive forces and the ability to resist dynamic impact (or scratching) [35].

**Adhesion testing** is often applied a coated surface and determine if the hydrophobic layer can adhere securely to the substrates. Testing the adhesion is usually the first measurement to be conducted regarding to durability evaluation due to lack of sufficient level of adhesion to a substrate will cause the detachment of the coating under a minor mechanical shear forces. In addition to surface adhesion, “internal adhesion” within the coating itself is also essential, whereby the cohesive forces between the constituents of the coating was also studied.

Tape peeling is a useful and straightforward means of removing material from a surface and has been used to test the adhesive strength of non-wettable coatings on substrates [217,236–243]. Generally, a tape is applied on the tested surface and it is pressed in order to eliminate air entrapment and to ensure uniform adhesive contact. Subsequently, the tape is peeled from one end vertically and the condition of the coated surface, whether the coating is totally removed or partially destructed, is examined. After individual peeling cycles, the hydrophobicity can be re-evaluated again. Tapes are often classified according to their strengths of adhesion force to a reference substrate, as reported as adhesion to steel surface in N/m. As this parameter (N/m) increases, the tape peeling becomes more destructive to the coating [35].

Cross-cut test is a peeling test which involves scoring marks on a target region of the coating forming a grid of small squares before applying the tape. The tape is then placed at a 45° angle across the grid and is subsequently removed. The brand of tape, adhesion time and grading should follow the ASTM D3359 procedure [237,239]. Adhesion strength rating (i.e. grade) are typically based upon the amount of material removed after the tape peeling; the standard ASTM D3359 uses the grades 5B to 0B, where coatings rated 5B exhibit the strongest adhesion to a substrate and 0B the weakest adhesion. This test can also be used to provide an evaluation of the brittleness of the coatings by examining the damaged patterns along the cut lines. Figure 11a shows adhesion
tests conducted on various silicone rubbers that exhibit different levels of adhesion to the substrate, followed by an indicative rating chart based on the ASTM D3359 [237,239].

Despite the importance of adhesive strength in practical considerations, most of the studies on superhydrophobic coatings do not report their adhesion performance. Steel et al. (2012) [228], Cholewinski et al. (2014) [240] and Xu et al (2015) [243] used tape peeling to evaluate the adhesion strength of their nanocomposite coatings, and Kumar et al. (2015) [236] followed the ASTM D3359 Cross-cut procedure for their samples. Their results will be summarised in Table 2, followed by a discussion.
Figure 11. Mechanical durability tests (a) Cross-cut tape peeling test on silicon coating and grading from ASTM D3359. Image is reprinted from [237]. (b) Typical linear abrasion test setup and photograph of the Taber linear abrader. Image is reprinted from Taberindustries.com (c) Typical Rotary abrasion setup and a photograph of the Taber abraser. Image is reprinted from Taberindustries.com (d) Sketch of the setup used to determine the stability of the surface against sand impact.

A common abrasion test [137,173,244–264] for coating can be performed by adopting linear shear abrasion with a solid abradant moving across the tested surface. Wear arises at the contact points between the abradant and the coated material. The abrasion eventually leads to alteration of the surface characteristics and loss of the non-wettability property.

Figure 11b shows a typical schematic of the commercial setup (Taber linear abrader) for performing the abrasion test and such setup was used by some research groups [254,258,261]. This
experimental setup consist of a horizontal arm holding a vertical cylinder that perform reciprocated motion in a linear direction while the speed and the distance can be adjusted. Different types of abradant material (e.g. sandpapers of different grades, poly(dimethyl siloxane) (PDMS), rough rubber, etc.) are chosen to attached to the bottom end of the cylinder which produce different degrees of mechanical wear. The tested sample is mounted and aligned parallel and in contact with abradant. The pressure applied on the tested surface can be adjusted by adding weights on to the vertical cylinder.

Alternatively, abrasion test can be carried out via a rotary system which was developed by Taber, Figure 11c, that involves mounting a flat square (or round) coated sample (area = ~100 cm²) to a turntable platform that is rotating on a vertical axis at a set speed. Two Taber abradant wheels, which are applying a specific pressure on the specimen surface. As the turntable rotates, the wheels are driven by the sample and they rub the surface in the opposite directions, along a circular track, while a vacuum system removes loose debris during the test, thus revealing the resultant abrasion track of approximately 30 cm² in area. The selection of abradant wheels is very important since they can produce very different types of wear, as is the loading pressure, Figure 11c.

The key performance features that can be measured in such abrasion tests include the number of cycles which should lead to a loss of superhydrophobic properties as well as the number of cycles to have the coating physically removed, exposing completely the substrate below. The Taber abrasion systems are recommended if test results are to compare under certain industrial standards, e.g. ASTM D4060 [265].

Xu et al. (2011) [245], Huovinen et al. (2012,2014) [173,256], Wang et al. (2013) [249,250], Zhou et al. (2013) [255], Tang et al. (2014) [263], Milionis et al. (2014) [260], Xue et al. (2015) [247] and Zhng et al. (2015) [252] all performed abrasion tests on their samples and results are summarised in Table 2. Unfortunately, it is difficult to draw a fair comparison between the durabilities of different coatings, due to variations in experiment setups/procedures and the adoption of different measuring parameters (applied pressures, contact areas, types/speed of motion, etc.) and in the tests.

Surface durability can also be tested under collisions or impact with solid or liquid [35]. In these dynamic impact tests [266–270] the surfaces are usually placed either horizontally or with a 45° tilt. The surface morphology can be significantly altered by these collisions so that their
superhydrophobic property can be changed. In these tests, microsize sand is used and it can provide relevant information whether the coating is suitable for use in outdoor applications where harsh environment are encountered. Sand impact tests can also simulate severe particle collisions in aerospace or wind farm applications. A typical experimental setup is shown in Figure 11d. The coated sample is tilted 45°, so that deposition of the sand after the impact can be avoided. The sand flows at a constant rate from a container placed at a given height from the surface. With increasing height or mass, the kinetic energy of the particles increases and therefore more damage would be done on the surface. The impact energy \( W_s \) of a solid particle is given by: 

\[
W_s = m_s g h = \frac{4\pi}{3} \rho_s R_s^3 g h.
\]

Here, \( \rho_s \) is the average density of the particles, \( g \) the acceleration of gravity, and \( R_s \) the mean radius of the particles.

Sand impact test has the advantage of not needing any sophisticated equipment and procedure. Therefore, many researchers such as Li et al. (2014) [269], Tang et al. (2014) [270], Zhang (2014) [268] Ipekci et al. (2016)[267] and Jiang et al. (2017) [266] adopted this method to evaluate the mechanical durability of their coatings. Their results were summarised in Table 2.

Scratching tests such as nanoscratching, pencil and blade/knife tests are also typically used for assessing the mechanical durability of coated surfaces [241,271–273]. During these tests, there is usually a sharp tip which is kept still and perpendicular in touch of the top of the surface, and the sample is slowly moved sideways. The force on the tip and moving speed are controlled. The force required to move the sample can be measured and if the test is repeated on the same scratch line, the force is expected to decrease until it eventually reaches a steady value when the coating is completed destroyed.

It is noticed that scratching test cannot replace abrasion, peeling or sand impact test, due to the fact it only causes changes in a relatively small area around the scratch line. Nevertheless, with the use of SEM, it does give useful information on the durability of the micro/nanostructure.

2.2.2. Chemical corrosion durability test

In addition to physical processes, such as pressure, abrasion, or peeling, chemical corrosion can also cause loss of superhydrophobicity due to the decomposition of low surface-energy materials. This must be taken into consideration when superhydrophobic coating are designed for practical application. For example, the coating is used on hulls of ships that contact sea water or outdoor
furniture which exposed to acidic rain, hydrophobic functional group of the coating might be damaged and loss of superhydrophobicity ensues.

Recently, researchers have begun to examine corrosion resistance of the superhydrophobic coating and have prepared anticorrosive superhydrophobic surfaces for applications [274–282]. However, there are currently no standard methods to evaluate the corrosion resistance of superhydrophobic surfaces.

The most common approach to access the chemical corrosion of the superhydrophobic coatings is to immerse the coated sample into strong acids, strong alkalis, sea water or NaCl solution. Samples are taken out and contact angle was measured periodically Coatings which developed by Luo et al. (2008) [282], Xu et al. (2010) [280], Wang et al (2013) [271], Zhang et al. (2011) [278] and Lee et al. (2012) [275] showed remarkable durability under corrosive condition, their results will be summarised in Table 2.

### 2.2.3. Liquid impact resistance tests

Liquid impact tests are also considered as a useful durability test to evaluate the performance of non-wettable surfaces [77,281,283–289]. The liquid can be in the form of sprayed micro-droplet, regular size droplet or liquid jet. These tests can mimic surface exposure to raindrop impacts commonly encountered in outdoor coating applications. During heavy rain in the summer, the rain droplets have the maximum diameter of 3-4 mm and could reach a maximum speed of 7–9 m/s when impacting a rigid surface on the ground [290,291]. A typical free-fall liquid impact experimental setup is very similar to the sand impact apparatus with the only difference being the liquid dispenser which replaces the sand container. The increase of the impact speed, the impact of the ejected liquid droplet on the surface becomes more destructive.

A spraying liquid impact test schematic and a photograph of this setup in Davis et al., (2014) [286] work are shown in Figures 12a and b respectively. High-flux and highspeed microsize (< 1mm) drops travelling at high speed (maximum of 25 m/s) were produced from a spraying nozzle, and subsequently impact on a moving surface below. Micro/nano surface morphology is threatened by the continuing impacted droplets with high pressure. In liquid jet test, spraying nozzle is replaced by a jetting nozzle, Figure 12c. The speed and diameter of the liquid jet, the distance to
of the sample and the impact can be adjusted. Jet impact creates maximum pressure at a particular small area and creating the biggest change for surface durability.

![Image](image.png)

**Figure 12.** Liquid impalement tests (a) Schematic and (b) A photo of the spray impact setup used to investigate rain impact resistance of superhydrophobic surfaces. Schematic and photo are modified/reprinted from [286]. (c) Schematic of the experimental setup for the jet or drop impact test [292]. (d) Schematic of UV accelerated weathering test rig setup, UV light (35 mV/cm², 10 min) Ozone (2.7 g O₃/h, 1 h), acid raid (1M H₂SO₄ aqueous spray) and alkane fog (1M NaOH aqueous spray). Schematic and photo are modified/reprinted from [293].

In some cases, superhydrophobic surface morphologies are not damaged by the impact of drops or jet but gradually a loss of their non-wettability due to a Cassie to Wenzel wetting-state transition. The penetration of the hierarchical protrusions on the non-wettable surface is expected during the impact event after repeated tests, and such occurrence probability increases with drop size, impact
speed or/and pressure. Cui et al. (2009) [281], Geng et al. (2014) [77], Huang et al. (2014) [284], 
Lv et al. (2016) [283] and Mundo et al. (2016) used droplet impact test to evaluate the durability of 
their coating, Davis et al. (2014) [286] and Xiong et al. (2014) [285] used spraying impact test and 
finally Zhang et al. (2014) [292] used jet impact test. Their results were summarised in Table 2.

2.2.4. Environmental durability tests

The environmental robustness of superhydrophobic surface is essential when they are designed 
for long-term outdoor application[192,293–301]. The environmental test can be carried out simply 
by placing the coated samples outdoor, exposed to the outdoor environment and test their 
hydrophobicity daily [300]. Alternatively, just like Zhang et al.(2011) [293] ‘s work, creating a test-
rig (Figure 12d) to simulate different outdoor condition, such as strong UV exposure (Sunshine), 
acidic rain, alkaline fog, and Ozone condition.

Previous study often used UV exposure durability to represents environmental durability, since 
acidic and alkaline resistance were often tested in chemical resistance test, and rain and fog 
condition were often tested in drop impact resistance test. As it was mentioned, in “Material 
selection” section, some polymeric material and micro/nanoparticle suffer from photo-
degradation due to their photocatalytic nature.

Wang et al. (2009)[192], L. Wang et al (2011)[298], Duan et al. (2011) [296], Wu et al. (2014) [295], 
Bai et al. (2016)[294] and Ellinas et al.(2016) [301] exposed their superhydrophobic samples either 
under sun or artificial UV exposure, in order to test the environmental durability of the samples. 
Their results will also be summarised in Table 2.

Other durability tests includes thermal stability (heat/elevated) tests [243,244,248,301], laundry 
wear/dry cleaning tests [253], oscillating steel ring/ball tests, and aerodynamic impact tests were 
designed by researchers for specific application purposes.
<table>
<thead>
<tr>
<th>Material</th>
<th>Fabrication Method</th>
<th>Mechanical Resistance: (Tape-peeling/abrasion/scratching)</th>
<th>Chemical resistance</th>
<th>Liquid impact resistance</th>
<th>Environmental durability</th>
<th>Others Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>J.Zimmermann et al. (2007)</td>
<td>Silicone nanofilament/PFDTS</td>
<td>CVD</td>
<td>-</td>
<td>Acid DEW</td>
<td>-</td>
<td>1 yr outdoor Fog test UV exposure</td>
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<tr>
<td>Luo et al. (2008)</td>
<td>PTFE/PPS</td>
<td>Spraying/Chemical Etching</td>
<td>-</td>
<td>H2SO4/NaOH: 7days</td>
<td>-</td>
<td>5 months in air</td>
</tr>
<tr>
<td>Cui et al. (2009)</td>
<td>SiO2 NP/Epoxy/ATPS</td>
<td>Dip coating</td>
<td>-</td>
<td>PH = 4-14 24 h</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Xu et al. (2009)</td>
<td>Cu plate/slive nitrate/n-octadecanethiol</td>
<td>Dip coating</td>
<td>-</td>
<td>PH = 1 and 14, 120 hrs</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Lin et al. (2009)</td>
<td>Epoxy/ATPS/ Silica NP</td>
<td>Dip coating</td>
<td>-</td>
<td>PH = 14, 1 day</td>
<td>Water flow: 10m/s, 5 mins</td>
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<tr>
<td>Xiu et al. (2010)</td>
<td>Silicon wafer/PU/Various NP</td>
<td>CVD/Sol-gel</td>
<td>Wiping abrasion: 3.5 kPa Sand impact: 30g, 30cm, 30s</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Wang et al. (2009)</td>
<td>ZnO NW/SiO2 shell</td>
<td>Sol-gel</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>UV exposure: 1 week</td>
</tr>
<tr>
<td>Ishizaki et al. (2010)</td>
<td>CeO2 film/FAS/TTST</td>
<td>Dip coating</td>
<td>-</td>
<td>PH = 1 to 14, 24 hrs</td>
<td>-</td>
<td>-</td>
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<tr>
<td>W. Duan et al. (2011)</td>
<td>CeO2 NP/DFTMs</td>
<td>Sol-gel</td>
<td>-</td>
<td>Sonication with ethanol</td>
<td>-</td>
<td>Good UV absorption</td>
</tr>
<tr>
<td>Material</td>
<td>Fabrication Method</td>
<td>Mechanical Resistance: (Tape-peeling/abrasion/scratching)</td>
<td>Chemical resistance</td>
<td>Liquid impact resistance</td>
<td>Environmenta l durability</td>
<td>Others Remarks</td>
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<tr>
<td>Rao et al.(2011)</td>
<td>Cu plate/MTES/ MeOH/NH₂OH</td>
<td>Sol-gel deposition</td>
<td>-</td>
<td>50% HCl: 100 hrs</td>
<td>-</td>
<td>3 months in air</td>
</tr>
<tr>
<td>Zhu et al.(2011)</td>
<td>PE/ Cu NP/ AgNO₃/ PFOTS</td>
<td>Dip coating</td>
<td>Sandpaper (1500 #): 10 cycles</td>
<td>-</td>
<td>-</td>
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<tr>
<td>CH, Xue et al. (2011)</td>
<td>ZnO/SiO₂ core/shell NP/PET</td>
<td>Spraying</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>UV chamber: 55 hr</td>
</tr>
<tr>
<td>Xu et al.(2011)</td>
<td>Cu mesh/slide nitrate/n-octadecanethiol</td>
<td>LBL</td>
<td>-</td>
<td>PH = 1 to 14, 24 hrs</td>
<td>-</td>
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</tr>
<tr>
<td>Xu et al.(2011)</td>
<td>LDPE/Nylon mesh</td>
<td>Templating</td>
<td>Taber linear abrasion: 8 cm/s¹ 32 kPa, 5520 cycles</td>
<td>-</td>
<td>Water pressure: 690 kPa</td>
<td>-</td>
</tr>
<tr>
<td>LL Wang et al (2011)</td>
<td>ZnO/SiO₂ rod/shell</td>
<td>LPL</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>UV chamber: 2 weeks</td>
</tr>
<tr>
<td>Zhang et al.(2011)</td>
<td>Al plate/PDES/Zn(NO₃)₂</td>
<td>Dip coating</td>
<td>Scratching test: 1.4N</td>
<td>-</td>
<td>-</td>
<td>3 months in air</td>
</tr>
<tr>
<td>JP Zhang et al. (2011)</td>
<td>Silicone nanofilament/PFDTS/TCMS</td>
<td>CVD</td>
<td>-</td>
<td>NaOH: 1 hr HCL: 1 hr</td>
<td>-</td>
<td>1 hr UV</td>
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<tr>
<td>Cho et al.(2012)</td>
<td>Al plate/HDFS</td>
<td>Chemical Etching</td>
<td>Abrasive film (1μm grade): 1kg load, 150mm distance</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Lee et al.(2012)</td>
<td>Cu NWs</td>
<td>CVD</td>
<td>Microtribometry: 300 mN Tape peeling: ASTM D3363 Pencil scratching test</td>
<td>PH = 2 to 13</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Material</td>
<td>Fabrication Method</td>
<td>Mechanical Resistance: (Tape-peeling/abrasion/scratching)</td>
<td>Chemical resistance</td>
<td>Liquid impact resistance</td>
<td>Environmental durability</td>
<td>Others Remarks</td>
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<tr>
<td>Steele et al. (2012) PMC / montmorillonite clay nanofiller</td>
<td>Spraying</td>
<td>Tape peeling:10 peels (3850 N/m)</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<tr>
<td>Xiu et al. (2012) Epoxy/Silica NP/ PFOTS</td>
<td>Plasma etching</td>
<td>Abrasive film: 225g load, 100mm distance.</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>In 45 °C water, 24 hrs</td>
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<tr>
<td>Park et al. (2012) PDMS/CNT</td>
<td>Photolithography</td>
<td>Rubber tip abrasion: 1.5N, 600 cycles.</td>
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<tr>
<td>Wang et al. (2012) PVDF/PTFE</td>
<td>Hot pressing</td>
<td>Sandpaper (320 #): 100 cycles</td>
<td>-</td>
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<td>-</td>
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<tr>
<td>Zhang et al. (2012) TMCS/ Silica NP</td>
<td>Dip coating</td>
<td>Scratching test: 0.8N</td>
<td>PH = 1 to 14</td>
<td>-</td>
<td>3 months in air</td>
<td>-</td>
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<tr>
<td>Wang et al. (2013) PTFE/RTVS/PDMS/TOES</td>
<td>Hot pressing</td>
<td>Sandpaper (320 #): 100 cycles</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<tr>
<td>Steele et al. (2013) Ti plate/PMC</td>
<td>Laser Etching</td>
<td>Taber linear abrasion: 3 cm$s^{-1}$, 110 kPa, 10 cycles</td>
<td>-</td>
<td>-</td>
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<td>-</td>
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<tr>
<td>Zhou et al. (2013) PTES/FeCl$_3$.6H$_2$O</td>
<td>CVD</td>
<td>Abrasive film: 260g load, 20mm distance, 600 cycles</td>
<td>PH = 2 and 14, 72 hrs</td>
<td>-</td>
<td>-</td>
<td>Fabrics</td>
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<tr>
<td>Barthwal et al. (2013) Al plate/PFOTS</td>
<td>Chemical Etching/Anodization</td>
<td>Tape peeling:10 peels / stamping (4 N)</td>
<td>-</td>
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<tr>
<td>Cholewinski et al. (2014) PDMS/SiONP/Epoxy</td>
<td>Dip and spin coating</td>
<td>Tape peeling:4 peels (~2000 N/m)</td>
<td>-</td>
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<tr>
<td>Chen et al. (2014) PS/FMS/TiO$_2$ and Silica NP</td>
<td>Spraying</td>
<td>Sandpaper:10 kPa, 10 cycles</td>
<td>-</td>
<td>-</td>
<td>UV: 24 hrs</td>
<td>-</td>
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<tr>
<td>Chao et al. (2014) PS/FAS/ Silica NP</td>
<td>Spraying</td>
<td>Air plasma damage:2 hrs</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>Selfhealing by heating</td>
</tr>
</tbody>
</table>

57
<table>
<thead>
<tr>
<th>Material</th>
<th>Fabrication Method</th>
<th>Mechanical Resistance: (Tape-peeling/abrasion/scratching)</th>
<th>Chemical resistance</th>
<th>Liquid impact resistance</th>
<th>Environmental durability</th>
<th>Others Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Davis et al. (2014)</td>
<td>PU/Organoclay/PM C</td>
<td>Spraying</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Davis et al. (2014)</td>
<td>PU/Organoclay/PM C</td>
<td>Spraying</td>
<td>-</td>
<td>-</td>
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<td>-</td>
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<tr>
<td>Huang et al. (2014)</td>
<td>SiO₂ NP /PFTO/Silic acid</td>
<td>Sol-gel</td>
<td>Pencil scratching test: 9H</td>
<td>-</td>
<td>Drop: 1.4 m/s, 20k drops.</td>
<td>Transparent</td>
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<tr>
<td>Huovinen et al. (2014)</td>
<td>PP</td>
<td>Photolithography</td>
<td>Tribometer:120kP/Compression meter: 20MP</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<tr>
<td>Li et al. (2014)</td>
<td>PAA/PAH/SPEEK</td>
<td>LBL/Spraying</td>
<td>Sand impact: 2m, 15 mins</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<tr>
<td>Tenjimbayashi et al. (2014)</td>
<td>EAC/Silica NP</td>
<td>Spraying</td>
<td>Sandpaper:40kPa, 1 cycles</td>
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<td>-</td>
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<tr>
<td>Tang et al. (2014)</td>
<td>Epoxy/acrylate copolymer/CaCO₃ NP</td>
<td>Brush painting</td>
<td>Sand impact:15 cm, 15g, 5 mins</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Tang et al. (2014)</td>
<td>PU/MoS₂</td>
<td>Spraying</td>
<td>Abrasive film: 0.5kg load, 100 mm distance.</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<tr>
<td>Geng et al. (2014)</td>
<td>TEOS/PDDA/PAA/ PSS/ Silica NP</td>
<td>CVD</td>
<td>4H pencil scratching test, Tape peeling:40 peels (~600 N/m), Sand abrasion: 50 cm,40 g</td>
<td>-</td>
<td>Drop: 1m/s, 4500 drops.</td>
<td>Transparent</td>
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<tr>
<td>Xiong et al. (2014)</td>
<td>SiO₂ NP/Fluorinated thiol-ene</td>
<td>Spraying/UV curing</td>
<td>Sandpaper (2000 #)/3.8mm/s, 350 cycles</td>
<td>PH=2 and 14, 24 hrs</td>
<td>Drop: 2m/s, 4160 drops</td>
<td>Transparent</td>
</tr>
<tr>
<td>Material</td>
<td>Fabrication Method</td>
<td>Mechanical Resistance: (Tape-peeling/abrasion/scratching)</td>
<td>Chemical resistance</td>
<td>Liquid impact resistance</td>
<td>Environmental durability</td>
<td>Others Remarks</td>
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<tr>
<td>L. Wu et al. (2014)</td>
<td>PU/fluoropolymers</td>
<td>Dip coating</td>
<td>A4 paper abration :100 cycles</td>
<td>NaOH:2 hr H2SO4: 24hr</td>
<td>-</td>
<td>Stronge UV :1 hr</td>
</tr>
<tr>
<td>Zhang et al. (2014)</td>
<td>PP/HDPP</td>
<td>Hot pressing</td>
<td>Sand impact: 2.8 ms⁻¹, 10g, 30 sec</td>
<td>-</td>
<td>Drop: 2.4 m/s</td>
<td>-</td>
</tr>
<tr>
<td>Zhang et al. (2014)</td>
<td>PP/PDMS/TiO₂ and Silica NP</td>
<td>Bulk Material</td>
<td>Sandpaper (800 #): self-healing</td>
<td>PH = 2,1 hr</td>
<td>-</td>
<td>UV: 5 hrs Selfhealing</td>
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<tr>
<td>Kumar et al. (2015)</td>
<td>TEOS/Glymo/FAS/ Silica NP</td>
<td>Spraying</td>
<td>Cross-cut adhesion test:2B-1B.</td>
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<td>UV Chamber: 72 hrs</td>
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<tr>
<td>Mundo et al. (2015)</td>
<td>PTFE</td>
<td>Plasma</td>
<td>-</td>
<td>-</td>
<td>Drop:2.05 m/s</td>
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<tr>
<td>Wang et al. (2015)</td>
<td>EP/MPVDF/FEP/CNT/ Silica NP</td>
<td>Spraying</td>
<td>Rotary abration: 1.4 MPa,0.47 m/s,150 mins</td>
<td>-</td>
<td>-</td>
<td>Blending test</td>
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<tr>
<td>Wang et al. (2015)</td>
<td>PFOTS/PDMS/Silica Np</td>
<td>CVD/Plasma</td>
<td>AFM scratching/Tribometer scratching</td>
<td>-</td>
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<tr>
<td>Wang et al. (2015)</td>
<td>Cu plate/NaOH/FAS</td>
<td>Chemical Etching</td>
<td>Sandpaper (800 #): 30g, 200mm</td>
<td>-</td>
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<tr>
<td>Li et al. (2015)</td>
<td>SU-8 3010</td>
<td>Photolithographic</td>
<td>Tape peeling:4 peels</td>
<td>-</td>
<td>-</td>
<td>Transparent</td>
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<tr>
<td>Xu et al. (2015)</td>
<td>PEDOT/Porous silica NP</td>
<td>Electro CVD</td>
<td>Tape peeling:2 peels Sand abrasion:20 cm,20 g</td>
<td>- Drop:4.43 m/s</td>
<td>-</td>
<td>Transparent</td>
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<tr>
<td>Xue et al. (2015)</td>
<td>FAS/Hydroxyl acrylic/ silica NP</td>
<td>Spraying</td>
<td>3M 610 tape peeling Sandpaper (2000 #): 2kpa, 25 cycles</td>
<td>PH = 1 and PH = 14,12 hrs</td>
<td>-</td>
<td>1kg Hammer impact test</td>
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<tr>
<td>N. Bai et al (2016)</td>
<td>OMMA/ZNO/STA</td>
<td>Spraying</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>UV: 3 hrs Air:5 weeks</td>
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<td>Material</td>
<td>Fabrication Method</td>
<td>Mechanical Resistance: (Tape-peeling/abrasion/scratching)</td>
<td>Chemical resistance</td>
<td>Liquid impact resistance</td>
<td>Environmental durability</td>
<td>Others Remarks</td>
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<tr>
<td>K.Ellinas et al. (2016)</td>
<td>COP/PFOTS</td>
<td>Plasma/CVD</td>
<td>-</td>
<td>-</td>
<td>60 cycles: UV, heat and moisture</td>
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<tr>
<td>Ipeki et al. (2016)</td>
<td>PS/FDTS/ silica NP</td>
<td>Spraying</td>
<td>Sand impact: 2.8 ms⁻¹, 10g-20g, 10-30 cm</td>
<td>-</td>
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<tr>
<td>LV et al. (2016)</td>
<td>PTFE/CNTs</td>
<td>Photolithography</td>
<td>-</td>
<td>-</td>
<td>Drop:2.4 m/s</td>
<td>-</td>
</tr>
<tr>
<td>Hoshian et al. (2016)</td>
<td>Al plate/PDMS/ TiO₂ NP</td>
<td>Chemical Etching/Spraying</td>
<td>Scotch Tape peeling: 10 cycles Sand peper: 100g, 10cm, 50 cycle Rubbing/KnifeCut : 10 cycles</td>
<td>PH = 1 and PH = 14, 6 hrs</td>
<td>Drop:7.6 m/s</td>
<td>UV: 1 hr</td>
</tr>
<tr>
<td>Xue et al. (2016)</td>
<td>PET/PDMS/ODA/THF</td>
<td>Dip coating</td>
<td>AATCCA Test Method 8-2001: 10k cycles. Air Plasms damge</td>
<td>PH = 1 and PH = 14,24 hrs</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Jiang et al. (2017)</td>
<td>Papers/Silicon wafer/FDTCS</td>
<td>Plasma etching/CVD</td>
<td>Sand impact:, 20g, 20-40 cm,30s</td>
<td>-</td>
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</tr>
</tbody>
</table>

**Table 2:** List of superhydrophobic coatings and their material fabrication method and durability performance (For all the durability tests, the conditions presented were the situation when the coatings lost their superhydrophobicity).
2.3. Applications

For superhydrophobic coatings, a number of applications such as self-cleaning and corrosion resistance surfaces, oil-water separation, anti-icing, anti-bacterial and so on have been explored. The development of individual applications requires extensive research of relevant theories, material selection, fabrication process and testing procedure.

Self-cleaning is considered the most direct application of anti-wetting surfaces since when a water droplet rolls of a superhydrophobic surface, it picks up and remove the dirt on the surface. These self-cleaning coated surfaces have been applied in industry as well as associated with our daily lives to reduce cleaning costs [157,158,171,192,206,217,220].

Corrosion reaction accounts for enormous wastage of metallic material every year. In 1998, the total annual direct cost of corrosion in the U.S. was ca. 276 billion dollar (ca. 3.2% of the US’s GDP) [302]. Traditional anti-corrosion methods including oil paint and treatment with chromium-containing compounds are harmful to human health and the environment, that have significantly limited their broad applications [30].

In the past three decades, researchers have found that superhydrophobic nanocomposite could be used to applied on various material surfaces to prevent corrosion. This method has attracted much attention both from basic research and practical points of view. The corrosion resistance mechanism of superhydrophobic nanocomposite coating is attributed to the chemical stability of the polymeric material (e.g. epoxy resin) and the existence of air pockets between the coating and corrosive solution, effectively blocking of the migration of corrosive ions (e.g. chloride ions in seawater)[29,30,183,222,276,277].

Superhydrophobic nanocomposite coatings which possess good light transmittance have broad application potential including glassware, outdoor windows, solar cell systems, camera lenses, etc. [24,111,121,127,161,233,242,284,303,304]. Transparency of a surface would be reduced as roughness increases (a key requirement of superhydrophobicity) due to light scattering [305]; that is to say, there are two confliction requirements to achieve a transparent superhydrophobic surface. According to Rayleigh [306], there are two different types of scatterings: Rayleigh scattering is negligible in the visible region (Wavelength = 390 nm – 700nm) when the roughness is far less than the irradiated light wavelength and Mie scattering occurs when roughness size is comparable.
to or greater than the irradiated light wavelength. Theoretical computation results indicate that Mie scattering increases exponentially and transparency significantly reduces with increasing roughness. Therefore, roughness at the scale of sub-100 nm would be more conducive to achieving superhydrophobic surfaces with higher transparency [307]. The transparent (anti-reflection) superhydrophobic nanocoating was used on solar cells as it could enhance optical absorption and remove dirt on the surface.

In the last few years, frequent leakages from oil pipes and drilling platforms (e.g. 2016 BP North sea oil spill) continued to threaten ecological systems. Therefore, to separate water from oil has become a major problem waiting for engineers to solve. Special wettability materials have been developed to attempt to solve this problem [188,215,255]. Some polymeric nanocomposite material appear to have superhydrophobicity and oleophilicity at the same time, and therefore these material can selectively filter or absorb oil from oil-water mixtures, due to the distinct difference in surface tension between water (72.8 mN/m) and oil (<30 mN/m).

Superhydrophobic surfaces were also used as an anti-icing solution [22,27,308,309]. Since superhydrophobic surface has air trapped inside surface textures and has a small water contact angle hysteresis, water droplet slides or bounce off easily before ice nucleation can take place at cold temperature [76]. An anti-icing performance study was carried out and the results showed the growth rate of frost on the superhydrophobic coating was about half of that on a bare Al surface [28]. This coating was silicon-oil-infused PDMS nanocomposite coating and applied by spraying or painting. Under -5 ℃ and saturated condition, the coated surface showed a reduction of ice adhesion strength about 3% of the value on a bare aluminium surface [28].

However, the connection between superhydrophobicity and icephobicity of surfaces is still currently under debate. Some researchers suggested that superhydrophobicity and icephobicity of surfaces are parallel rather than directly related [310–312]. The absence of a standard to characterise ice adhesion strengths, the differences in the preparation of ice samples and testing procedure may all be reasons for the uncertainty. The process of icing upon a superhydrophobic surface is quite complex, due to different surface morphology [310]. Despite recent research had led to a better understanding of the icing phenomenon, the basic freezing mechanism, ice nucleation and growth and ice adhesion strengths are still needed to be studied.
Superhydrophobic surfaces can also be used for reducing growth of bacterial for medical devices or food packaging, due to the fact that bacterial grows significantly quicker under wet environments [17,313]. Silver nanoparticles in a superhydrophobic nanocomposite further enhance the antibacterial effect, due to the release of silver cations ($\text{Ag}^+$). It has been suggested that upon the penetration of $\text{Ag}^+$ ions into the bacterial cell, the DNA molecule loses its replicability, eventually leading to killing the bacteria.

### 2.4. Literature review conclusion

Over the past decade, publications regarding the development of superhydrophobic surfaces have significantly increased. In this review, I first gave a summary of the recent progress in the synthesis of a range of different superhydrophobic surfaces using a wide variety of material and fabrication approaches. It is followed by demonstration of different techniques that researchers used to evaluate the durability of the surface in many aspects. Finally, the applications of these superhydrophobic surfaces were also presented.

Indeed, there are relative advantages and disadvantages of different material and fabrication approaches for artificial superhydrophobic nanocomposite coating. Carbon-based and silica-based inorganic materials usually have excellent chemical resistance in both acidic and alkaline conditions, as well as they provide multifunction such as transparency and high thermal (or electrical) conductivity to superhydrophobic surfaces [214,314–316]. Metallic oxides, such as $\text{ZnO}$, $\text{TiO}_2$, $\text{SnO}_2$, are common materials exhibiting a wide range of surface morphologies like nanorods, nanotubes and nanoplate. Polymeric matrix have their own advantages such as simple fabrication, structural flexibility and controllable thickness. However, there are also disadvantages involved, for example, the problem of metallic oxide UV corrosion, the high price of carbon nanotubes or graphene, the toxicity and brittleness of organic polymers, the expensive experimental set-up of photolithography and most of the fabrication approaches are not suitable for large-scale applications.

Regarding durability testing, a wide range of tests have been reported and claimed that a non-wetting surface was “durable” in many aspects. However, researchers who have been working on non-wetting materials and coatings applications still have got have a unified and standardised way to report the robustness of their coatings. For instance, in order to test the surface wear abrasion resistance, some researchers used sand impact test and some used Taber abrasion test. The results
from two different tests are not comparable even they both aim to represent wear abrasion resistance. In order to make meaningful comparisons, it is suggested that the researchers should establish ways of conducting durability tests that are close to industrial standards (ASTM, IOS, etc.) developed for coatings and painting industry. Also, durability tests for a superhydrophobic coating should cover as many aspects as possible, that would not only assist engineers to identify the potential applications but also help the further development the products.

After reviewing the superhydrophobic surface related research from the past decade, gaps in the current knowledge of ‘developing superhydrophobic nanocomposite coatings’ are identified:

(1) Most of the material and approaches which are selected to fabricate superhydrophobic nanocomposite coatings are limited to laboratory scale and not suitable for industrial production.

(2) Many superhydrophobic coatings suffers from bad mechanical and chemical durability. Nanocomposite with self-similar nature can be used to create superhydrophobic coatings and should have better mechanical/chemical durability. However, it rarely have been studied.

(3) Superhydrophobic coating will lose its anti-wetting properties and become hydrophilic once the liquid penetrate into its the micro- or nanotexture. Therefore, a superhydrophobic coating with good liquid impalement resistance is needed to be developed.

(4) There is a trade-off between superhydrophobicity and optical transparency. To what extent one could introduce transparency to superhydrophobic coatings by understanding the size and material properties of the nanoparticles?

Accordingly, the research objectives are set as follow:

(1) Develop and fabricate nanocomposite superhydrophobic coatings which are inexpensive, durable and can be used for large-scale application
(2) Design and perform experiments which are close to industrial standards to test the coated surface durability in different aspects including mechanical, chemical, impact resistance and environmental. Try to discover the key factors of a long lasting superhydrophobic coating.

(3) Analyse and discuss the test results and exploit the potential coating applications via integrating transparency to the superhydrophobic coating.

In order to achieve these objectives, I started with picking a series of material including different micro/nanoparticle and polymers to form nanocomposite coatings. Material selection is based on experience from previous researchers, different nanocomposite and polymer were used. Bearing in mind that each individual selected material might have its own weakness. However, these weaknesses can be compensated via mixing material matric with different properties. For instant most metallic oxide particles are brittle therefore sensitive to mechanical stress, and hence mixing metallic oxide particles into a soft polymer matrix such as epoxy or PMC can help to improve coating overall mechanical durability.
3. Experiment

This chapter is divided into three main parts. (1) a list of materials which are used to fabricate one- (or two) step micro/nanocomposite superhydrophobic coatings and the equipment (or set up) which is required to fabricate these coatings. (2) Fabrication procedures of micro/nanocomposite superhydrophobic coatings. (3) Mechanical, chemical, liquid impalement, environment resistance, and optical tests and procedures.

3.1. Material and equipment

**Micro/nanoparticle :**

(1) Silicon (IV) oxide (SiO\(_2\), amorphous, 99.9% metals basis, 80 nm APS nanopowder), from Sigma-Aldrich, Inc.

( Fume silica with diamater of 20 nm was firstly tried due to it is intrinsically hydrophobic. However, it has difficulty of mixing with the water-based solvent. Therefore, amorphous Silicon (IV) oxide which can be easility dispersed into water was used)

(2) Cerium Oxide (CeO\(_2\), 99.5% metals basis, 15-30 nm APS powder), from Sigma- Aldrich, Inc.

( CeO\(_2\) js intrinsically hydrophobic and maintain hydrophobic in harsh enviroment [198])

(3) Aluminium oxide (Al\(_2\)O\(_3\), 99.5% metals basis, 13 nm APS nanopowder) - procured from Alfa Aeser, Inc.

( Al\(_2\)O\(_3\) is one of the most common nanoparticle has been used to fabricate superhydrophobic nanocomposite, It is relatively inexpensive and can easility dispersed into water)

(4) Multi-walled Carbon nanotubes (CNT, multi-walled, thin and short, <5% metal oxide), from Sigma-Aldrich, Inc.

( CNT is used to improve the dispersion quality of the nanocomposite solution and increase the surface roughness of the coating.)

(5) Polytetrafluoroethylene(PTFE) nanoparticle powder (1 \(\mu\)m particle size), from Sigma-Aldrich, Inc.

(PTFE is considered the material has the lowest surface energy, it is used to despersed into epoxy to form superhydrophobic nanocomposite. SEM results indicated that the actual size of the nanoparticles are around 200 nm)
Polymers:
(1) Water-based commercial fluoro-acrylic polymer, Capstone™ ST-100, from DuPont™ Inc.
(2) Commercial epoxy resin (AIRSTONE™ 760E), from Dow.

Solvent:
(1) Deionized water (18.2 megohm), from Alfa Aesar, Inc.
(2) Isopropyl alcohol (≥99.7%) from Sigma-Aldrich, Inc.
(3) Acetone (ACS reagent, ≥99.5%), Alfa Aesar, Inc.

Other Chemicals
(1) CTAB (hexadecyltrimethylammonium bromide), from Sigma-Aldrich, Inc.
(2) Commercial perfluoropolyether (Krytox oil™) from Sigma-Aldrich, Inc.
(3) Heptfluorobutyric acid (≥99.0%), from Sigma-Aldrich, Inc.
(4) Diethylenetriamine (ReagentPlus®, 99%), from Sigma-Aldrich, Inc.
(5) HNO₃ solution (70%, purified by redistillation), ≥99.9% trace metals basis, from Aldrich.
(6) HCL solution (ACS, reagent 37%), from Sigma-Aldrich, Inc.
(7) NaOH solution (50% in water) from Sigma-Aldrich, Inc.

Regular Laboratory supplies:
Microscopic glass slides (L × W × T, 76 mm × 26 mm × 1 mm) and Aluminium plates (L × W × T, 10 cm × 10 cm × 0.5 mm) are used as coating substrate, different sizes of beakers and pipettes were used for liquid transfer, fumed cupboard, etc.

Equipment
(1) Spraying guns: IWATA Eclipse BSC air-brush (0.5 mm nozzle), IWATA Air Gunza AZ40 air-brush (0.8 mm nozzle), IWATA LPH-80 (1 mm nozzle).
(2) Air supply and control: 20L Nitrogen gas tank and 0-12 bar BOC gas regulator, from BOC.
(3) Ceramic-top hot plate/magnetic stirrer (0-550°C, 0-1500 RPM) from IKA, Cole Parmer.
(4) Ultrasonic prob processor (Cole-Parmer 130-Watt, 44347 model) from Cole-Parmer.
(5) Ultrasonic bath (Grant instrument, XUBA Analog 1.5, L 0-70 °C) from Fisher scientific.
(6) Syringe pump (Cole-Parmer Single-syringe infusion pump), from Cole-Parmer.
(7) CMOS camera (Thorlab, model DCC1240) from Thorlab.
(8) High-speed camera (Phantom v411, 2014 vers) from Phantom.
3.2. Coating Fabrication

3.2.1. PTFE/Epoxy resin based nanocomposite (PKFE) coating

Epoxide resin was chosen as the polymer matrix in this study due to its mechanical/chemically robust and good adhesive property [19,32,294]. Fluorinated epoxide curing agent was used to reduce the surface energy of epoxide resin. Furthermore, PTFE particle was chosen to mix with epoxide resin to form nanocomposite, to reduce the overall surface energy, and at the same time increasing the surface roughness, therefore superhydrophobicity should be achieved.

Synthesis of fluorinated amine curing agent:
First, 0.01 mole diethylenetriamine was dissolved in 10 ml deionized water in a 100 ml beaker and stirred at 125 rpm on a magnetic stirrer plate. Separately, 0.01 mole heptafluorobutyric acid was dissolved in 10 ml deionized water and added drop-by-drop to the stirred diethylenetriamine solution. The mixing should initiate the fluorination reaction. After having added all the heptafluorobutyric acid solution, the resulting mixture was heated to 100 °C to evaporate all the water content and to obtain the fluorinated amine (F-amine). The F-amine so obtained was used as a hardener for epoxy curing, Figure 13.

Nanocomposite coating preparation:
The following steps were used to obtain a stable polymer/nanoparticle dispersion: firstly, 2.0 g of bisphenol A based epoxide was dissolved in 5 ml of acetone, and separately 10.5 g PTFE
nanoparticles were dispersed in 30 ml of acetone, both by vigorous magnetic stirring at 1000 rpm for 10 mins. The amount of PTFE particles was varied to evaluate the role of particle loading on the coating properties. The epoxy solution was then mixed with the PTFE nanoparticles suspension and the mixture was stirred vigorously for 15 mins to obtain a PTFE/epoxy suspension. Next, 0.3 g of perfluoropolyether (Krytox®) was added to PTFE/epoxy suspension. The mixture was stirred (stirrers were driven magnetically) for 20 mins at 1000 rpm, then sonicated in an ultrasonic bath for 15 mins at room temperature followed by stirring again for another 10 mins to obtain a PTFE/Krytox/epoxy dispersion that could be stored in sealed glass bottles at room temperature for more than a month.

Before the coating preparation, 1.5 g of F-amine, synthesized as described above, was dissolved in 10 ml acetone by stirring for 5 mins at 300 rpm. The F-amine solution was then mixed with the PTFE/Krytox/epoxy suspension. The mixture was stirred for 5 mins at 1000 rpm, sonicated for 15 mins followed by a final 5 mins stirring at 1000 rpm to obtain a well dispersed PTFE/Krytox/epoxy/F-amine suspension ready to be applied on to the substrates (e.g. glass, metal, plastics, polymer composite materials, etc.) through the use of any of common coating techniques such as spraying, brushing or rolling. After applying onto the substrate, in each case, as a final step the coating was annealed in air at ~120 °C for ~1 hour to remove all the solvents and to complete the epoxy curing process (Figure 13a).
Figure 13. PKFE and oxide/PMC-base nanocomposite coatings fabrication process. (a) Schematic illustration of the fabrication process for PTEF/epoxy resin based superhydrophobic coating (PKFE).

(b) Schematic illustration of the Oxide/PMC based superhydrophobic coating.
3.2.2. Oxide/PMC-based nanocomposite coating

Oxide nanoparticles are often used to fabricate superhydrophobic surface due because 1) many of them are very suitable for further chemical treatment to reduce surface energy, 2) they can provide sufficient micro/nano-roughness and 3) they are easy to obtain. Poly(perfluoroalkyl) methacrylate copolymers (PMCs) are used for the polymeric matrix not only because it has a low surface energy and a good adhesion to substrate, and it is also water-based and thus is of environment-friendly nature.

**SiO$_2$ based superhydrophobic coating:**

0.3 g of SiO$_2$ nanoparticles and 0.02 g of carbon nanotubes (CNT) were dispersed in 10 ml of de-ionised water using a high-power ultrasonic probe for 15 minutes. Subsequently, 1.2 g of Capstone ST 100 was mixed with the aqueous dispersion of CNT/SiO$_2$, and stirred (stirrers were driven magnetically) for about 60 minutes at 80 °C. The polymer dispersion was then cooled down to room temperature by placing the solution in an ultrasonic bath for 15 minutes. Thereafter, ~30 - 40 ml of isopropanol was added to the polymer dispersion, and resultant solution was stirred for ~2 hours to obtain the final polymer nanocomposite dispersion, Figure. 13b.

**CeO$_2$ based superhydrophobic coating:**

0.35 g of CeO$_2$ nanoparticles and 0.02 g of carbon nanotubes (CNT) were dispersed in 10 ml of de-ionised water using a high-power ultrasonic probe for 15 minutes. Subsequently, 1.2 g of Capstone ST 100 was mixed with the aqueous dispersion of CNT/CeO$_2$, and stirred for about 60 minutes at 80 °C. The polymer dispersion was then cooled down to room temperature by placing the solution in an ultrasonic bath for 15 minutes. Thereafter, ~30 - 40 ml of isopropanol was added to the polymer dispersion, and resultant solution was stirred for ~2 hours to obtain the final polymer nanocomposite dispersion.

**Al$_2$O$_3$ based superhydrophobic coating:**

Al$_2$O$_3$ nanoparticles were firstly functionalised by mixing them with 0.05 g of CTAB and stirred with 0.02 g of carbon nanotubes in 10 ml of de-ionised water at room temperature (~25 °C) for an hour. Then 1-1.2 g of Capstone ST100 was added into the mixture and kept stirring for 40 mins on the hotplate with its surface temperature set to 80 °C for between 40 mins and 60 mins. The rest of the procedure was the same as CeO$_2$ based superhydrophobic coating.
3.2.3. Spraying polymer nanocomposite coating

Glass substrates (or Al) were cleaned by immersing into ethanol for a sufficient amount of time (4-6 hours). For PFKE coating, the dispersion was sprayed using an airbrush: IWATA LPH-80 (1 mm nozzle), from a distance of ~20 cm. During spraying, the back pressure was regulated to maintain at 2 bars.

For Oxide-based nanocomposite coating, a glass substrate was firstly spin-coated with 1 ml of Capstone ST-100, which served as a primer. Coated glass slides were cured at 100 °C for 15 - 20 mins, and subsequently cooled down to room temperature. Then the coating dispersion was sprayed using an airbrush from a distance of ~20 cm with a nozzle diameter of 0.5 mm. During spraying, a back pressure of 3 bars was maintained. The coating thickness was controlled by varying the number of passes. Finally, the coated glass slide was cured at 150 °C for 30 mins.

3.3. Surface characteristics and robustness tests

3.3.1. Surface characteristics

The two key requirements for superhydrophobic surfaces are low surface energy and sufficient roughness. Fourier transform infrared spectroscopy (FTIR) with a universal attenuated total reflection (ATR) was used to analyse the chemical composition of the surface and to make sure the existence of a hydrophobic functional group(s). Scanning electron microscope was used to observe the surface morphology of the coating in micro/nanoscale. The SEM results give researchers some ideas of the roughness level of the surface and damage condition after the surface has undergone various robustness tests.

3.3.2. Wettability test

The hydrophobic performance of the coatings were analysed by measuring the $\theta_A$ and $\theta_R$. This was done by using an in-house setup which was basically made up of a light source, the specimens stand and a camera as shown in Figure 14a. A water droplet was dispensed and withdrawn from the surface of the coated specimens using a programmable syringe pump through a clinical needle, where the tip was filed down to a flat finish.
As the camera captures a video of a water droplet being dispensed and withdrawn from the specimen’s surface, the advancing and receding points are identified and a screenshot of those points were taken. The $\theta_A$ and $\theta_R$ were then measured using a MATLAB® image analysis program.

### 3.3.3. Mechanical durability tests

**Tape peel test (adhesion test):**
A strong bonding tape (VHB, 3M, with adhesion to steel value of 2,600 Nm$^{-1}$) was used to test the adhesion strength of the coatings. The tape was applied by rolling a 4 kg steel roller on the tape twice, followed by waiting for 90 seconds and then peeling off – the tape application and peeling-off comprised one cycle. The process was repeated with advancing and receding contact angle measurements following each cycle. A fresh piece of tape was used for each peel-off cycle.

For cross-cut (ASTM D3359-17) tape tests, cross hatch engravings were created on the coatings at 2 mm spacing using a sharp razor blade, followed by tape application using the 4 kg steel roller and peel-off (Figure 11a). After tape application, following the ASTM standard, 90 seconds were allowed to elapse before peeling off. These cross-hatch adhesion tests were performed using Elcometer 99 tape (adhesion to steel: 642 Nm$^{-1}$) and the VHB tape. In each case, following tape peel-off, the water droplet roll-off test was performed by placing a ~10 µL drop on the tested region and gradually tilting the coated sample.

**Taber abrasion test:**
Abrasion tests were performed following ASTM D4060, using a Taber abrasion machine (see Figure 11c.) at three different loads, 150 g, 200 g, and 250 g. The abrasion test samples comprised of coated 10 cm × 10 cm glass plates. Following the ASTM standard, each rotation of the substrate was counted as one abrasion cycle. The coatings’ advancing and receding contact angles as well as thickness were measured as a function of Taber abrasion cycles. Any abrasive particles or coating fragments appearing on the samples were rinsed off before thickness and the contact angles were measured.

**Sand abrasion test:**
250 g of sand grains (industrial sands grains from Travis Perkin, D < 0.5 mm) were dropped from 15 cm height onto a 30° tilted surface for 60 seconds. Sand grains slid down from the coated samples and recollected for the next cycle. $\theta_A$ and $\Delta \theta$ were measured after each cycle. Abrasion
tests were performed until the coatings lost their superhydrophobic property, by indicating high \( \Delta \theta \) values.

### 3.3.4. Chemical corrosion durability tests

The polymer nanocomposite coated glass slides were immersed in concentrated acidic solution (HNO\(_3\), HCl or Aqua regia solution) or alkaline solution (NaOH solution). Contact angle measurements (\( \theta_A \) and \( \Delta \theta \)) were performed on glass slides by taking them out from the solution, followed by drying. The measurements were taken after 2, 15, 30, 60 and 120 minutes of immersion in the solution.

![Diagram](image)

**Figure 14 (a)** Wettability tests were carried out by measuring the \( \theta_A \) and \( \theta_R \), the flow rate of syringe pump speed is set as slow as possible (0.03 L/h, 0.25 mm diameter needle). Drop impact test was carried out by using the same set-up, but the distance between the needle and surface was increased, therefore the droplet free-fell after detached from the needle and hit the surface with a certain speed.
Figure 14 (b) In Jet impact test, syringe pump was replaced by a high-pressure nitrogen tank with an electronic pressure valve therefore high-speed jet can be formed. The COMS camera was also replaced by a high-speed camera. Therefore the impact moment could be captured.

3.3.5. Liquid impalement resistance tests

Droplet impact test:
Water droplets of diameter of ~2.5 mm, which were generated using a fine needle fitted to a syringe pump, were dropped from different heights on horizontally positioned coated samples. The impact event was captured by using a high-speed camera. The impact images were analysed via MATLAB® and impact speed was calculated by using the law of free fall. The highest speed impact speed was 4.5 ms\(^{-1}\).

Jet impact test:
Pneumatic forcing of liquid through nozzles of different diameter were used to obtain stable and controllable high speed water jets (Figure 14b). An electronic on-off valve was connected to the high pressure nitrogen gas cylinder which was used to force water through a nozzle using a needle/syringe assembly. The supply pressure was regulated to within 0.1 bar resolution, with a maximum value of 11 bar.
Different water jet velocities were obtained by adjusting the gas pressure. Two different nozzles with a nominal diameter of 0.25 mm and 2.5 mm were used; the jet diameters were assumed to be the same as the nozzles. Due to system transients, upon application of the control signal on the electronic on-off valve, the gas back pressure on the piston inside the syringe was expected to ramp up to the set pressure. This transient process caused a time-dependent rise in jet speed before levelling off to a steady rate corresponding to the applied pressure. To reveal this transient process, the motion of the piston/water interface inside the cylinder during typical jet impact test was recorded by using a high-speed camera. The motion of the piston could be used to determine the jet speeds through simple mass conservation calculation, with the knowledge of cylinder and nozzle diameters.

3.3.6. Environmental / UV resistance

Polymer nanocomposite coated glass slides were placed inside a chamber fitted with an UV lamp of intensity \(~5\, \text{W/cm}^2\) in room condition with a relative humidity of 40%. \(\theta_A\) and \(\Delta\theta\) were measured on glass slides on a regular interval of time. The tests were conducted over a period of 20 days.

3.3.7. Optical characteristics tests:

The optical properties of the nanocomposite coating were tested using photonic countering measurement for light transmittance and haze measurements for light scattering.

**Photonic countering measurement:**

The photonic countering measurement system is consisted of a pointed light source (Ocean Optics, Halogen, Light source), with integrated optical amplification (Ocean Optics, HL-2000-FHSA). Coated glass samples with different coating composition and thickness were placed between the light source and a photonic high-sensitivity spectrometer (Ocean Optics, HR 2000+). The light source pointed to the spectrometer and released a beam for 2 seconds. The photonic spectrometer then measures the amount of light and transforms the data collected by the spectrometer into digital information. A spare glass slide was used as a reference to calculate the light transmittance percentage.
Haze measurements:
Light that is scattered upon passing through coated samples can produce a hazy field when objects are viewed through the sample. Haze can be measured by using set up and procedure according to ASTM 1003D [317] and ASTM 1044D [318] which included a compact fibre optic spectrometer, light source with integrated optical amplification and collimation lens, custom haze measurement sphere with diffuse transmission port and optional sample attachment clips. The sphere was mounted on a breadboard with an alignment track to aid positioning. The scattering data were analysed by a MATLAB® programme, with values for the percentage (±0.5%) of light scattered beyond a 1.4° and 4° ($\theta$) from the normal. Coated glass slides with different coating composition and thickness were tested under room temperature.
4. Experimental results and discussion

In this chapter, the wettability performance of different nanocomposite coatings on different substrates are presented first. All nanocomposite coatings achieve superhydrophobicity with the nanoparticles providing the required surface roughness and the polymer to reduce the overall surface energy [18]. Spectra results of FTIR are used to reveal the chemical compositions of the coatings and SEM image to show the surface morphology.

The relative composition of the nanoparticle and polymer is a critical factor, since over-use of polymer will cause a reduction of the surface exposure of the nanoparticles, thus leading to a reduction of the surface roughness and resulting in a relatively less hydrophobic surface. Therefore, in section 4.1, a study on how the “nanoparticle/polymer ratio” would affect coating hydrophobicity is carried out, in order to determine an “optimum” nanoparticle/polymer composition to achieve the best hydrophobicity.

In section 4.2, a series of durability tests results including mechanical, chemical, environmental and liquid impalement are presented, follows by thorough results analysis. Discussing the reasons for good durability performances, failure mechanism and more importantly suggestions of how to improve the coatings.

In section 4.3, three commercial available sprayable superhydrophobic coatings: HIREC 450, NeverWet and Ultra-Ever-Dry, were used to compare with the PKFE and oxide nanocomposite coatings on their durability (adhesion strength, abrasive resistance, chemical corrosion resistance and liquid impalement resistance).

In section 4.4, the optical properties of the oxide nanocomposite coatings are shown, follow by the discussion of factors that affect light transmittance and scattering of the coating.
4.1. Surface wettability and characteristics

4.1.1. Surface wettability and morphology

The hydrophobic performance of a surface is represented by the dynamic wettability characteristics of a water drop, i.e. its advancing contact angle ($\theta_A$) and contact angle hysteresis $\Delta \theta = \theta_A - \theta_R$, also known as the droplet rolling-off angle [57].

When using a camera to capture the images of a water droplet being dispensed and withdrawn from a coated surface, the advancing (or receding) points can be identified as shown in the screenshot, Figure 15a. The $\theta_A$ and $\theta_R$ can then be measured using a MATLAB® code as known circle fitting, where a circle is fitted onto the droplet and the contact angle is the angle of the tangent of that circle that passes the advancing/receding point.

The code works by first asking the user to define the contact line (i.e. the coating surface) by selecting two points, “A” and “B”, Figure 15a. The circle is then defined by selecting three appropriately spaced points, “P”, “Q” and “R”, on the water droplet. The code will then generate the circle by calculating the location of the centre of the circle, “C” and its radius, as below. This is done by first generating the lines “PR” and “PQ”. Two lines respectively perpendicular to “PR” and “PQ” are then constructed, intersecting at point “S”. The coordinates of the centre $(x_c, y_c)$ of the circle and the length of its radius is then determined using, regardless the location of the reference point.

\[
\begin{align*}
x_c &= \frac{x_P + x_S}{2} \quad \text{and} \quad y_c = \frac{y_P + y_S}{2} \\
\text{then} \quad \text{radius} &= \sqrt{(x_c - x_S)^2 + (y_c - y_S)^2}
\end{align*}
\]

The intersection point between the circle and the contact line, “T” is then identified and the line perpendicular to line “CT” is drawn, where the contact angle can then be measured. The accuracy of this measurement mainly depends on the quality of the image, measurement error is estimated to be around $\pm 5^\circ$; furthermore, the wetting area can also be determined, if needed.
Figure 15 Wettability measurement and SEM image of surface morphology for PKFE and oxide/PMC-base nanocomposite

(a) An image taken during a droplet advancing on the PKFE coating surface and MATLAB® code is used to determine the contact angle.

(b) $\theta_A$ and $\Delta\theta$ measurement of PKFE and 3 oxide-based nanocomposites. All $\theta_A$ are shown above 150° and $\Delta\theta$
lower than 10°, suggesting all surfaces are superhydrophobic (c) SEM images of PKFE and 3 oxide-based nanocomposites, showing their surface morphology. The last two SEM images are the enlarged images of the circled area, showing the agglomeration nature of CeO$_2$ and self-assembly nature of Al$_2$O$_3$ particles.

The nanocomposite coating was first sprayed on a glass slide, and the results show that the hydrophilic glass substrate surface changes to a superhydrophobic surface for all the four tested coatings, with a high $\theta_A$ and a low $\Delta\theta$, as shown in Figure 15b.

The $\theta_A$ among these four nanocomposites coatings were quite similar, with a range between 158° to 167°, and the $\Delta\theta$ range is between 2° to 5°. As mentioned, the difference of hydrophobic performance is strongly relating to the surface morphology and chemical composition. Therefore, SEM was employed to observe the surface morphology of these coatings.

It is clear that the morphology of SiO$_2$ and Al$_2$O$_3$ were quite similar, but these two have rather unique features when compared to the other two coatings (PTFE and CeO$_2$). For the PKFE coated surface, PTFE particles which had a size of ~200 nm assemble compactly, forming a rough surface. In this image, the polymer (epoxy resin) which were used to stick the particles together cannot be explicitly seen. The slight “inhomogeneity” was believed to be caused by the inconsistency of the spraying process. For the SiO$_2$ nanoparticles (~80 nm) and PMC nanocomposite, the alignment of SiO$_2$ nanoparticles were observed to be more organised, forming a more homogeneous surface, thus resulting in a rougher coating when compared to the PKFE coated surface, due to the self-assemble nature of SiO$_2$ nanoparticles [172,319]. This was clear from the results that SiO$_2$ coating has a larger $\theta_A$ and a lower $\Delta\theta$ than the PKFE coating.

Regarding the CeO$_2$ nanoparticles (~15 - 30 nm)/CNT and PMC nanocomposite, a relatively non-homogenous morphology was observed when compared to the previous two. CeO$_2$ nanoparticles show an agglomeration nature, and therefore, some area have a higher nanoparticle concentration. Polymer (PMC) layer was visible in the SEM image and porous structures were formed during the annealing process when nanoparticles quickly assembled and the polymer film broke up. This morphology of CeO$_2$/CNT/PMC nanocomposite was a good example of the hierarchical structure; the polymer pores offered a microscale roughness and certain agglomerated particles provide a nanoscale roughness. The variations in their morphology features depended on the material characteristics such as particle size, nature of the particle and polymer types.
SEM images can provide information that is needed when applying certain theories that were developed by other researchers for estimating the wetting state of these coated surfaces. For example, the determination of solid fraction (\(\phi\)) requires particle sizes/numbers from the SEM images; the (\(\phi\)) of an evenly distributed nanocomposite surface such SiO\(_2\) nanoparticles mixed PMC coating can be estimated by "\(\phi \approx N\pi d^2/4A\)" , where respectively “\(N\)” is the number of particles and “\(d\)” is their diameter and "\(A\)” is the selected area. For Figure 15b , \(\phi \approx 0.75\), where particle number was 2408, acquired from “ImageJ” using circular particle analysis [320], \(d \approx 0.08 \mu m\) (SiO\(_2\)) and \(A \approx 16.25 \mu m^2\). The capillary pressure which is preventing water liquid from penetrating the morphology can be calculated as:

\[
P_c = -\left(\frac{4\phi}{d(1-\phi)}\right)\gamma \cos \theta
\]

\(P_c \approx 1231 \text{kPa}\) , where for \(\gamma\) (surface engery) and \(\theta\) (water contact angle) for PMC is respectively 24 mN/m and 110\(^\circ\) [219]. A typical water droplet (50 mg, diameter \(~ 2.5 \text{ mm}\) [290,291], a contact area based on \(\theta\) of 150\(^\circ\) will have a static pressure of \(~1 \text{kpa}\) which is far less than \(P_c\), implying that the drop will experience difficulty spread and penetrate the coating.

Applying the above equation to porous micro roughness, as in Figure 15b for CeO\(_2\) coating, “\(d\)” is taken as the pore diameter (shadow represents pores)and “\(\phi\)” can be obtained by “ImageJ” via grey-scale measurement [321]. \(P_c \approx 66 \text{kPa}\) ,where “\(\phi = 0.45\)”, “\(d = 0.2 \mu m\)”, “\(\gamma = 24 mN/m\)”, and "\(\theta = 110^\circ\) [219]. Thus the static pressure of a typical water droplet would not be far too lower than \(P_c\), suggesting that there is a chance for it to penetrate.

### 4.1.2. Surface chemical composition

Fourier transform infrared (FTIR) spectroscopy was used to assess the compositions of the PKFE and oxide nanocomposite coatings Figure 16. Different hydrophobic function groups with low-surface-energy can be selectively identified from the results.

Epoxy resin (E) was selected as the polymer matrix to form nanocomposite with a nanoparticle due to its roughhouses and good adhesion nature. However, many commercially available epoxy has rather high surface energy and low water contact angle (WCA), Figure 16a. As mentioned in
“Section 2.1.3”, Xiu et al.’s [173] work, O\textsubscript{2} plasma and fluoroalkyl silane treatment was applied on top of the epoxy in order to create roughness and reduce surface energy. However, the issue of this approach was hydrophobic performance significantly degraded after the top surface was abraded. In this study, fluorination procedure was carried out on the epoxy resin resulted in low-surface energy throughout every layer of the coating. FTIR spectroscopy can be used to monitor the introduction of low surface energy functional group during the fluorination procedure.

A standard FTIR normally scans from 400 cm\(^{-1}\) to 4500 cm\(^{-1}\) wavelength, however researchers in particular noticed that there are many peaks within the spectra of the longer-wavelength in the region of 400 cm\(^{-1}\) to 1500 cm\(^{-1}\), which usually referred as the fingerprint region.

Though it is usually very difficult to identify any specific functional groups in this region, it does contain valuable information. The pattern of the absorbance peaks is unique to individual molecules, meaning that the data from an unknown sample can be compared to the IR spectrum of known standards in order to make a positive identification.

The epoxy resin backbone was connected (grafted) with low-surface-energy fluoropolymers via using fluorinated amine curing agent which was synthesized by reacting diethylenetriamine and heptafluorobutyric acid fluoropolymers. Fluorinated epoxy resin (FE), was formed and WCA increased to 80\(^\circ\), Figure 16a. Then, a selective, perfluoropolyether was blended into the FE (KFE), improving hydrophobicity (WCA increased to 90\(^\circ\)and introducing mechanical flexibility. After these steps, the FTIR spectra showed that the relevant peaks for function groups \(-\text{CF}_2\) (~1,150 – 1,250 cm\(^{-1}\)) and \(-\text{CF}_3\) (~550 – 650 cm\(^{-1}\)), proving that the fluorination procedure was successful. FTIR spectra also indicated the peaks of fluorinated function groups (~\text{CF}_n\)) were enhanced further after mixing with PTFE particle (PKFE) resulting in a WCA of 162\(^\circ\).

Additionally, the grafting and blending technique were safe and environmentally friendly due no involvement of any toxic organic solvents or by-products. Water is the only synthesis by-product from epoxy fluorination and evaporated at 100 °C in the progress. Therefore, there is no obvious O-H bond peak in the final coating FTIR spectra. (FTIR can also be used in detecting the increase of moisture content on the surface during environmental test, which will be discussed later.)

The overlapping of peaks within the fingerprint region is causing difficulty of identifying individual functional group. Therefore, in order to acquire further composition information of the coatings,
a full spectra analysis is often required, Figures 16b and c show the FTIR spectrum of the two oxide nanocomposites, Al₂O₃ and SiO₂ based. Both spectra show two absorption peaks at 1144 cm⁻¹ and 1200 cm⁻¹ which are attributed to the symmetric and asymmetric stretching vibrations of CF bonds in the perfluoro groups \((CF₃ - (CF₂)ₙ)\) of Capstone ST 100 [219,322]. A strong absorption peak at \(\sim 1750\) cm⁻¹ shows a clear signature of C=O groups of CNT in both spectra. Rest of the peaks at 2310 and 2350 cm⁻¹ in the Al₂O₃ based nanocomposite’s spectrum were attributed to the Al₂O₃ nanoparticles [323]. The 640 cm⁻¹ peak in the SiO₂ based nanocomposite’s spectra indicated the existence of the silica nanoparticle.

The use of FTIR spectra for chemical composition is essential in superhydrophobic nanocomposite study. Particularly when off-the-shelf commercial products are used, in our case, Capstone ST 100. FTIR spectra can reveal the composition of these products which is often protected from customers as a business secret. According to the FTIR spectra results, I could estimate the Capstone ST 100 is consisted water and poly(perfluoroalkyl methacrylic) copolymer (or perfluoroacrylic polymer). The presence of fluorinatated functional groups \((CF₃ - (CF₂)ₙ)\) that had lower surface energy than its polymeric backbone would segregate to the surface in order to reduce the overall surface energy. When the surface was uniformly covered with fluorinated array, a very low energy surface could be achieved. Moreover, further adjustment could be performed on the polymer if it is needed, based on the functional group information which is provided by the FTIR spectra analysis.
Figure 16. FTIR measurement shows chemical composition of PKFE and oxide/PMC-base nanocomposite. (a) Epoxy resin (E) before fluorination, with a water contact angle of ~43°. Fluoropolymer-grafted epoxy resin (denoted as FE resin), the WCA increased to ~80°. Blending the perfluoropolyether into the FE resin (denoted as KFE resin); the \( \theta_w \) further increases to ~93°. Incorporating PTFE particles to obtain nanocomposite coating (denoted as PKFE coating) with a \( \theta_w \) of ~162°. Follow by a FTIR spectra’s fingerprint region of pure epoxy resin, FE resin, KFE resin and the PKFE coating (all samples for Fourier transform infrared spectroscopy were...
hardened and dried at 100 °C for 1 hr. (b) and (c) Full FTIR spectra of oxide nanocomposite coatings (Al2O3 based and SiO2 based).

4.1.3. Nanoparticle concentration

Controlling the percentage composition of the nanocomposite is important due to its significant influence on the wettability of the surface as well as its durability. Therefore nanocomposites with varied PTFE nanoparticle concentrations were prepared in order to determine the optimal value required for achieving the best possible mechanical robustness while maintaining the superhydrophobicity. The surface morphology of some sample coatings with different particle loadings was examined under SEM.

As shown in Figure 17a, the SEM revealed that surface roughness increases with increasing the nanoparticle concentration that directly affects the surface wettability. Therefore the variations in the PKFE and oxide-based nanocomposites’ θA and Δθ with the nanoparticle concentration was explored and plotted in Figure 17b.

For the PKFE nanocomposite coated samples, superhydrophobicity was achieved at nanoparticle loadings exceeding 30 wt.%, and the superhydrophobicity further increased up to a point with loading around 75 wt.%. Beyond 75 wt.% the poor dispersion quality of the coating suspension resulted in visibly “unstable and dusty” (i.e. with loose particles on the surface) coatings of reduced roughness, also with an insufficient quantity of the polymer for binding the particles together. This phenomenon was reflected by a slight decrease in θA and an increase in Δθ with an increase in particle loading from 75 wt.% to 80 wt.%. Overall, for PKFE, 75 wt.% particle loading was considered to be the optimal nanoparticle concentration for superhydrophobicity.

The optimal nanoparticle concentration for oxide-based nanocomposites was determined by both the size and nature of the particle [16,178]. Due to the self-assemble nature of SiO2 nanoparticles, only 75 wt.% nanoparticle concentration (particle to PMC polymer ratio is 3 to 1) was required to achieve superhydrophobicity.

However, at least 83 wt.% of CeO2 nanoparticle concentration (particle to PMC polymer ratio was 5 to 1) was required to achieve superhydrophobicity due to the agglomeration nature of the particles. The concentration of CeO2 could be reduced to 75 wt.% by blending in a very small
amount (10 wt.% of the original weight of CeO$_2$ nanoparticle) of CNT, as CNT not only introduced extra roughness but also improved CeO$_2$ nanoparticle dispersion.

During oxide-based nanocomposites solution preparation, the $\pi$-bond and $\pi$ electrons of the acrylic group from the copolymer can be delocalized by the vacant 4f orbitals which were provided by the oxidation state 2 of the metal oxide nanoparticle ($\textit{SiO}_2$, and $\textit{CeO}_2$). Since in CNT, the carbon particle had vacant p orbitals which also led to the delocalization of $\pi$ electrons, thus facilitating the mixing of copolymer and metal oxide nanoparticle, resulting in better dispersion of the solution, coating homogeneity and a longer storage time.

Figure 17b shows the hydrophobicity of the nanocomposite improved with the increase of nanoparticle concentration, but it also suffers from particle overdose at 83 wt.%. Therefore, in this work unless otherwise stated, the PKFE coatings and oxide based nanocomposite were prepared with their optimal nanoparticle concentration.

SEM can be used to estimate the thickness by imaging the cross-section of the coating, Figure 17c. It is worth mentioning that for those particles that were particularly hard to disperse, and if the nanoparticle concentration is low, the surface roughness can be increased via applying more coating material (more spray passes) on the surface at initial stage, resulting in an improved hydrophobicity. However, this method was only effective when the thickness is relatively small; for nanocomposite, once the coating is built up, surface characteristics should be unchanged regardless of the increase of thickness.

Nevertheless, coating thickness and nanoparticle concentration significantly affected the optical properties and durability of the nanocomposites coatings, mechanical durability in particular. In the following section, experimental results of different durability tests, e.g. mechanical, chemical, environmental, liquid impingement resistance will be presented and discussed.
Figure 17. Particle concentration and coating thickness affects wettability (a) CeO₂ based nanocomposite coated surface with 30 wt.% particle concentration (left) and 75 wt.% (right). (b) At low concentration 30% wt.% both PKFE (left) and oxide-based (right) nanocomposite cannot achieve superhydrophobicity due to lack of roughness. The glass substrate was initially roughened by sandpaper manually, then applied the 30% wt.% PKFE coating, superhydrophobicity is achieved. (c) The SEM image of the cross-section of a CeO₂ based nanocomposite with low nanoparticle concentration and low thickness, demonstrates that surface is inhomogeneous which resulted in low hydrophobicity. However, with the increase of thickness (spraying), more material is deposited on the surface therefore hydrophobicity improved.
4.2. Durability test results and discussion

Durability of superhydrophobic coatings is a critical issue for applications such as outdoor photovoltaic cells or self-cleaning windows. A durable coating not only can shorten the maintenance period but also reduce the associated costs. Therefore, a series of durability tests were carried out, covering mechanical aspect (e.g. adhesion, abrasion, solid impact), chemical aspect (e.g. strong chemical immersion), environmental aspect (e.g. UV exposure, long-term storage) and liquid impingement resistance aspect (e.g. drop impact, jet impact). All experiments on the nanocomposite coatings were performed following closely various industrial standards. Discussion on the coatings’ durability and how to improve the coating durability further would be addressed.

4.2.1. Mechanical durability

Adhesion is an important consideration for coating development since lack of sufficient adhesion to the substrate will cause the coating unsuitable for almost any kind of applications. However, adhesion tests have rarely been reported, compared to other mechanical durability testing (Table 2), and they were to be carried out first in this study.

A peel-tape testing on a cross-hatched surface (ASTM D3359) was performed. There are specific tapes suggested for this type of test but generally those with the highest adhesion strength are considered most suitable. This crosshatch test is relatively easy to perform and can provides a simple standardized assessment of substrate adhesion.

In the second adhesion test, the hydrophobicity performance (\(\theta_A\) and \(\Delta \theta\)) was re-measured after tape peeling cycles. The coating that retains its superhydrophobic properties must have significant adhesion to the substrate and internal adhesion. However, it can be difficult to interpret explicitly the reason of failure since it is not easy to assess which of the following two mechanisms that degrades the wetting properties. First, the partial deposition of the adhesive tape material onto the surface (i.e. the surface chemistry may change). Second, the partial destruction of the surface (i.e. removal of micro or nano-features that will change the surface geometry and/or chemistry). In order reduce the adhesive tape material which may left on the tested surface, the tested surfaces were rinsed with water after every peeling cycle.
Figure 18 Substrate adhesion (peeling) test results (a) Application of a strong adhesive tape on to the PKFE coating. (b) Water drops beaded up on the surface and rolled off easily even after 30 tape peel cycles (c) Outcome of crosshatch tape peel test performed on a PKFE coated glass plate (10 cm * 10 cm) with Elcometer 99 tape in accordance with ASTM standard D3359-17, showing no coating peel off. Water droplets still beaded up and rolled off easily from the tested region. (d) Crosshatch test with the VHB tape showing less than 5% damaged. (e) $\theta_A$ and $\Delta \theta$ were measured after each cycle (Elcometer 99 tape) for oxide-based nanocomposite coating. (f) Repetitive tape (VHB tape) peeling test was performed on PKFE coating and $\theta_A$ and $\Delta \theta$ were measured every 10 cycles.

The ASTM standard (D3359-17) adhesion cross-hatch tests were performed on all nanocomposite coatings using two different types: a standard Elcometer 99 (adhesion to steel: 642 Nm$^{-1}$) and the high-tack VHB tape (2600 Nm$^{-1}$). The Elcometer 99 tape did not remove any coatings, and none
or less than 5% of the coating was removed by the VHB tape and together with the observation that water drops rolled off easily from the tested area for an inclination angle of less than 5°; these all suggested the wetting capability survived the adhesion tests, Figure 18a, b and c.

The cross-hatch tape tests were not entirely suitable for metal oxide nanocomposite due to the polymeric matrix being transparent, resulting in the difficulty of identifying any removal coating material on the tapes. Therefore, repetitive tape application and peel-off cycles were only used to assess the wettability degradation (Figure 18d).

As shown in Figure 18c, $\theta_A$ decreased and $\Delta \theta$ increased after individual peels. At the end, insufficient surface roughness caused the surface to lose its superhydrophobicity due to both the flattening of the surface by the roller and the removal of coating material by peeling (see later Figure 21d). As expected, the durability against peeling could be improved by increasing the thickness of the coating; the 5-spray-pass coated sample lasted for only 3 peeling cycles, but the 15 passes coated sample remained superhydrophobic after 7 peeling cycles. If the coating is thick, a new layer with similar structure became exposed once the previous layer of got removed; this represented the benefit of using nanocomposite coatings as having similar structure throughout the coating depth.

For completeness, the repetitive tape peeling test was also performed on the PKFE nanocomposite coatings using the high-tack VHB tape. Figure 18b shows a single peel-off did not affect the drop contact and sliding angles, thus providing a first indication of the coating robustness. It was noted that ten peel-off cycles would cause a slight reduction in $\theta_A$, from 158° to ~155° and a slight increase of hysteresis ($\Delta \theta$) from 3° to 4° (see Figure 18f). However, the coating maintained excellent water repellency even after 30 tape peel-off cycles, Figure 18f; this is also evident from there being virtually no change in the coating morphology (see later Figure 21c, respectively for fresh and tape-peeled coatings) and the complete bouncing of a water drop impacting at ~0.22 m/s$^{-1}$.

For improving the coating adhesion to the substrates some good practices should be followed: (1) Increasing the surface roughness of the substrate by abrading by sand-paper or etching by chemical so that the applied coating can “lock” better to the substrate. (2) Cleaning the surface properly by various solvents (e.g. piranha solution) or O$_2$ plasma, to eliminate oil or other hydrophilic substance (3) Ensure chemical compatibility of the coating with the substrate by introducing appropriate
materials or primers. (4) Post-curing can also help sometimes to improve the adhesion to the substrate, depending on the polymer used [110].

Rubbing between a superhydrophobic surface with another solid surface is a common everyday occurrence and therefore abrasion is considered important for characterizing mechanical durability of the coatings. The linear abrasion test is currently the most popular durability evaluation method. Based on the pervious studies [35,245,254,261] that investigated the wearing durability of superhydrophobic surfaces, it is recommended to employ a downward pressure of at least 10 kPa against the surface during the test. Under such testing conditions, the surface should withstand tens or even hundreds of abrasion cycles to be judged as robust.

In this study, the abrasion resistance of the coatings was tested first using Taber abrasion technique based on the ASTM standard, where loaded wheels were abraded against the PKFE nanocomposite coated substrates, mounted on a rotary platform (see Figure 19a). The changes in the coating’s $\theta_A$ and thickness with cycle number are plotted in Figure 19b for three different loads. Each abrasion data point (averaged) and error bar (for example, in Figure 19c) was obtained from distinct measurements on three coating samples and at least at three different locations on each. After 100 abrasion cycles, the $\theta_A$ of the PKFE coating remained above 150° for loads of 150 g (~15 kPa) and 200 g (~20 kPa) and reduced to ~146° for 250 g (~25kPa , Figure 19b). This represented the abrasion rate was progressively getting higher with increased abrasion loads. Note that in each case, $\Delta \theta$ remained under 10°.

The abrasion-resistance and the water-repellence were attributed to the multi-fluorination strategy, which enables the PKFE nanocomposite coatings to maintain their texture even while being degraded by abrasion. Micro/nanostructures with low surface energy extending through the entire coating depth, therefore even when the top layer was abraded away, a new layer would expose with a similar hydrophobicity performance, until the coating was completely worn out (Figure 19c).
Figure 19. Abrasion resistance (Taber) test results (a) Picture of Taber abrasion machine featuring the abrasive wheels and mounted PKFE coated glass plate. (b) The change in $\theta_a$ and the coating thickness reduction with Taber abrasion cycles with three different abrading loads. $\theta_a$ remained at $\sim 155^\circ$ at 150 g load, $\sim 151^\circ$ at 200 g and $\sim 146^\circ$ at 250 g, even after 100 abrasion cycles. (c) Water drops beaded up on the PKFE coating even after 100 abrasion cycles and could easily be rolled off. The circular abraded region is also clearly visible due to the reduction of coating thickness from abrasive wear. And the schematic illustration of a PKFE coating which can still sustain superhydrophobic after abrasion. (d) Effect of nanoparticle loading on the hydrophobicity and wear resistance of the PKFE nanocomposite coating. Error bars were obtained from distinct measurements on 3 different coating samples and at least at 3 different locations on each.

Additionally, the effect of nanoparticle concentration/loading on abrasion resistance was investigated thoroughly to see whether the optimal concentration for mechanical durability also
matches well with that for wettability. The results presented in Figure 19b shows the coating $\theta_A$ before and after 100 cycles of Taber abrasion. The figure also shows the variation of thickness reduction with particle loading during abrasion test. The trend of $\theta_A$ of the coating after 100 abrasion cycles follows closely with that of the fresh surface, though quantitatively the $\theta_A$ decreases consistently across different loading values. When the loading increases to beyond 75 wt.%, the $\theta_A$ of the abraded surface continue to increase as opposed to that observed on a fresh coating.

Below 75 wt.%, the thickness reduction of the abraded coating increases slightly and steadily with increasing particle loading. However, from 75 wt.% to 80 wt.% loading, there was a sharp increase in thickness reduction.

PTFE nanoparticles influence wear resistance of the PKFE coating in two ways. Due to their lubricity and softness, PTFE reduced the wear coefficient of epoxy resin [324] and thereby helping to reduce the wear of the coating. However, as the particle loading went up, the mechanical robustness should decrease due to the softness of PTFE and relatively weak interfacial bonding between PTFE nanoparticles and the epoxy resin; the quality of nanoparticle dispersion also went down at very high particle concentration as noted from some visibly rougher coatings. Above 75 wt.%, they became the dominating factors, resulting in a sharp reduction in coating thickness during abrasion test (Figure 19d). Overall, it appears that a 75 wt.% particle loading was an optimum value for both water wettability and abrasion wear resistance.

Based on these experimental results, some general recommendations for improving the abrasion resistance could be made: (1) to achieve low-surface energy throughout the entire coating layer (2) to reduce the wear coefficient by controlling the hardness of the micro/nanostructure. (3) to ensure that strong interfacial bonding between nanoparticles and polymer. (4) to ensure good quality of nanoparticle dispersion.

Furthermore, it is suggested that to test the coated surfaces with different abradants in order to examine the different types of wear that might occur on a surface; for instance, using a rubber (smooth, resilient), a textile (smooth, deformable) or a vitrified (sandpaper) material can provide a more comprehensive overview of the surface's response to various abrasive actions. In this work, due to limited resources and time, only the rubber wheel was used.
Unfortunately, all the oxide-based nanocomposite coatings were found to be not strong enough to withstand the Taber abrasion, and they all lost their superhydrophobicity after only 1-2 cycles of abrasion under 250g load. Therefore, \textbf{sand abrasion test} was performed instead, by exposing the coated surface to sand impact. According to what have been reported so far, recommended conditions for sand impact test include releasing sand particles above the coating with the following steps: particle diameters of approximately 200 µm, release heights of 20 to 50 cm, and exposure time of 1-5 minutes with 40 – 50 g total mass of released particles. After performing these tests, if the surfaces still exhibit a high $\theta_A$ and low $\Delta \theta$, they can be considered as mechanically durable superhydrophobic materials [266–268,270].

A camera was used to record the process of 250 g of sand grains (industrial sands grains from \textit{Travis Perkin}, D $<$ 0.5 mm) impacting the surface within 60 seconds, after they were dropped from a 15 cm height. Sand grains slid off from the coated samples (tilted at 15° to horizontal) and recollected for the next cycle, Figure 20a. Wettability performance, $\theta_A$ and $\Delta \theta$ were measured after each impact cycle, up to 7 cycles, and superhydrophobic quality of the all oxide nanocomposite coatings exhibited a deteriorating trend with increasing abrasion cycles. For the Al$_2$O$_3$ coating, the $\theta_A$ reduced to 149° while $\Delta \theta$ was found to increase to 10° after 7 cycles of sand abrasion. The rest of the nanocomposites had similar performance, losing their superhydrophobicity after 6-7 impact cycles. Most of the tested coatings have a thickness $\sim$10 µm, but some were done with thickness $\sim$1-2 µm. The results showed all coatings with thickness of $\sim$1-2 µm lost their superhydrophobicity after 1-2 cycles.
Figure 20. Solid impact resistance (sand) test results (a) Sand impact test on Al₂O₃ based nanocomposite coating, 250 g of sands was dropped 15 cm from above the coated surface and slide down within ~60 seconds. After the sand impact test, water droplets were placed on the surface, making sure they rolled-off and their self-cleaning property remained. (b) Hydrophobic performance of three oxide composites during sand impact tests. The performances are rather similar among these coatings; all of them lost their anti-wetting property after 6-7 cycles due to the damage to the surface morphology.
All the mechanical durability tests carried out were intended to assess the nanocomposite in three areas: adhesion to the substrate, the capability to resist tangential abrasive forces and the ability to resist solid dynamic impact. A coating will be considered mechanically durable if it maintains its static anti-wetting state and low water adhesion properties after the test cycles.

In relation to mechanical durability, it is essential to understand the mechanisms that can cause a loss in superhydrophobic performance via the experimental results. In general, the top surface of the coating is damaged or removed by external forces during peeling, abrasion or solid impact.

The Cassie Baxter state on the superhydrophobic surface might be destroyed due to the change of surface morphology and chemical composition. A subsequent transition to the energetically more favourable Wenzel state occurs, where the liquid now penetrates into the rough asperities, touch the substrate and inducing the strong pinning effects, eventual the surface change to hydrophilic. Therefore, preserving the surface morphology and chemical composition become the most important aspect for mechanical durability.

The surface morphology of superhydrophobic coatings can be quite different. The Cassie–Baxter wetting state requires at least one scale of micro- or nanoroughness and the hydrophobic performance can be further enhanced if both are employed, forming a hierarchical structure. The micro/nano/hierarchical structure support the droplet on the upper part of the surface so that numerous air pockets are formed on the droplet-substrate interface.

The height of the structure must exceed a threshold value, which can vary for different types of textures (see Section 1.1.2), in order to suspend the liquid surface in air between two neighbouring peaks, to maintain a Cassie–Baxter state. The wetting state transition happen once the height is below the threshold value and the non-wettability will be lost. Such a height reduction can happen when textured surfaces undergo mechanical abrasion. E.g. the height of the micro-features of the PKFE progressively decreasing during abrasion until it goes below the threshold, resulted in a Wenzel wetting state. The morphology of the PKFE coating after 100 abrasion cycles of (250 g load) was presented Figure 21a, showing a plastic deformation spot.

Sand impact not only reduced the height of the micro/nano/hierarchical structure but also created large cracks on the surface. Figure 21b shows the SEM image of the surface structure after 7 cycles of sand abrasion. Both the micro and nanostructure were damaged by the sand grains. Not only
particle deformation could be seen but also some cracks could be found. It was believed that when the size of the crack was small, it would create some extra roughness which can contribute towards superhydrophobicity [35]. However, when the cracks grew larger, they could lead to Wenzel state wetting transition hence with a reduced superhydrophobicity.

Figure 21. (a) A SEM image of the morphology of the PKFE coating after 100 abrasion cycles of (250 g load); the surface roughness was decreased due to the height of the morphology being reduced by abrasion. (b) A SEM image of a coated surface after sand dropping abrasion, showing the flattened or damaged surface structure by sand. (c) A SEM image is showing the morphology of the PKFE coating after 30 tape-peel cycles, with no observable damage to the coating morphology. (d) A SEM image of the oxide nanocomposite coated surface after 7 tape peels,
showing some damaged areas by tape peeling (e) A hydrophobic surface coating on a rough pattern may get easily worn off, and hydrophilic bulk material is exposed as a result. (f) If rough features are fabricated from hydrophobic material, no hydrophilic pinning sites can be introduced due to wear. (Schematics are modified and reprinted from [35])

Preserving the surface chemical composition is also a very essential aspect for mechanical durability. Loss of any functionality due to a change in the surface chemistry by mechanical wear depends on the degree of the bulk homogeneity of the coating. If the coating is chemically homogenous throughout the bulk (the whole coating) and unless the entire coating is removed (down to the substrate), no loss of chemical uniformity will appear. Figure 21c shows the SEM image that even after 30 tape-peel cycles, the surface homogeneity of the PKFE coating still remained unchanged.

Some of the two-step commercial superhydrophobic coatings, such as Never-wet or Ultra-ever-Dry, uses surface functionalization strategy to induce anti-wetting properties. The removal of the thin upper layer is enough to lose the desired surface chemistry. This is a major concern in terms of durability since very thin monolayers that are usually on the molecular to nanoscale level tend to be removed easily by the application of even minor abrasive or adhesive forces.

In this study, high nanoparticle concentration would cause an increase amount of loose particles and a reduction of binding strength between particles. Under such conditions, surface homogeneity and chemical composition was hard to maintain, resulted in fast degradation of superhydrophobicity, Figure 21d. The superhydrophobicity degradation which related to a change in surface chemical composition, as presented schematically in Figure 21e, while Figure 21f shows a loss in geometric topology.

The most common strategy for improving mechanical durability is to employ surfaces that can withstand physical (adhesive, abrasive, impact) forces while retaining the surface morphology features and the hydrophobic chemical composition. The abrasion test for the PKFE coating shows that after 100 abrasion cycles the total thickness of the removed material was 160 µm. Unlike in the oxide cases where the non-wetting properties disappeared almost instantly after one to two cycles, there was a gradual decrease of the θ, with increasing abrasion cycles for PKFE. This is probably due to the fact that the surface becomes smoother while maintaining its hierarchical texture.
The coating was able to maintain its non-wettability even after 100 abrasion cycles due to its self-similar nanostructure that essentially keeps the desired morphology and mechanically durability even upon abrasion. The above implies that the thickness of the superhydrophobic nanocomposite coating is strongly related the mechanical durability.

4.2.2. Environmental and Chemical (corrosion) durability

In addition to mechanical wearing, corrosive or chemical process such as weathering, UV irradiation and chemical etching can also cause nanocomposite coatings to loss their superhydrophobicity. This phenomenon is mostly caused by the decomposite (degradation) of the low surface energy material. This must be taken into consideration when material are designed/selected for specific applications. For example, electrolyte corrosion might occur when the nanocomposite coatings are to be used on the hull of ships that are in contact with sea water. Another example, nanocomposite coatings that are consisted of photocatalytic polymers/particles will experience photo-degradation and lost its anti-wetting property if exposed under strong sunlight.

Worst of all, decomposition of nanocomposite coating in most cases is an irreversible process, once the coated surface lost its superhydrophobicity, and recoating is often required [229–231]. Therefore, a series of tests on the superhydrophobic coating’s long-term storage, outdoor exposure (UV light exposure), strong acid/alkalis were carried out accordingly in this study.

The storage time for the coating solution and coating was investigated first. Due to both PKFE and oxide nanocomposite using an evaporative solvent (acetone, isopropanol/water), both coating solutions have to be stored in a seal glass bottle. The PKFE dispersion was highly stable and could be stored under room condition for more than 1 month. Whereas, the oxide nanocomposite solution can maintain stability for only one week due to particle precipitation. All the coatings can maintain superhydrophobicity in room condition for more than 6 months after they were applied to the substrate.

An UV chamber which fitted with an UV lamp of intensity ~5 W/cm² was used to simulate sunlight exposure, in a room condition with a relative humidity of 40%. Two type of nanocomposite coatings: SiO₂ and Al₂O₃ based were tested.
Figure 22. UV chamber test results for (a) Al₂O₃ based and (b) SiO₂-based nanocomposite coating. Al₂O₃ based nanocomposite coating remained superhydrophobic after 20 days whereas SiO₂-based lost its anti-wetting property after 10 days. FTIR spectra was taken for (c) Al₂O₃ based (d) SiO₂ based nanocomposite coating. Referencing moisture content FTIR (e) show that the O-H peak is located between 3000 - 3700 cm⁻¹ and H-O-H peak is located between around 1700 cm⁻¹ [325]. (f) After 10 days of UV chamber test water droplet pinned on the surface and failed to recede.
Figure 22a, shows under UV radiation, the hydrophobicity of the Al₂O₃ based coatings gradually degraded over the time, but with a $\Delta \theta$ remains below $\sim 10^\circ$ even after 20 days of exposure. SiO₂ based samples lost its low hysteresis as its value was increasing, and finally the water droplet pinned on the sample after 10 days (Figures 22b and f). This phenomenon might be explained by the PMC polymer being damaged by the UV light, and then the exposed SiO₂ particles (in amorphous and porous form) started collecting moisture from the humid environment [325–327].

Figure 22d, FTIR revealed that for the SiO₂ based coating, the two peaks between 3000 - 3700 cm⁻¹ and between around 1700 cm⁻¹ increase significantly over the 10-days UV exposure. Based on a referencing FTIR spectra for water (moisture), the increase of intensity of these peaks indicated that water (moisture) content of the SiO₂ based coating increased significantly after 10 days.

Al₂O₃ based samples appeared to have a better durability against UV and moisture exposure, remaining as superhydrophobic for $\sim 20$ days and collecting a small amount of moisture when compared to SiO₂, as reflected by a smaller increase of the peaks, Figure 22e. Due to the limitation of time and resources, UV tests were not performed on PKFE.

All my nanocomposite coatings were also developed with chemical robustness in mind. Thus, to assess harsh chemical corrosion resistance, a concentrated acid, nitric solution (HNO₃, 70%) and a 1M basic sodium hydroxide (NaOH) solution, and an even aqua regia (a mixture of highly concentrated hydrochloric acid (HCl) and nitric acid (HNO₃) in a 3:1 volume ratio — a strongly acidic and very potent oxidizing solution) were used respectively. Although such extreme harsh chemical corrosion is not very common in practice, it is a meaningful way to establish the coating chemical robustness.

Furthermore, the first obvious application of a superhydrophobic coating is to prevent liquid penetration on a surface and reach the substrate under the coating, when the coating is placed underwater or corrosive solution, Therefore, stability against immersion in liquids is very important for the successful implementation of superhydrophobic surfaces in shielding applications, e.g. ship hull coating.
One point needs to be made clear here. The robustness of a surface against immersion is measuring the penetration of a liquid into the surface structure when the surface is immersed in the liquid due to hydrostatic pressure. This must not be confused with composition changes caused by chemical corrosion that renders a superhydrophobic surface losing its non-wettability. The study only focused on the latter examining the chemical stability of low surface energy coatings after immersion in corrosive liquids. Therefore, tests were performed by dipping the coated glass slides into the chemical solutions, and over a certain time period, the coating stability is evaluated by taking the sample out of the liquid, measuring the $\theta_A$ and $\Delta\theta$ after rinsing with water and drying.
Figure 23. Chemical (corrosion) resistance test results for (a) The Al$_2$O$_3$ based nanocomposite coating maintained superhydrophobic for up to 2 hours and no measurements of hysteresis were possible. (b) Test results of aqua regia corrosion for the PKFE nanocomposite and $\theta_A$ is maintained above 150° after 60 mins. (c) test results for NaOH solution (1 M) corrosion and the superhydrophobicity is maintained after 12 hours. (d) Morphology of the PKFE coating after 60 min in aqua regia solution (e) Morphology of the PKFE coating after 12 hours in 1 M NaOH solution. The error bars denote standard deviations, obtained from distinct measurements on three different coating samples and at least at three different locations on each.

Figure 23a showed that the oxide samples remained superhydrophobic after having been immersed in nitric acid (PH = 1) for $\sim$120 mins. It was found the $\theta_A$ degraded gradually over immersion time
and finally droplets were seen to be pinning on the surface after 2 hours, indicating the loss of surface superhydrophobicity.

Preliminary test of the PKFE coatings showed no significant degradation of hydrophobic property in nitric acid solution, and therefore further tests using aqua regia, a more corrosive acid solution, were carried out. The results are shown in Figure 23b and the coating maintained a $\theta_A$ of greater than 150° after 60 min of immersion. Addition tests with 1 M NaOH for 12 hours of immersion showed (Figure 23c) that within experimental error, the $\Delta \theta$ of $\sim 10^\circ$ or lower was maintained. SEM images (Figures 23d and e) show no noticeable damage. One of the main reasons for such excellent chemical resistance is due to the inherent chemical inertness of our rationally selected PKFE nanocomposite constituents.

Environmental or chemical damages on superhydrophobic coating are mostly via changing or decomposing the chemical composition of the material that might impair its physical properties. Therefore, an in-depth understanding of the coating’s chemical properties is essential, and follow-up analysis of the degraded nanocomposite coatings, caused by environmental or chemical damages, is necessary. In this study, nanocomposite coatings are prepared with various type of nanoparticle (e.g. PTFE, SiO$_2$, Al$_2$O$_3$ and CeO$_2$) and different polymers (e.g. epoxy resin, PMC, perfluoropolyether (PFPE)) and the environmental and chemical stability in chemical perspective are discussed as follow.

As mentioned in Section 2.1.3, TiO$_2$ and ZnO have been widely used in the superhydrophobic nanocomposite. These inorganic white pigment nanoparticles have also been applied for UV blocking, e.g. textile fabrics to provide UV protection. For TiO$_2$ and ZnO, their direct-band-gap and semiconductor characteristic make them a good absorber, having an excellent UV-blocking of the whole spectrum of UV-R (both UVA and UVB fall into the regions of 315-400 and 280-315 nm, respectively, of the solar spectra).

In addition, the photo-oxidative ability of TiO$_2$ and ZnO must be also considered. Photo-oxidation of TiO$_2$ and ZnO is driven by their photocatalytic nature, derived from the formation of photogenerated charge carriers (hole and electron). This phenomenon happens upon the absorption of ultraviolet (UV) light corresponding to the band gap, Figure 24a. The photogenerated holes in the valence band diffuse into the TiO$_2$ (or ZnO) surface and react with the adsorbed water molecules, forming hydroxyl radicals ($\cdot$OH), Figures 24b and c.
Figure 24. Photogeneration phenomenon mechanism for metallic oxide-based nanocomposite (a) Schematic illustration of the formation of photogenerated charge carriers (hole and electron) upon absorption of ultraviolet (UV) light. (b) Combined reduction-oxidative model for the photonic induce hydrophilic effect after TiO$_2$ particle exposed to UV irradiation. The reducing and oxidizing regions are spontaneously formed: (1) when oxygen is absent, protons are reduced to produce interstitial hydrogen atoms with no organic compound present; (2) when oxygen is present, the latter is reduced to superoxide or hydrogen peroxide with no organic compound present; (3) when oxygen is absent, protons are again reduced, while oxidation of organic compound occurred; (4) when oxygen is present, the latter is again reduced, while oxidation of organic compound occurred. In (1) and (2), holes react with water to produce a variety of possible hydrophilic moieties, such as (•OH). (c) Schematic illustration of mechanism of photo-induced hydrophilicity. (d) Hydophobic TiO$_2$ coated samples were change to hydrophilic after UV irradiation.
The photogenerated holes and the hydroxyl radicals oxidize the organic molecules nearby on the TiO$_2$ surface. Meanwhile, electrons in the conduction band participate in reduction processes, which typically react with oxygen molecules in the air to produce super-oxide radical anions (O$_2$ $•^-$), Figures 24b and c. (The trapped electron $e_{tr}^-$ and hole $h_{tr}^+$ react with acceptor or donor molecules, respectively.) [328–330].

The wettability of TiO$_2$ (or ZnO) nanocomposite surface changed dramatically under UV-light irradiation. The surface changed to hydrophilic due to chemical conformation changes of a surface. Most of the holes were subsequently consumed by reacting directly with adsorbed organic species or adsorbed water, creating •OH radicals as previously described. Nevertheless, a small proportion of the holes were trapped at the lattice oxygen sites and would reacted with TiO$_2$ itself, which would also weaken the bonds between the lattice titanium and oxygen ions. Since the water molecules can interrupt these bonds, the new hydroxyl groups would be formed (Figure 24c). The singly coordinated OH groups produced by UV-light irradiation are thermodynamically less stable and have high surface energy, thus leading to the formation of a hydrophilic surface.

Moreover, in the of TiO$_2$ photo-electro-chemical mechanism, surface oxygen vacancies are created at the bridging sites of TiO$_2$, resulting in the conversion of Ti$^{4+}$ sites to Ti$^{3+}$ sites, and Ti$^{3+}$ is considered to be favourable for dissociative water adsorption, forming hydrophilic domains. Wang et al. (1997) experimentally demonstrated a TiO$_2$ nanoparticle based hydrophobic sample transform to a hydrophilic surface after UV radiation (Figure 24d).

Therefore, SiO$_2$ and Al$_2$O$_3$ particles were chosen in this study due their smaller photosensitivity than ZnO, since the bands gap of SiO$_2$ (9 eV) and Al$_2$O$_3$ (6 eV) are much larger.

(For further information on photocatalysis, see Hoffmann et al. (1995) [331], photo-electron-chemical mechanism for different metal oxide is described in detail.)

Polymers such as PMMA, PS, PVC are often used to form superhydrophobic nanocomposite. However, these material also suffer from photodegrading when get exposed to the sun for a long time. Photodegradation includes photodissociation, the breakup of molecules into smaller pieces by photons, irreversible change of a molecule's shape, and the additions of other atoms or molecules. A common photodegradation reaction is oxidation.
Photooxidative degradation of polymers, which includes processes such as chain scission, crosslinking and secondary oxidative reactions, takes place via radical processes. For instance, poly(vinyl chloride) (PVC) products can be attacked by UV light at wavelengths greater than 250 nm as their spectrum energies are sufficient to cleave the C-Cl bonds in the PVC molecules. This will lead to photodegradation, resulting in the formation of long conjugated-double-bond (polyene) sequences, (CH=CH)$_n$, and subsequent discoloration of the PVC.

In the presence of oxygen, an oxidation reaction can develop simultaneously to form carbonyl groups in the PVC chains that also suffer from cleavages and cross-linking. These structural changes due to direct UV exposure compromise the physical and mechanical properties as well as the wettability, making the surface hydrophilic. PMMA and PS degrade in air when exposed to sunlight as the photonic energy is sufficient to cause the breakdown of the polymeric C-C bonds, and as a consequence further photolysis and/or dissociation of side group occurs.

Photostability can be achieved through the addition of special chemicals, such as light stabilizers or UV stabilizers, that can slow down or prevent photo-degradation. Comparing to TiO$_2$ (3.27 eV) and ZnO (3.37 eV), CeO$_2$ has a relatively small band gap (3.1 eV), corresponding to about 400 nm, meaning that CeO$_2$ can almost absorb light in the entire UV region. This fact makes CeO$_2$ a good UV absorber. After CeO$_2$ gets dispersed into the polymer, it engages with the first step of the photooxidation process, that is, it absorbs the harmful UV radiation before it reaches the photoactive chromophoric species in the polymer molecule (300–400) nm. Thus, the energy dissipates in a manner that does not lead to polymer photosensitization. More importantly, unlike TiO$_2$ and ZnO, CeO$_2$ is not a photocatalyst, and therefore the surface wettability will not be significantly affected by UV irradiation. In the work of Pattamasattayasonthi et al. (2011) [332], CeO$_2$ was mixed into PVC polymer, resulting in a significant improvement of UV stability without compromising the surface wettability.

Another method of enhancing photostability is by introducing fluorinated functional groups. Because C-F is the most stable bond among all possible carbon-element bonds (Figure 25a), the introduction of fluorine atoms into polymer structures improves their chemical stability, in addition to providing weather resistance as a consequence of photochemical stability, solvent and oxidation resistance attributed to fluorinated groups.
Acrylic polymers are often used for the formulation of protective coatings, due to their film forming nature and excellent adhesion [333–335]. Acrylic and methacrylic monomers with fluoroalkyl groups in the side chain can be acquired by acylation of the parent fluorinated alcohol with acrylic or methacrylic acid chloride, provided that at least one methylene group is linked to the alcoholic hydroxyl. These monomers can be homo- or co-polymerised by a free-radical mechanism allowing design of a vast class of partially fluorinated polymers with properties tailored to different applications, depending on the length of the fluorinated chains, on the copolymer average composition and on the overall fluorine content. Capstone St-100 which contains poly(perfluoroalkyl methacrylic) copolymer was selected for the superhydrophobic nanocomposite coating. Not only because it is expected to have good adhesion, film forming and low surface energy properties, but also the photo and chemical stabilities due to the strong fluorinated chain and high fluorine content.

A superhydrophobic nanocomposite is said to be chemically stable if it is not particularly reactive in the environment or during normal use and retains its superhydrophobicity on the timescale of its working life expectancy. In particular, the anti-wetting function is retained in the presence of air, moisture, corrosive material, etc. Superhydrophobic nanocomposite coatings have many potential outdoor applications. Therefore, UV chamber test was used to simulate the under moisture and sunlight conditions. Later on, immersion of the coated surfaces into strong acid or alkaline solution could test their corrosion resistance, evaluating whether the coating can survive under harsh condition such as acid rain or polluted sea water.

Polymer chemical (corrosion) resistance correlates strongly with the the number, the relative position of the chemical groups along the chain. Strong acid or alkali attacks the polymer often causing chain-scission, including side-group scission, which involves the rupture of the primary valence bonds, followed by cleaving the parallel bond strength between the atoms. The bond energies of carbon-fluorine (C-F) and carbon-hydrogen (C-H) are respectively about 116 and 97 kcal mole⁻¹. Therefore, the polymers and nanoparticles, such poly(perfluoroalkyl) methacrylate copolymers, fluorinated epoxy resin and polytetrafluoroethylene (PTFE), used in this study which contains($C_n$) – ($CF_n$)ₙ would be more resistant to chemical degradation than polyethylene that contains ($CH$) – ($CH$)ₙ.

Polymeric degradation can cause the change of physical parameters such as molecular weight, molecular weight distribution, crystallinity, chain flexibility, crosslinking, branching, etc., that will
eventually affect the overall physical properties of the polymer e.g. hardness. For example, a drop in the molecular weight of the polymer, which leads to weaker inter-chain forces, thus lowering the mechanical strength and softening point, and increasing susceptibility to solvent and chemical attack.

Generally speaking, crystalline polymers which have high melting points are more stable towards oxidative and chemical attack than their amorphous counterparts. Because of the higher energy input is required to overcome both intermolecular and intramolecular forces, which can lead to chain stiffening [336]. These forces influence how the crystalline (as opposed to amorphous) polymers behave towards thermal, chemical or oxidative degradations.

Crosslinking introduces strong primary valence restraints preventing the separation of the chains from one another as well as constraining main chain movements. This led to an invariably increases of stiffness, creep resistance, brittleness, thermal and chemical stability. The crosslinking density (number of crosslinks per unit weight or volume) and type of crosslinks, (e.g. length, flexibility, chemical) control the extent of stability. As for the chemical nature of the crosslinks, carbon-carbon (C-C) crosslinks tend to be more stable towards thermal and chemical attacks than sulfur-sulfur crosslinks (S-S). Shorter crosslinks increase stiffness as well as giving rise to denser structures, which contribute to greater thermal and chemical stability.

For polymers which has branched structure tend to oxidize more readily than those which have linear structures. The oxidation rate increases with the degree of branching. These have been attributed to steric factors that tend to weaken intra- and inter-molecular forces. Polymer branching also encourages the crystalline formation among closed packing structures [336]. The creation of tertiary carbons is also a result of branching. As a result, hydrogen atoms bonded to tertiary carbons are more susceptible to chemical attack than the hydrogens bonded to primary or secondary carbons.

In summary, polymers which has strong bond energy (such as C-F), branched structures and in crystalline form should be more chemically stable than polymers which have weak bond energy (Such as C-H), linear structure and in amorphous form.
(Factors such as secondary valence bond strength, backbone rigidity, or copolymerization, etc can all relate to polymer degradation, Hawkins (1984) and Hamid (2000) will provide more information.)

(a) **Bond Energies, Kcal mole⁻¹**

<table>
<thead>
<tr>
<th>Bond</th>
<th>Energy</th>
<th>Bond</th>
<th>Energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>C–F</td>
<td>116</td>
<td>Cᵦᵦ–H</td>
<td>100</td>
</tr>
<tr>
<td>C–H</td>
<td>97</td>
<td>Cᵦᵦ–N</td>
<td>110</td>
</tr>
<tr>
<td>Si–O</td>
<td>106</td>
<td>Cᵦᵦ–O</td>
<td>107</td>
</tr>
<tr>
<td>C–C</td>
<td>83</td>
<td>Cᵦᵦ–Cᵦᵦ*</td>
<td>100</td>
</tr>
</tbody>
</table>

(b) **Diethylenetriamine**

(i) Summary of bond energy of typical bonds in polymers.

(ii) Mechanism of fluorinated amine

(c) **Fluorinated epoxy**

**Figure 25.** Mechanism of fluorinated amine curing agent synthesis and hardening (PKFE coating).

(a) Summary of bond energy of typical bonds in polymers. (b) Mechanism of fluorinated amine
curing agent synthesis. (i) Heptafluorobutyric acid reaction with diethylenetriamine. (ii), Excess heptafluorobutyric acid reaction with diethylenetriamine. (c) Hardening mechanism of epoxy in PKFE coating.

After reviewing the possible failure mechanisms of the polymer due to UV irradiation and chemical attack, the loss of superhydrophobicity of the nanocomposite coating can be explained. The presence of highly stable C-F bonds in PMC and fluorinated epoxy resin can improve the chemical and photochemical stability [337–340]. Therefore, the Al₂O₃ based nanocomposite could maintain its superhydrophobic after 2 weeks of UV exposure and PKFE lasted 2 hours immersing in Aqua Regia solution. However, after a longer period of UV irradiation (~20 days), the degradation mainly occurred on the tertiary position of acrylic units of the PMC, followed by extensive chain scissions, resulted in the loss of superhydrophobicity as explained by Chianotore et al. (2001) [337]. They researched on the photochemical stability and photo-degradation pathways of main-chain and side-chain fluorinated poly(meth)acrylate-based copolymers, studying the mixture of two copolymers: 1H,1H,2H,2H perfluorodecyl methacrylate and 2-ethylhexyl methacrylate (XFDMA-EHMA). It underwent a large molecular weight loss (25%) after 15 days, implying that the degradation of the fluorinated poly(meth)acrylate.

Moreover, for the silica-based nanocomposite coating, the surface properties of amorphous silica, which is considered to be a moisture adsorbent, depend in general on the presence of silanol groups (Si-O-H) on the particle surface. Silanol groups are formed during synthesis of the silica or as a result of rehydroxylation of dehydroxylated silica when it is treated with water or aqueous solutions. With a sufficiently high concentration, these groups turn the coated surface hydrophilic. The OH groups act as the centres of molecular adsorption during their interaction with adsorbates capable of forming a hydrogen bond with the OH groups, or, more generally, of undergoing donor-acceptor interaction. In this study, the silica-based nanocomposite coating was exposed to UV light in a chamber (relative humidity = ~40 %) for a long time. The humid environment and photonic-degraded polymer increased the hydroxyl groups absorption for silica nanoparticle, resulted to a hydrophilic surface.

The conversion of linear epoxy resins to the three-dimension cross-linked structures was possible via hardening reaction [341]. The epoxy polymer within the PKFE nanocomposite was hardened/cross-linked/cured by reacting with a polyamine-diylenetetramine. It is expected that during the chemical resistance test, the acids attack not only the unreacted NH₂ and NH groups,
but also N groups that always exist in the molecular epoxy-resin network formed in the hardening process. Therefore, a high-molecular epoxy resin was chosen due to its lower fraction of N groups. Bearing in mind of this, as long as the hardening process was performed using diethylenetriamine, easily attackable positions, represented primarily by noncarbon atoms or groups, Figure 25b, are often created.

By mixing the heptafluorobutyric acid with diethylenetriamine solution, fluorination was initiated through reaction of carboxy group with amine. Chemically stable carbonyl group and fluorous group were created, Figure 25b. The epoxy resin was harden by the fluorinated amines at 100 °C, new bonds appeared, some functional groups decayed, and the epoxy resin structure underwent changes, all the changes are reflected by the chemical and mechanical properties of the hardened material. At the beginning, the primary aminic hydrogens enter into the first-stage reaction with the epoxide groups. This reaction runs at a substantially higher rate than the subsequent reaction of secondary polyaminic hydrogens with the residual epoxide groups. The epoxy hardening mechanism is illustrated in Figure 25c, depicting the reaction of epoxide groups with the secondary amines in the F-amine.

The theoretical quantity of polyamine needed can be calculated when the contents of epoxide groups in the resins are known. Moreover, people who fabricate PTFE coatings should pay attention to avoid “overdosing” of diethylenetriamine. The hardening process is ran by reaction of primary amino groups. Overdosing will create a considerable number of non-reacted secondary amino group and may give rise to the appearance of linear macromolecules. These linear macromolecules is considerably vulnerable to corrosive attack therefore the overall chemical stability would be compromised.

Another critical factor regarding the extraordinary chemical stability of the PKFE nanocomposite coating is that it contains 75 wt.% (particle loading) of PTFE particle. The chemical resistance of PTFE is outstanding, partly because of the strength of C-F bonds, and there are no solvents which could dissolve PTFE at room temperature [336].

Moreover, although photodegradation test was not done on PKFE coatings, epoxy resins were considered possessing aromatic groups with strong absorption in the UV range (about 300 nm), making epoxy structures vulnerable to UV degradation. What happens after the degradation of the fluorinated polymer is also a concern. Copolymer with a long perfluoroalkyl group might break
down into perfluorinated acids, which may represent a toxic threat [178]. Therefore, further study should be carried on examining what chemicals would be released when these fluorinated nanocomposites degraded.

4.2.3. Liquid impalement resistance

For liquid impalement resistance of the superhydrophobic nanocomposite coatings, water drop and jet impact tests were used. The drop impact tests were performed by releasing individual water droplets from a certain height to enable gravity led acceleration of the droplets and achieve different impact speeds. Figures 26a to d show the drop impacts on PKFE and oxide nanocomposite coatings at different speeds. These high-speed images captured the key features of the droplet impact process at 3-4 different speeds on different samples. At low speed (e.g. 1 ms$^{-1}$ in Figure 26), the impact is characterised by droplet spreading, recoil and complete bounce off from the surface. At higher speeds, the impact $W_e$ is high enough for the droplet to splash and atomize.

As the Figure 26 shows, at $\sim$2.6 ms$^{-1}$ to $\sim$4.6 ms$^{-1}$ the droplet atomized upon impact and the resulting droplet fragments spent much less time on the substrate; down to $\sim$8.0 ms compared to 15.3 ms at $\sim$1 ms$^{-1}$, i.e., more than 50% reduction in contact time. This phenomenon is due to atomization (splashing) of the droplet following the impact at a relatively high liquid Weber number ($W_e$) = $\rho V^2 d/\gamma_{LG}$, where $\rho$ denotes the liquid density, $\gamma_{LG}$ is the liquid/gas interfacial tension, $V$ is the impact speed and $d$ is the characteristic length scale, taken as the diameter for both the jet and droplets in this study (the $W_e$ values are shown in the Figure 26) [324]. The reduction in contact time observed here at high $W_e$ is distinct from the reduction in contact time through surface texturing or the observed scaling of the contact time with drop resonance timescale, both of which have been obtained through impact studies at low $W_e$ numbers (typically < 102) [75].

Once the droplet impact speed exceeded a limit, water would penetrate the coating texture and caused liquid impalement which could be observed typically as either a tiny remnant droplet (viewed from the side) or as a liquid patch (viewed from the top) [76,342]. The impalement speed for different oxide nanocomposite coating was recorded and shown in Figure 26d. The liquid impalement speed was affected by the particle type and size, and the coating thickness. Figure 26d shows that for 5-10 um thick Al$_2$O$_3$ nanocomposite coatings the impalement speed was $\sim$4.2 ms$^{-1}$, and for 1-2 um CeO$_2$ nanocomposite coating, it was $\sim$2.5 ms$^{-1}$. 
Figure 26. Liquid impalement resistance (droplet impact) test results (a-c) Water droplets bouncing and atomizing upon impact on PKFE coating at different speeds. (a) Impact speed ~1.0 ms⁻¹, water droplet does not break up. (b) Impact speed ~2.0 ms⁻¹, water droplet starts to break up and the main body of the droplet bounces off, but few very small water droplets scatter on the surface. These droplets were highly mobile on the surface. (c) Impact speed ~4.6 ms⁻¹, water droplet atomizes (breaks up) upon impact and its substrate contact time is reduced dramatically. Note the substrate contact is made in the second image in each row. Thus, contact time (starting from second image in each row) is ~8.0 ms⁻¹ at the impact speed of ~4.6 ms⁻¹ as opposed to from ~15.3 ms for ~1 ms⁻¹. (d) Droplet impact on the Al₂O₃ nanocomposite coating respectively with impact speed of 1.9 ms⁻¹, 2.6 ms⁻¹, 3.2 ms⁻¹ and 4.2 ms⁻¹. With the increase of impact speed, droplet behaviour after the impact changed from recoil and rebound to shatter and bounce off. (e)
Impalement impact speed for different oxide based nanocomposite at which small droplet fragments pinned on the surface.

Note that unlike the oxide nanocomposite coatings, on the PKFE coatings after drop impact and splashing, no signs of liquid impalement into the surface texture was observed. The high atomization and splashing as well as reduction in contact time are beneficial when designing, say in anti-icing superhydrophobic surfaces. [75,76,343]

Let’s revisit some of the theories from Chapter 1 and compare them with the experimental observations, regarding the maximum drop impact pressure and the capillary pressure of a textured surface.

\[
P_{\text{max}} = 0.88 \left( \frac{R \mu_g^{-1} V^7 \rho_l^4 \gamma}{St \pi} \right)^{\frac{1}{3}} \quad \text{and} \quad P_C = -\left( \frac{4 \phi}{d(1 - \phi)} \right) \gamma \cos \theta
\]

where \( R \) is the droplet radius, \( \mu_g^{-1} \) is the air viscosity, the \( St = \mu_g / VR \rho_l \) is the Stokes number, \( \rho_l \) is the liquid density, \( Ca = \mu_g V / \gamma \) is the capillary number, \( P_0 \) is ambient pressure, and \( \phi \) is the solid factor of the surface.

For a water droplet which has a \( d = 2.5 \) mm and impact speed of \( V = 4.5 \) m/s, the \( P_{\text{max}} \) can be calculated as \( \sim 806 \) kPa where \( \mu_g = 1.85 \times 10^{-5} \) kg/ms, \( \gamma = 72 \) mN/m, \( \rho_l = 997 \) kg/m\(^3\). The \( P_C \) was estimated in Section 4.1.1, based on the SEM images and textured analysis. For the nanoscale homogenous surface such as \( \text{Al}_2\text{O}_3 \) or \( \text{SiO}_2 \) based nanocomposite coating, the \( P_C \) was estimated \( \sim 1200 \) kPa which is quite close to the impalement pressure. For the porous and aggregation structure such as the \( \text{CeO}_2 \) based coatings, which has a \( P_C = \sim 66 \) kPa and the surface was predicted to fail the drop impact test.

The experimental result did match very well with the theoretical prediction, \( \text{CeO}_2 \) based 1-2 \( \mu \text{m} \) coatings has the impalement speed of \( \sim 2.5 \) m/s in the experiment, the \( P_{\text{max}} \) can be calculated as \( \sim 83 \) kPa at this speed, which is larger than \( P_C = \sim 66 \) kPa. As expected, the impalement speed was found to increase with the thickness for the \( \text{CeO}_2 \) based nanocomposite (Figure 26e), due to the increase of surface roughness and the increase in \( P_C \).
Surface roughness and $P_C$ can also be improved by forming a hierarchical (microscale and nanoscale) structure. In general, a rougher surface or a complex surface structure will increase the $P_C$, and subsequently improve impalement resistance. If two surfaces have a similar solid fraction ($\varnothing$) (i.e. a similar $P_C$), the surface which has smaller gaps between the asperities (or particles) both at micro and nanoscale will have a better impalement resistance [77].

Droplet impalement and impact characteristics (contact time, spreading/recoiling manner and splash transition) are not only determined by the surface texture and impact speed. Other factors such as surface/droplet temperature also play an important role. Regarding this topic, Deng et al. (2010) [77], Bird et al. (2013) [344], Liu et al. (2014) [345] and Lv et al. (2016) [346] worked systematically and discussed the dynamics of droplet impact on superhydrophobic surfaces.

The attainable droplet impact speed is a function of height which was limited to $\sim 1.5$ m in the current set up. The PKFE nanocomposite coating repelled droplets and showed no sign of liquid impalement at $4.6$ $\text{ms}^{-1}$. Thus, for reaching a higher liquid impact speed, water jet tests were employed. The setup shown schematically in Chapter 3, Figure 14 was used to obtain a stable and controllable high speed water jet. A nitrogen gas cylinder connected to an electronic pressure valve was used to provide pressurised gas to force water through a nozzle/syringe assembly. With a nozzle diameter of $2.5$ mm (water jet diameter was $\sim 2.5$ mm), $4$ ml of water could be discharged in $\sim 380$ ms – allowing the high-speed camera to record the process. This is equivalent to an average jet speed of $21$ $\text{ms}^{-1}$ ($\text{We} \sim 15,000$).

The supply pressure of the gas cylinder was set at $11$ bar and the supply line to the syringe set-up was equipped with an on-off valve which was electronically controlled via a computer. When the valve was signalled to open, the piston accelerated up to a point after that it began to slow down. The motion (time-distance data) of the piston/water interface inside the cylinder was recorded by using a high speed camera, to be used to determine the jet speeds through simple mass conservation calculations based on the cylinder and nozzle diameters.

The time $\Delta t$ for the piston to move by a distance of $\Delta h$ was taken from the recording, and the jet speed ($V$) can be determined by using $\pi D^2 \Delta h / 4 = \pi d^2 V \Delta t / 4$, where $D$ is the cylinder diameter, $d$ the nozzle (jet) diameter. By calculating the jet speed over several successive intervals, the maximum speed of the test could be noted. The same test was repeated several times to obtain an
average value of those maximums. This gave a maximum impact speed of 35.1 ms\(^{-1}\) (Figure 27), for a gas pressure of 11 bar, with a corresponding \(W'_{\text{el}} \approx 43,000\).

The PKFE surface showed no signs of liquid impalement. This was the highest \(W'_{\text{el}}\) achieved on a superhydrophobic surface to the best of my knowledge. After water jet impact, small water droplets were observed to bounce off from the impact spot, indicating the intactness of water repellence even at such a high jet impact speed of \(\sim 35\) ms\(^{-1}\) (Figure 27).

**Figure 27.** Liquid impalement resistance (Jet impact) test results (a) Water jet velocity calculation by recording the piston/water interface motion.
Figure 27. Liquid impalement resistance (Jet impact) test results (b) Highest jet impact speed tested on a superhydrophobic surface. The top row images capture the jet impact test. The bottom row images capture a remaining water droplet from the nozzle—well after the jet impact test—impacting on the substrate and bouncing off completely, indicating an absence of surface damage. The setup enabled testing of PKFE nanocomposite coatings up to a highest jet impact speed of 35.1 ms\(^{-1}\) with the corresponding \(W_e/\theta_i\) ~43,000—the latter \(W_e/\theta_i\) points to the highest ever impalement resistance reported. After the water jet impact test, the surface showed no signs of damage or impalement. This was also tested by water drop roll-off tests and measuring the restitution coefficient at the location of jet impact. (c) The 2.5 mm diameter water jet was at laminar regime at low speed and change to full turbulent when the speed reached ~20 ms\(^{-1}\).
The impact of water jets of 0.25 mm and 2.5 mm diameter respectively were recorded, for different pressure settings. The corresponding impact speeds and We₈ values were determined, and the jets at different speeds were classified into different regimes (Figure 27c). The finer jets (0.25 mm diameter) atomize following substrate impact at high speeds, while the larger jets form an axisymmetric flow trajectory as marked by the dashed line seen in Figure 28a. The ability of the PKFE coatings to withstand repeated jet impact was tested by subjecting them to a 0.25 mm jet at 25 ms⁻¹ 20 times, for ~10 s each time. No damage was found to incur.

The PKFE coatings were also tested with impacting jets (0.25 and 2.5 mm diameter, respectively) striking the surfaces inclined at 45° for jets) using up to ~35 ms⁻¹ and We₈ ~43,000 for the 2.5 mm diameter jet. The speed was at the upper limit achievable in our set-up and the corresponding We₈ is already 4 – 10 times higher than in recent works [343][347]. Post-jet impact contact angle measurements were made at the impact region, showing a θₐ of 159° (Figure 28b). SEM was also employed to examine the surface morphology (Figure 28c) and no observable damage was noted.

To be assertive of a lack of liquid impalement into the surface texture, droplet impact was performed again at the same region, and the result confirmed a complete rebound. Additionally, low speed droplet impact tests were used to determine the coefficient of restitution [348] before and after the jet impact tests. In analogy with a rubber ball bouncing off from a rigid surface, the restitution coefficient for a droplet bouncing off a surface is defined as the ratio of droplet speed at the point of lift-off during a rebound to the droplet speed just before impact [348]. High speed videos of the droplet impact on the PKFE coating were digitised and processed by MATLAB® to obtain the impact and lift-off velocities. The results are plotted in Figure 28d, which shows the restitution coefficients measured from both the fresh PKFE and post-highspeed jet impact coatings.
Figure 28. Liquid impalement resistance (restitution coefficient) test results (a) A high-speed water jet impacting on a coating with a speed of $\sim 21 \text{ ms}^{-1}$ and $\text{We}_{l} \sim 15,000$; the maximum speed tested on the surfaces was $\sim 35 \text{ ms}^{-1}$ ($\text{We}_{l} \sim 43,000$). (b) A water drop on a post jet impact tested
PKFE surface, Scale bar = 2.5 mm. (c) SEM image of the morphology of a water-jet-impacted PKFE surface, showing a rough structure with no damage. Scale bars, 10 µm (left) and 1 µm (right).

(d) The restitution coefficient of a rebounded droplet measured before and after the high-speed jet impact test, plotted as a function of drop impact speeds (the corresponding Weber numbers are plotted as top horizontal axis). Larger error bars at low speeds were due to the position errors in the image processing, as it was difficult to judge whether the droplet had completely lifted off. At higher speeds (> 0.3 ms⁻¹) the restitution coefficient before and after jet impact was rather comparable, reflecting a lack of liquid impalement into the PKFE surface texture.

Note that these experiments were performed with slightly smaller droplets (diameter ~1.9 mm) and at lower impact speeds to avoid large variability in the droplet shape during droplet transit, which affected the restitution coefficient measurements [349,350]. Error bars were obtained from measurements on 3 different coating samples at no less than 3 different locations for each sample. The error bars are larger at low impact speed due to greater positional errors, as also reported in the experiments by Richard et al. (2000) (2002) [348,349]. At progressively higher speeds, the restitution coefficient for both the fresh and post-impact PKFE coatings seem to stabilize at ~0.9. Such a high value of restitution coefficient corresponds to low adhesion of the surface towards the droplet and a lack of liquid impalement during jet impact, as observed in this study. The Figure 28d also shows two horizontal lines, at respectively restitution coefficients of 0.91 and 0.85, that correspond to lossless, spherical (0.91) or elongated (cylindrical, 0.85) lift-off of the droplet after impact [348–350].

Pressure balance analysis was first performed to understand why a coating has a strong impalement resistance. Similar to the droplet impact, impalement of liquid into a hydrophobic surface texture is resisted by capillary pressure that can be expressed as $P_c = -\left(\frac{4\theta}{d(1-\theta)}\right)\gamma\cos\theta$. The liquid meniscus impalement is favoured when the combined dynamic and water hammer pressures due to the liquid impact is larger than $P_c$. The dynamic pressure can be expressed as $P_d = 0.5\rho V^2$. The water hammer pressure originates from the liquid compressibility, as defined by $P_{wh} = kZ_eV$ given in Maitra et al. (2014) [76], where $k$ is an empirical constant and $Z_e$ is the effective acoustic impedance of the liquid and substrate (coating) system and can be written as:
The effective acoustic impedance is a combination of liquid and substrate acoustic impedances, $Z_l$ and $Z_s$, respectively, and is defined as the product of its density, $\rho$, and speed of sound through it, $c$. The subscripts $l$ and $s$ denote the liquid and the substrate, respectively. Typically, water hammer pressure is much larger than the dynamic pressure and, therefore, controls the liquid meniscus penetration into the texture. For further insight, $Z_e$ can be written in a normalized form as:

$$Z_e = \frac{Z_l Z_s}{Z_l + Z_s} = \frac{\rho_l c_l c_s \rho_s}{\rho_l c_l + c_s \rho_s}$$

For rigid substrates (i.e. $Z_l \ll Z_S$), thus, the right-hand side of the equation becomes unity and we can write the water hammer pressure to be:

$$P_{wh} = k Z_l V = k \rho_l c_l V$$

This equation is often used in the literature [324] for rigid substrates. However, for light and flexible substrates/coatings, the approximation of $Z_l$ being much smaller than $Z_S$ will not hold. To illustrate this, the normalized effective acoustic impedance ($Z_e/Z_l$) is plotted against the normalized substrate acoustic impedance ($Z_s/Z_l$) as seen in Figure 28d, and zones of flexible and rigid substrates are marked in orange and blue colours, based on the data of various material from Onda Corporation [351]. Clearly for flexible substrates and coatings, the effective impedance was lower than that for rigid substrates; this would reduce the magnitude of $P_{wh}$.

The flexibility of the PKFE coatings was demonstrated by spraying it on paper. Even, having crushed the coated surface multiple times manually, the superhydrophobicity of the surface remained. The flexibility arises due to the homogeneous blending of the fluorinated epoxy with perfluoropolyether (Krytox) and soft PTFE nanoparticles. The softness of these coatings is in fact enhancing its impalement resistance. During impact of a droplet or a jet on a substrate, the impalement of the liquid meniscus into the surface texture is primarily influenced by a transient peak in the water hammer pressure ($P_{wh}$), which depends on the acoustic impedance of the liquid/substrate combination.
In $P_{wh} = kZ_e V$, since the $P_{wh}$ is directly related to $Z_e$, a reduction in $Z_e$ would result corresponding in a same percentage drop in water hammer pressure.

Figure 29. Liquid impalement resistance is affected by coating softness (a) Variation in normalized effective acoustic impedance with changes in the normalized substrate acoustic impedance. Flexible substrates or coatings clearly have lower effective acoustic impedance, which
will reduce the peak water hammer pressure on these substrates. (b) Droplets were placed on top of the inclined coated substrate (oil-infused PKFE or just PKFE).

A fused silica was taken as an illustrative example of a relatively rigid, which has a similar $Z_s$ of aluminium but a much lower $Z_s$ when compared to harder metal/alloy such as titanium, stainless steel. The water hammer pressure for the latter will correspondingly be even higher on these substrates. At room temperature, as in this study, for water $Z_s \sim 1.5$ MRayl, for epoxy $Z_s \sim 3$ MRayl, for PTFE $\sim 3$ MRayl and that for fused silica $\sim 12$ MRayl (data were obtained from Onda Corporation [351]). In Figure 29a, epoxy (similar to PKFE coating) and fused silica as a typical rigid substrate are marked. The effective normalized acoustic impedances for epoxy and fused silica (see Figure 29a) are 0.67 and 0.89, respectively. The difference is as much as $\sim 25\%$, helping to explain the excellent liquid impalement resistance shown by the PKFE coatings.

A recently proposed way for achieving liquid repellence [352] was to use immiscible oil-infused (oil: perfluoropolyether) textured surfaces to achieve low $\Delta \theta$. In this study, though perfluoropolyether (that is, Krytox 1506 oil) is used, but it was for the purpose of creating a softer PKFE coating instead of exploiting the immiscibility of the oil with water for water repellency.

An experiment was performed to observe the droplet motion on the PKFE coating and the experiment was repeated when the PKFE coating was oil-infused. The infusion was done by gently smearing a few drops of Krytox on the PKFE coating, as demonstrated in Figure 29b. The results show a much faster droplet motion on the PKFE coating compared to the infused surface, confirming a much higher drop adhesion with the oil infused surface due to oil viscosity [353]. Therefore, my strategy to blend oil (Krytox) in the coating formulation has a clear benefit.

### 4.3. Comparison with commercial sprayable superhydrophobic coating

The PKFE and metal oxide composite coatings is used to compare with three different commercial superhydrophobic coating in terms of durability. The $\text{Al}_2\text{O}_3$ based coating used in the comparison is $\sim 15 \mu\text{m}$ thickness, prepared following the procedures presented in Section 3.2, with the optimum particle concentration ratio. (In Figure 30, presenting the comparative data, this coating is denoted as $\text{Al}_2\text{O}_3$ based.)
The three different commercial material used are: NTT-AT HIREC 450 from Japan, Ultra-Ever Dry and NeverWet from Euro/U.S.A, which were all prepared by spraying, in accordance with the supplier’s guidance. Ultra-Ever Dry and NeverWet are two-part coatings, i.e., they used first a primer for adhesion improvement. This is in contrast to PKFE, Al₂O₃ based and HIREC 450, which are all one part sprayable formulations, and thereby offer an advantage in field application.

**Figure 30.** The PKFE and oxide based coating were used to compare with several commercial available sprayable superhydrophobic coatings (HIREC 450, Neverwet and Ultra-Ever Dry). Al₂O₃ based 15 um thickness coating was chosen to represent oxide-based coatings. Al₂O₃ based and HIREC 450 are one part coatings just as PKFE, whereas NeverWet and Ultra-Ever Dry are two-part coatings, requiring a primer layer. (a) Tape peel cycles sustained by coatings before reaching a contact angle hysteresis ($\Delta \theta$) beyond 10°. PKFE performance is 4-6 times better than the rests including the oxide-based coatings. (b) A number of Taber abrasion cycles with a loading of 250 g, survived before $\Delta \theta$ increasing beyond 10°; PKFE is about twice as good compared to the next best coating. Al₂O₃-based coating lost its superhydrophobicity after 1-2 cycles. (c) Results of NaOH
exposure tests, with PKFE showing excellent chemical corrosion resistance and nearly one order of magnitude better the rests. (d) Jet impalement tests show critical impalement speeds and $W/e$ for other coatings (see also the inset), whereas PKFE remains dry (indicated by the green arrow) up to maximum attainable jet speed and $W/e$ in our setup; demonstrating well over an order of magnitude improvement. Error bars were obtained from distinct measurements on 3 different coating samples and at least at 3 different locations on each.

The comparison was presented in Figure 30, following the procedures outlined previously in the “experimental section”. Figure 30a shows the number of repeated tape peeling cycles that a coating could sustain before the contact angle hysteresis ($\Delta \theta$) increased to above $10^\circ$, which is taken as losing superhydrophobicity. Whereas the oxide-based nanocomposite and commercial coatings survived an average of 5-7 cycles, PKFE coatings lasted for 30 cycles, representing a 4-6 folds improvement. It is worth mentioning that the Ultra-Ever Dry started to show signs of physical damage after 5 peeling cycles, and the primer layer (adhesive layer) was fully detached from the glass substrate after ~7 peeling cycles.

As it is shown in Figure 30b, PKFE coatings survived 80 abrasion cycles (under the Taber abrasion test) at a load of 250 g, which was nearly twice as good as the Ultra-Ever Dry coatings that lasted about 45 abrasion cycles and was nearly four times better than the NeverWet coatings. The HIREC 450 and oxide-based nanocomposite coatings appeared fragile against the Taber abrasion, most likely due to the vulnerable surface morphology.

Figure 30c shows the results of chemical corrosion resistance tests. PKFE maintained superhydrophobicity ($\Delta \theta < 10$) after 12 hours of 1M NaOH exposure, but the oxide nanocomposite and all the commercial coatings got damaged in a couple of hours at most. HIREC 450 fell apart in 5 minutes likely due to chemical reaction between the coating and the alkane. PKFE coatings seem to have much better chemical robustness; demonstrating nearly an order of magnitude better resistance to NaOH exposure.

The results of jet impact tests are presented in Figure 30d, showing the maximum jet speed (hatched bars) tested and the corresponding $W/e$ (filled bars). Note the green arrow above the bars for PKFE coating is meant to indicate that the maximum of impalement resistance (jet speed) for PKFE coatings has not been reached due to experiment limitation. For the oxide nanocomposite and commercial coatings, the jet diameter was of 0.25 mm and each of these coatings showed
liquid impalement when a certain speed was reached. The liquid impalement was tested by placing a droplet at the location of impact and assessing whether the droplet rolled off at a tilt angle (10°). The PKFE coatings were also tested repeatedly with 0.25 mm jets but showing no signs of impalement. Figure 30d presented the jet speed and $W_e$ for the PKFE coatings using a 2.5 mm diameter jet, which corresponded to a maximum tested $W_e$ of ~43,000, an again no impalement was seen. The inset shows the impalement $W_e$'s achieved for other coatings; PKFE coating clearly demonstrated well with an order of magnitude improvement.

4.4. Optical properties of the oxide nanocomposite coatings

In consideration of potential industrial applications such as solar panel or package wrapping, some hydrophobic coatings might require to be translucent or even transparent [19,354]. As a matter of fact, one of the most challenging aspects is to prepare a transparent superhydrophobic coating, knowing that the requirements for transparency and surface roughness are generally conflicting. While the surface roughness is a prerequisite to achieving superhydrophobicity, it may also lead to opacity due to undesired light scattering which is a function of roughness and the refractive index of the materials. Therefore, a careful control of the roughness and a proper matching the refractive index of the coating materials with the substrate are critical to achieve both high transparency and superhydrophobicity.

Many transparent and superhydrophobic coatings have been developed via using different material and fabrication approaches [24,307,355]. For instant, Xu et al. (2012) [355] created a superhydrophobic nanocomposite coating made from the assembly of fluorinated hollow SiO$_2$ nanoparticle (100 nm) via dip coating that had a 92% optical transmittance. In their study, 3-aminopropyltriethoxysilane (ATPS) was used to control the aggregation of the hollow SiO$_2$ nanoparticles; with an increase of ATPS concentration, surface roughness increases significantly (more aggregation and larger roughness size). This resulted in better hydrophobic performance, but a poorer optical transmittance.

It seems the keys to acquire both the transparency and superhydrophobicity at the same time are using small enough nanoparticles which are far less than the wavelength of the irradiated light (wavelength ~ 390 nm–700 nm) and using a transparent polymer. The oxide-based nanocomposite
coating meets both of these requirements. Therefore, a series of optical properties (transparency and scattering) tests are performed on the coatings.

**Figure 31.** Transparency test results for oxide-based nanocomposites. (a) Different coated samples were placed between a light source and spectrometer. The light source was placed ~10 cm away and pointed at the spectrometer which is used to measure the amount light. (b) Transmittance measurement of 4 different composition oxide nanocomposite coating with the same thickness. The measurement was taken respected to uncoated glass (assuming uncoated glass is 100% transmitted). (c) Transmittance measurement of SiO$_2$ based coating with different thickness, 5 passes created ~1-2 µm thick coating and 15 passes created 5-10 µm.

Optical tests were carried out on oxide nanocomposite coated substrates with a commercially available optical set-up, figure 31a. Figures 31b and c presented the optical transmittance around the visible region. Transparency of a surface will be reduced as roughness increases because of light scattering. Therefore, surface morphology, the refractive index of the material and the number of passes (thickness) of the coating are the key factors. 5 passes of spraying created a 1 –
2 \mu m coating and sufficient roughness for superhydrophobicity. At these thicknesses, silica based nanocomposite (with or without CNT) coatings gave an optical transmittance over 90%, due to the fact that silica nanoparticles have a refractive index of \(~1.5\) (being the lowest among the chosen three material, whereas \(\text{Al}_2\text{O}_3\) is \(~1.8\) and \(\text{CeO}_2\) is \(~2\) [356,357]). The surface SEM images also indicated that the dispersion quality of silica nanoparticle was good, resulting in a homogenous surface.

The polymer (PMC) which was used in the oxide nanocomposite is considerably transparent in nature with a low refractive index of \(~1.35\) [340]. However, the increase of spraying passes (coating thickness) was found to lead to an increase in surface roughness and complexity, resulting in an increase of light scattering and a loss of transparency. The transmittance dropped to \(~0.84\) from 0.92 when the thickness was increased to \(5 - 10 \mu m\).

It is noticeable that, the graphs for the “5-pass silica based nanocomposite” (with or without CNT) appear to be comparably flat, whereas the others 5-pass oxides and the 10, 15-pass silica based nanocomposites appear to be more sensitive to changes in wavelengths. The reason for this might be explained as that \(\text{Al}_2\text{O}_3\), \(\text{CeO}_2\), and CNT which were used in the nanocomposite have higher light absorption, thus affecting the light transmittance.

Mie scattering is expected once the particle size (roughness size) is comparable to or greater than the irradiated light wavelength (\(~100\) nm), resulting in a hazy image [307]. Haze measurement can be performed according to ASTM D1003, measuring the portion of incident light scattered by more than \(2.5^\circ\) (Wide-angle-light-scattering) through the coated specimen. Haze is expressed in percentage, and the lower the Haze value, the higher the visibility. If Haze value is greater than \(30\%\), the material is diffusing, figure 32a.
Figure 32. Schematic of hazemeter and claritymeter. (a) Spectrometer (or photocell) was installed on the wall within a sphere enclosure and used to measure the light scatter $\theta > 2.5^\circ$ after it passed through the coated surface. High Haze value cause a blurring image. (b) Claritymeter measured light scattering $1.3^\circ < \theta < 2.5^\circ$ which is referred as narrow-angle scattering. The set-up is similar to the Hazemeter except the spectrometer was installed at the back of the sphere and the coated sample was placed next to the light source.

Source: ASTM 1003D

Source: ASTM 1044D
Agglomeration of particles would result in poor coating dispersion which in turn affects narrow angle light scattering. Narrow-angle scattering causes the image to blur more as the distance between sample and detector is increased [305]. ASTM D1044 [318] demonstrated a standard procedure to measure the light scattered between 1.3% to 2.5% and evaluated the narrow-angle scattering by calculating the “Clarity” of the surface, Figure 32 (b). “Clarity” is expressed as

\[
Clarity = 100\% \times \frac{(T_{1.3^\circ}) - (T_{4^\circ-2.5^\circ})}{(T_{1.3^\circ}) + (T_{4^\circ-2.5^\circ})},
\]

where \(T_{1.3^\circ}\) is light transmittance within \(1.3^\circ \pm 0.1^\circ\), and \(T_{4^\circ-2.5^\circ}\) is the light transmittance between \(4^\circ\) and \(2.5^\circ\) [318].

Haze measurements (Figure 33a) show that the “SiO\(_2\) (No CNT) 5 passes” sample has the best haze performance (14%). After the introduction of CNT, Mie scattering increased due to the increase of roughness; haze performance reduced to 23%. The other two oxide particles mixed CNT nanocomposite samples has similar Haze performance between 17-23%. The increase of thickness would significantly boost the light scattering due to the increase of surface roughness and complexity. CeO\(_2\) nanoparticles have agglomeration nature and CeO\(_2\) based samples become optically diffusing (Figure 33a, Haze = 30%) when the coating thickness increased to 5\(\mu\)m – 10\(\mu\)m.

Figure 33a shows the “SiO\(_2\) (No CNT) 5 passes” sample had a as high as 70% clarity and the coated sample can be easily seen through (Figure 33b). After the introduction of CNT, the particle sizes (roughness size) increased which led to a 14% of clarity reduction, (Figure 33a). It was suggested that CeO\(_2\) particles agglomerated and resulted in forming lumps of particles and an unevenly distributed surface, which led to low clarity.
Figure 33. Optical properties measurement for different type (thickness) of oxide-based nanocomposites. (a) Haze and clarity measurements of different oxide-based coated samples, accurate to ± 1%. (b) Nanocomposite with different nanoparticle and different thickness coated samples were placed on a printed paper. (c) Different coated sample with different clarity were placed 20 cm above a printed paper. (Camera was placed 10 cm above samples)

The light scattering behaviour of the coatings can be explained by Rayleigh and Mie scattering theories depending on roughness. Assuming that surface texture is formed by spherical, non-absorbing (dielectric) particles which redirect the incident light. According to Cho et al. (2010) [358] and Kerker’s (1969)[359] work, when light passes through a surface with roughness
dimension of sub-wavelength of the light, Rayleigh scattering occurs and the intensity of the scattered light, I, is

\[ \frac{I}{I_0} = \frac{1 + \cos^2 \theta_{\text{light}}}{2s^2} \left( \frac{2\pi}{\lambda} \right)^4 \left( \frac{n^2 - 1}{n^2 + 1} \right)^2 \left( \frac{d}{2} \right)^6 \]

where \( I_0 \) is the intensity of the incident light, \( s \) is the distance between the particle and the detector, in this study \( s = \sim 10 \text{ cm} \), \( d \) is the diameter of the particle, \( \theta_{\text{light}} \) is the scattering angle (\( \theta_{\text{light}} = 0^\circ \), when measuring transmittance) , \( \lambda \) is the wavelength of light and \( n \) is the refraction index of the particle.

Meanwhile, refractive index (n) which is a dimensionless number and defined as the ratio of the speed of light in vacuum and the phase speed of light in the material, affect Mie scattering significantly. Increasing the refractive index (n) of the materials increases the Mie scattering cross section. Therefore, in order to reduce the Mie scattering, particles and polymer which have low refractive indexes should be preferentially considered.

Polymethacrylate materials have relatively high refractive indexes, e.g. PMMA (\( n = 1.490 \)) compared to some of the highly fluorinated polymers. For example, Poly(1H,1H-heptafluorobutyl methacrylate) has a lower refractive index of 1.386 and the PMC used in this study has a refractive index of 1.35 [340]. Moreover, it is well known that the refractive index of a polymer can be tuned by copolymerization of two appropriate monomers [340]. A new fluorinated poly(meth)acrylate-based copolymers with transparent nature can be achieved by reducing the refractive index of primary materials according to the composition of the copolymer.

As seen from Figure 34a, when the roughness is less than 100 nm, Rayleigh scattering in the visible region (\( \lambda \approx 550 \text{ nm} \)) is negligible for different materials, including PMC (\( n = 1.35 \)), SiO\(_2\) (\( n = 1.43 \)), Al\(_2\)O\(_3\) (\( n = 1.77 \)) and CeO\(_2\) (\( n = 1.9 \)). However, the scattering intensity increases significantly when roughness is greater than 100 nm, resulting in a decrease of light transmittance.

When the roughness is comparable or larger than \( \lambda \) (\( \sim 700 \text{ nm} \)), Mie scattering predominates and the total scattering cross sections was defined in Penndorf (1957) [306] as,

\[ \sigma_M = \pi r^2 K_{\alpha,n} \]
where $K$ is a dimensionless coefficient that depends on the refraction index ($n$) and the size parameter ($\alpha = 2\pi r/\lambda$). Mie et al. (1908)[360] derived $K$ as:

$$K\{\alpha, n\} = \left(\frac{2}{\alpha^2}\right) \sum_{1}^{\infty} (2m + 1)[|a_m|^2 + |b_m|^2]$$

which leads to the Mie scattering cross section:

$$\sigma_M = \lambda^2 / 2\pi \sum_{1}^{\infty} (2m + 1)[|a_m|^2 + |b_m|^2]$$

$a_m$ and $b_m$ are the Mie coefficients, representing the magnetic and electric multipoles of order $m$, respectively. This function $K$ has been computed and the numerical values are presented in Penndorf (1957) [306]. In his work, 5 different materials were presented with $n = 1.33, 1.4, 1.44, 1.486$ and 1.5 and Mie scattering cross section with respect to the different particle sizes are shown in Figure 34b. This figure shows the total Mie scattering increases exponentially with the increase of particles diameter. The refractive index ($n$) affects the gradient of the curves, contributing to the over exponential increase of the Mie scattering.
Figure 34. Theoretical analysis for Mie (Rayleigh) scattering (a) Rayleigh scattering in the range of visible light ($\lambda \approx 550$ nm) is determined by the particle size. When the particle size remains under 100 nm, light transmission stays high. (b) Mie scattering cross sections from materials with different refractive indices was contributed by particle diameters. $K\{\alpha, n\}$ was obtained from in Penndorf (1957) work [306]. (c) Mie scattering cross sections as a function of the distance between detector and sample with different refractive indices. (d) The Mie scattering cross section as a function of sample to detector distance from $\text{SiO}_2$ ($n = 1.43$) of different diameters [361].

When increasing the distance between sample and detector, $s$, the total flux of Mie scattering cross section decreases significantly (see Figures 34c and d). This phenomenon explains that many previous publications intended to present the transparent coatings by placing the sample right on top of a printed paper, the Mie scattering is minimised. In this study, clarity measurements were performed, the distance between sample and detector was deliberately increased. Therefore, more
Mie scattering is introduced and large particle Mie scattering (Narrow-angle scattering) can be taken into consideration, Figure 33c.

The presented data above are obtained based on other researcher’s formulation which adopted the assumption of dealing with spherical particles in the air. In reality, the light scattering can be much more sophisticated due to the various environmental factor (e.g. temperature), irregular shapes of the surface and gradient of the refractive index of the materials. Nevertheless, these theoretical data offer useful guidance in designing transparent, superhydrophobic coatings.
5. Conclusion and future work

Artificial superhydrophobic coating can potentially tackle real-world problems. For instance, self-cleaning property of superhydrophobic coating can reduce outdoor facilities maintaining costs and protect metal surface from corrosion. Previous study shows Superhydrophobic surface can be fabricated by combining the adequate surface roughness and a low surface energy.

There are many ways to fabricate artificial superhydrophobic surface such as lithography, chemical vapour deposition, electrochemical spraying, layer by layer, wet chemical reaction, and so on. Most of the fabrication methods, such as lithography, require expensive equipment and are mainly applicable for small flat and rigid surfaces. Therefore, I selected the spraying nanocomposite coating approach which is considered a scalable, economical and easily accessed approach.

A wide variety of materials have been selected by researchers to make nanocomposite coating, due to their respective advantages. Carbon-based and silica-based nanoparticles often have excellent chemical resistance and good thermal stability. Metallic oxide particles, such as ZnO, TiO$_2$, Al$_2$O$_3$, are common materials existing in a wide range of forms like nano-rods, nanotubes and nano-needles, that enable different morphologies to be achieved. In addition, low surface energy polymers such as poly(methyl methacrylate) (PMMA), polydimethylsiloxane (PDMS), polystyrene (PS), and poly(perfluoroalkyl) methacrylate copolymers (PMCs) and epoxy resin, have many advantages such as simple fabrication, structural flexibility, controllable thickness, good adhesion and low cost.

Also noted were some disadvantages of various materials, such as problems associated with oxide dispersion in solution, the high price of carbon nanotubes or graphene nanosheet, and durability such as the photo-degradation of certain organic polymers. Therefore, developing appropriate fabrication approaches and suitable durability tests become extremely important. Researchers have developed many procedures to evaluate the durability of superhydrophobic coatings, including mechanical, chemical (corrosion), UV resistance, water impalement resistance, etc. Many nanocomposite coatings previously developed failed in these durability tests due to either the fragile morphology got damaged or change of surface chemical composition.
Bearing these challenges in mind, the main objective of this study is to design and fabricate a nanocomposite superhydrophobic coating based on easily accessible off-the-shelf material and simple spraying approach. The coating should be applicable for both large- or small-scale application, relatively cheap and environmental friendly, as well as being durable.

In this study, the first superhydrophobic coating I made is the PKFE nanocomposite which is Polytetrafluoroethylene particle mixed with Kytox oil and Fluoropolymer-grafted epoxy resin. Accordingly, various tests to assess the surface characteristics and durability of the superhydrophobic coatings were designed, based on industrial standard (ASTM). Experimental apparatus and procedures were described in detail. Three aspects of mechanical durability of the coatings were tested: adhesion to the substrate (or inner adhesion), linear abrasion and solid impact. ASTM standard (D3359-17) adhesion cross-hatch tests were performed on PKFE coatings and showed no significant removal of the coating material, using the standard recommended tape (adhesion to steel: 642 Nm⁻¹) and strong VHB tape (adhesion to steel: 2600 Nm⁻¹). Furthermore, PKFE coating shown slightly decrease of hydrophobicity after 30 repeat peeling cycles when using the VHB strong tape. The strong adhesion of PKFE is because of fluorinated epoxy having an excellent adhesion property.

The linear abrasion test was performed by using ASTM standard Taber machine, under an applied load of 250 g, and PKFE coatings maintain their superhydrophobicity after 100 cycles of abrasion. The volumetric superhydrophobic nature of the PKFE coating leads to the phenomenon that the thickness and hydrophobic performance only decrease slowly with abrasion cycles. SEM results showed that the loss of superhydrophobicity was mostly caused by physical force, damaging the delicate micro/nano texture of the surface. Nanocomposite coatings were found to show mechanical durability due to being a volumetric superhydrophobic material. Moreover, the mechanical durability could be improved even further by e.g. carefully manipulating the flexibility of the coating.

To test the chemical corrosion resistance of the PKFE coating, aqua regia (a mixture of highly concentrated hydrochloric acid (HCl) and nitric acid (HNO₃) in a 3:1 volume ratio) was used. PKFE coating was found to be able to sustain its superhydrophobicity after 2 hours of aqua regia and 24 hours of sodium hydroxide solution. The strong chemical resistance of the PKFE and
Oxide-based nanocomposite coating were due to the presence of the chemically stable fluorinated groups in the polymers.

The raining condition was simulated by performing a liquid drop impact test. No sign of impalement was shown on the PKFE coatings during the droplet impact test (drop impact speed up to ~4.5 ms\(^{-1}\)). A more aggressive water jet impalement test was used, the PKFE coatings were found to be able to withstand impact with a maximum jet speed of 32.5 m/s, without any sign of liquid impalement. The excellent impalement resistance could be attributed to the flexible nature of the epoxy used in the coating. The PKFE was compared with some commercial coatings. The results demonstrated that the PKFE coatings are four times better in adhesion, a factor of two times better in abrasion resistance and possess about an order of magnitude better in chemical and high-speed liquid impact resistance.

Despite PKFE coating demonstrated remarkable robustness in many aspects, it is limited to many applications such as car window due to its opaque and solvent based nature. Therefore, the second approach of water-based oxide nanocomposite coating was developed. By controlling the size of the nanoparticle (< 100 nm) and choosing material low refractive index transparent superhydrophobic coating can be achieved. Silica based nanocomposite provided ~90% of optical transparency and passed the standard mechanical durability and liquid impalement tests. However, it lost its superhydrophobicity after exposed to UV light after 10 days. FTIR results indicated the Silica based nanocomposite was gathering the moisture after the PMC got damage by UV. Therefore, Al\(_2\)O\(_3\) and CeO\(_2\) nanoparticle are used to replaced SiO\(_2\) and CNT is added to improve the dispersion quality of the coating.

Transparent, scattering and clarity tests were performed on the oxide nanocomposite coatings. The SiO\(_2\) based samples had an optical transmittance of over 90% with coating thickness of \(e 1 – 2 \mu m\). However, it was also shown that the transparency decreased as number of spray passes increased which causing a corresponding increase in the surface roughness and light scattering. ASTM standard Haze and Clarity measurements were used to evaluated wide and narrow angle light scattering, and SiO\(_2\) based samples showed a 14% haze and 71% clarity. Experimental results indicated that the increase of coating thickness, particle agglomeration and measuring distance all led to poor Haze and Clarity performance. In practice, low clarity results in the transmitted image to blur more as the observation distance was increased and low Haze results in the transmitted image become fuzzier.
The major contribution of this work can be concluded as followed:

- Developing robust superhydrophobic nanocomposite coating while maintaining saleability. It is achieved by combining the chemically stable and self-similar nature of nanocomposite, as well as discovering soft material can enhance liquid impalement resistance. The PKFE can withstand impact with a maximum jet speed of 32.5 m/s which is best liquid impalement resistance have ever recorded and these results have been published in Nature Material. Other researchers can be benefited from this work by following the material selection and experiment procedure to produce durable superhydrophobic coating for fundamental liquid-solid interaction study and everyday life application.

- Water based oxide nanocomposite coating was developed with different nanoparticles. It has the advantage of having facile fabrication process, using all off-the-shelf material, using water as the solvent and can achieve superhydrophobic and transparent at the same time.

- One of the most challenging aspects is to prepare a transparent superhydrophobic coating, knowing often the requirements for transparency and surface roughness are generally conflicting. The trade-off between superhydrophobicity and optical properties were systematic study on the water based oxide nanocomposite coatings. The optical properties: transmittance, haze and clarity can be controlled by nanocomposite coating thickness, dispersion quality and total refractive index. This study can provide valid information to engineers and researchers when are designing new transparent superhydrophobic coatings for specific applications.

Future work should concern more in-depth analysis of particular superhydrophobic failing mechanisms; new proposals to try different material and fabrication methods to achieve multifunctional coating. This thesis has been mainly focused on developing robust superhydrophobic nanocomposite coatings. Therefore, there are some ideas which relate to integrating multifunction into robust superhydrophobic surface I would like to try in the future.

- Thermally and electrically conductive superhydrophobic coating have been developed in the past by employing thermally/electrically conductive material (particle and polymer) [362–365]. Carbon-based material such as carbon nanotube, graphene or carbon black are often used, the key factors of achieving good thermally/electrically conductive are the
carbon-based material concentration and dispersion quality in the conductive polymer matrix. By systematically study these two factors, good thermally/electrically conductivity could be integrated into the robust superhydrophobic coating.

- Nanocomposite superhydrophobic coatings has excellent abrasion resistance due to the volumetric self-similar nature. With a well-dispersed solution and appropriate fabrication method, bulk superhydrophobic can be achieved. Moreover, theoretically speaking, the superhydrophobic nanocomposite solution can be used as “ink” in 3D printing process. Therefore, a superhydrophobic bulk with a unique shape or structure can be created. The main challenge will be controlling the viscosity of the “ink” and the curing process.
6. Bibliography


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7. Publications and Conferences record

Publication:

(1) Peng C, Chen Z and Tiwari M K 2018 All-organic superhydrophobic coatings with mechanochemical robustness and liquid impalement resistance Nat. Mater. 17 355–60

Conference records:

(2) “Robust superhydrophobic coating” and “Metallic nanotexture surface for water jet impact resistance and anti-frost application”. Results was presented at The 31st Edition of the International Conference on Surface Modification Technologies (SMT 31), Belgium.

(3) “Synthesis and characterization of polymer nanoparticle based stable superhydrophobic coatings using environmental benign chemicals” Results was presented at UK Colloids 2017 Conference, Manchester

(4) “Superhydrophobic coating for spray cooling application” Results was presented at 15th UK Heat Transfer Conference, London.