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# Approaches for Evaluating and Engineering Resilient Superhydrophobic Materials

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#### Abstract

Superhydrophobic materials rely upon highly rough surface morphologies in order to maximise water repellency, and requires surface features on the micro/nanoscale. These tremendously small surface structures are inherently physically weak, relative to characteristics of bulk materials. This limits the real-world applicability of many superhydrophobic surfaces, as degradation and loss of superhydrophobicity readily occurs upon exposure to anticipated stimuli. Consequently, there is an absence of long-lasting commercial products, but instead rely upon frequent regeneration. These materials demonstrate a tremendous potential for application in a range of areas, including antifouling, self-cleaning, drag-reduction, anti-icing, etc. To realise application on these fields, superhydrophobic resilience must be maximised. This chapter summarises evaluation methods and engineering procedures in attaining resilience, both are highly important in the development of robust materials.

**Keywords:** superhydrophobic, resilience, evaluation, engineering, degradation, microstructure, chemistry

## 1. Introduction

Superhydrophobic materials exhibit potential real-world application that encompasses a wide range of commercial sectors [1–3]. This is a result of properties inherent to superhydrophobic surfaces, including; self-cleaning, antibiofouling, drag-reduction, and oil-water separation. State-of-the-art research provides a tremendous breadth of superhydrophobic coatings and membranes reported within the literature [3]. However, there is a noticeable absence of commercial solutions currently available. The majority of superhydrophobic products concentrate on short-term treatments, which require reapplication of the coatings to retain functionality [4, 5].

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The short-term nature of many applied superhydrophobic surfaces stem from the architecture required to induce extremely water repellent properties. The two major features of these materials are; (i) an inherently water repellent surface chemistry, and (ii) a highly rough surface microstructure [6–8]. The latter of these necessitates a surface structure composed of micrometre, or nanometre, sized features—which are fundamentally physically weak structures. Therefore, commercial products that impart superhydrophobicity tend to degrade overtime, deteriorating at a faster rate as the intensity of the application increases [9].

The major challenge facing researchers aiming for applicable materials is surface fragility, and routes for engineering resilience. This chapter aims details the nature of superhydrophobic degradation, and monitoring techniques, in addition to required materials tolerances, and a summary of approaches to achieving resilience.

## 2. Superhydrophobic surface degradation

#### 2.1. Chemical/physical degradation

The loss of superhydrophobic properties can stem from changes to surface chemistry, or the loss of tapped air at a surface (e.g. by degradation of surface roughness), or a combination of these factors [10, 11]. Understanding the cause of the loss of superhydrophobicity enables the targeting of specialised surface design for resilience enhancement.

#### 2.1.1. Surface chemistry changes

The surface chemistry of a material determines its Young contact angle; this value is a measure of wetting for a flat ideal surface [12]. The Young contact angle feeds into the main surface wetting models; Wenzel, and Cassie-Baxter [13, 14]. As most superhydrophobic materials are fabricated with an inherently water repellent coating, any deviation from this will lead to an observed reduction in water contact angle (WCA – **Figure 1**) [6]. This is demonstrated by the covalent attachment of self-assembled monolayers (SAMs), where the strength of SAM-surface binding is an extremely important consideration with respect to coating longevity. Another factor that affects the stability of surface bound molecules is molecular size, whereby variation in the size of these molecules can either enhance, or impair their relative stabilities [15]. Chemical robustness can be ensured through the utilisation of energetically stable surface chemistry, or the incorporation of hydrophobic coatings that exceed the thickness of a monolayer [16, 17].

Another pathway that includes surface chemical change is surface fouling, especially when considering real-world application. This issue can be seen when biofouling, or chemical contamination (e.g. hard water staining) is a concern [18, 19]. Surface fouling can be controlled through solutions to particular contaminants, however the success of a particular approach is very much dependent on the operational environment of the materials [20].

#### 2.1.2. Physical degradation

A lowering in WCA achieved by a superhydrophobic surface is anticipated when the overall surface roughness is reduced [1–3]. However, a WCA reduction would be also expected



**Figure 1.** A demonstration of the effect of SAM surface coverage on the resultant WCA. This theoretical example utilises ideal Youngs WCAs for the complete SAM coating, and bare substrate of 110°, and 60° respectively [12–14].

through any unfavourable alteration of the water-surface wetting interface (e.g. loss of trapped air) [21]. This can be reasoned through examining the roughness terms in the Cassie-Baxter surface model, where  $f_1$  represents the liquid-solid interfacial unit area (akin to the 'roughness factor' within the Wenzel model), and where  $f_2$  represents the liquid-air interfacial unit area (a 'roughness factor' for the air trapped at the interface). Therefore, any change to the solid roughness (e.g. surface microstructure damage) is reflected by a reduction  $f_1$ , and the removal of air causing a reduction in  $f_2$  (**Figure 2**) [14].

The removal of trapped air, without any additional surface variation, can be considered a form of recoverable degradation (covered in Section 2.2), if this air is allowed to re-enter the surface porosity [22]. However, recovery from physical damage (i.e. scratching, material removal, or flattening) cannot be achieved simply, unless engineered into the surface components (e.g. self-healing materials—Section 4.3). Resilience to this type of damage requires is a key engineering challenge within superhydrophobic research (detailed in Section 4).

#### 2.2. Recoverable degradation

As outlined in the previous section (Section 2.1.2), not all degradation is results in a permanent change in wetting behaviour [22]. The removal of trapped air, transitioning from Cassie-Baxter to Wenzel type wetting, can result in a change in the way water interacts with the surface, in addition to the loss of superhydrophobicity (**Figure 2(iii)/3**) [23]. This air can be removed physically (*via* hydrostatics), additionally it can also be slowly dissolved by water over time [24, 25]. Hydrostatic removal can occur when water interacts dynamically with the surface (e.g. water impact, turbulent surface flow, etc.), whereas air solvation most commonly



**Figure 2.** Scheme showing the effect of variation of surface roughness and trapped air  $(f_1/f_2)$  on the on the WCA for a surface. Where; (i) is the original superhydrophobic surface wetting (i.e. Cassie-Baxter), (ii) shows the partial removal of roughness features, (iii) demonstrates the Cassie-Baxter to Wenzel transition (*NB*;  $f_1$  increases), and (iv) complete removal of all surface features. The schematic presumes a consistent surface chemistry [12–14].

occurs when superhydrophobic materials are submerged underwater for extended periods. In either case, once air is reintroduced and the Cassie-Baxter state is regained, surface hydrophobicity (i.e. WCA, hysteresis, etc.) will return to the original state (**Figure 3**) [22].

#### 2.3. Degradation analysis

The optimisation of a materials resilience can be facilitated through understanding the nature of superhydrophobic degradation (changes to; surface chemistry, microstructural damage, or recoverable degradation), within the context of the type of resilience testing used, or degradation stimuli applied [26]. The following section details commonly used degradation, and degradation analysis protocols.

#### 2.3.1. Degradation protocols

A commonly used approach in testing the physical robustness of superhydrophobic materials includes an array of scratch or abrasion testing methods [26]. In the literature, this ranges from arbitrary scratching of the surface with a blade or scalpel, to quantitative abrasion testing compatible with industrial standards (e.g. linear abrading) [26–28]. Arbitrary testing methods (e.g. blade scratching) can provide a good indication of surface resilience, particularly if the exact specifications of testing are reported (**Figure 4**). However, many examples throughout the literature do not provide adequate detail to assess materials resilience (e.g. blade testing; blade type, blade dimensions, scratch protocol—force applied/blade travel/etc., or indication



**Figure 3.** SEM/photos of substrates fabricated to probe the Cassie-Baxter to Wenzel wetting transition, and their wetting behaviour. The ridge surface structures (A) facilitate superhydrophobicity *via* the trapping of air (B). Once fully wetted, the surface demonstrates a direction dependent WCA variation (C/D). The original WCA are regained when samples are dried and retested.

of reproducibility) [27]. Another commonly used method employs adhesive tape, which is applied to the superhydrophobic material and then removed to cause surface damage. Although this may provide some insight into surface resilience, the techniques are associated with many variables (e.g. adhesive strength, tape application/removal protocols, surface microstructure, etc.) imparting a level of uncertainty to the testing. In contrast, quantitative abrasion tools are able to provide a reproducible method of surface degradation (**Figure 4**). While providing an objective indication of the magnitude of surface roughness. The utilisation of a commercial linear abrader has been shown to provide details of; abradant type/size/ contact area, and abrasion force/velocity [28].

These testing examples focus in the physical degradation of the surface material (i.e. the flattening of surface roughness), subsequently affecting surface hydrophobicity. Recoverable degradation (without surface damage) is less often probed, however several literature protocols have been developed [30]. One example of probing the Cassie-Baxter to Wenzel transition, is the use of water-surface compression apparatus. This utilises a parallel plate configuration, where water is place between two superhydrophobic surfaces which are then progressively moved closer together (**Figure 5**). The result is a surface tension induced pressure increase at the interface, which progressively squeezes air from the surface microstructure (hence transitioning from Cassie-Baxter to Wenzel wetting). The pressure required for the wetting transition is a measure of the stability of the superhydrophobic trapped air stability [31]. An example aimed at accessibility uses water bouncing to characterise superhydrophobic



**Figure 4.** Physical degradation protocols utilising arbitrary surface abrasion (A—weighted abrasion cycling), and quantitative industrial abrasion (B—linear abrader) [27, 29].

resilience. The technique enables an assessment of trapped air stability, however does not require the use of specialised equipment (e.g. parallel plate set-up) [32, 33].

The use of dynamic water interactions with superhydrophobic surfaces has been employed to examine both physical degradation, and the reversible removal of air at the water-solid interface. This includes water flow, and water-surface collisions, and ranges from arbitrarily flowing water across a surface, to quantitative techniques (e.g. sheer stress endurance) [34–37]. Water sheer has been shown to be provide the conditions for testing reversible and non-reversible degradation, while offering in situ monitoring of surface hydrophobicity (detailed in Section 2.3.2—**Figure 5**). The application of water sheer stress provides a direct measurement of the materials resilience to water flow across the surface [34]. In contrast, the wider relevance to other forms of degradation (e.g. scratch resistance) can only be considered with some amount of ambiguity [27].

The development of highly resilient superhydrophobic materials is a key concern within the research field [1–3]. Tremendous progress has been made in the engineering of materials

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Figure 5. Recoverable degradation testing, via parallel plate pressuriser (A), and cone-on-plate rheometry (B) [31, 34].

robust enough to survive real-world application (summarised in Section 4). However, the lack of standardised testing, through the use of arbitrary (e.g. scalpel scratch testing), or semiquantitative (e.g. abrasive drag testing) techniques, hinders potential advancement, as this leaves some literature open to interpretation. As mentioned within this section, quantitative techniques are able to provide an accurate indication of materials resilience to a particular stimulus. In many cases, further analysis is required to provide a comprehensive indication of robustness. This ambiguity pushes the development of a standardised testing regime, which takes into account a range application-specific testing protocols, particularly if a material is targeted at broad real-world application.

#### 2.3.2. Degradation analysis protocols

The degradation pathways (detailed in Section 2.3.1) inflict a range of chemical, structural, and recoverable changes on superhydrophobic materials [26]. For physical/chemical changes, post degradation analysis is most commonly employed, as in situ monitoring of surface roughness (macro/nanoscale features), and surface chemistry is not trivial [38–40]. The reversible removal of air can be successfully tracked using in situ monitoring, as it is suitable to the dynamic wetting/drying of the surface microstructure [41]. The following section highlights the range of analysis techniques available for monitoring these types of degradation:

#### 2.3.2.1. Surface chemistry alteration

Changes to surface chemistry can be tracked in two main ways; (i) analyse the result of the changing surface chemistry, or (ii) directly characterise surface chemistry [42, 43]. Primarily, WCAs can be used to estimate the variation in hydrophobicity [42]. This is relatively straightforward, however due to the WCAs connection to both surface chemistry, and surface roughness, morphological effects must also be monitored to specify the nature of chemical change [10]. Direct characterisation of surface chemistry can be conducted using a multitude of techniques [43]. Vibrational spectroscopies (e.g. infrared/Raman) provide a non-destructive indication of surface functionality and are commonly employed. Monitoring of surface chemistry is important particularly when environmental degradation pathways are likely, such as superhydrophobic materials constructed from photocatalytic materials (e.g. Titanium dioxide, TiO<sub>2</sub>). TiO<sub>2</sub> nanoparticles are commonly used for superhydrophobic coatings, as they are commercially applicable (white pigment utilised worldwide) and can be easily functionalised to induce hydrophobicity. TiO<sub>2</sub> is a semiconductor, which can produce highly active species which break down organic species on the surface (i.e. coatings required for superhydrophobic materials) [44]. Therefore, a reduction in the amount of hydrophobic surface coating can be tracked using infrared, in addition to the resultant reduction in observed WCA (Figure 6) [45, 46]. X-ray photoelectron spectroscopy is a highly sensitive technique, able to distinguish changes in elemental composition, surface contamination, and can be combined with depth profiling. However, the technique is not widely accessible (i.e. costly equipment that requires supportive infrastructure), it also requires samples to be exposed to vacuum, which may limit its applicability. Quantitative analysis of XPS intensities has been demonstrated to provide understanding of film thicknesses and stoichiometries. Utilisation over extended periods can provided an extremely detailed interpretation of surface chemistry degradation [47].

#### 2.3.2.2. Surface microstructure change

Changes to surface morphology can be investigated by the interpretation of 2D representations, or more accurately from quantitative 3D techniques. A simple approach to assessing changes to surface roughness is optical microscopy, however comprehensive assessment can only be made by using techniques such as confocal imaging as this provides a 3D representation [48]. Optical

Profilometry provides 3D topological information, able to facilitate analysis of surface damage, material displacement, in addition to other surface changes (e.g. self-healing materials). The technique is however limited to the analysis of relatively large surface features (i.e. >0.4  $\mu$ m), due to diffraction limits of visible light [49]. 2D representations at higher resolution can be made using electron microscopy (**Figure 7**). Scanning electron microscopy (SEM) is very commonly used in the analysis of superhydrophobic morphology (**Figure 7**). Partial 3D interpretations can be attained through using tilted views of surfaces within SEM, however this does not provide reliable quantitative data [44, 50]. Contact profilometry can be used to provide 3D morphological data, and higher sensitivity analysis through atomic force microscopy (AFM—**Figure 7**) [51, 52]. These are similar techniques aimed at different morphological scales, with contact profilometry aimed at solely microscale roughness, and AFM able to measure nanoscale features.



**Figure 6.** The degradation of surface bound molecules (stearic acid), monitored using infrared spectroscopy, on the surface of mesoporous  $TiO_2$  films (A), and concentration analysis for steric acid degradation under UV light irradiation (B) on TiO<sub>2</sub> coatings formed under various conditions (1–3) [45].



Figure 7. Surface change assessment techniques. Includes; confocal optical microscopy (left), side-on SEM imaging (centre), and AFM (right) [50, 54, 55].

These techniques (contact profilometry/AFM) lack the ability to resolve surface features it cannot make direct contact with, as they both use probes mounted perpendicular to the materials surface [53]. In addition, the ability to gain accurate/valuable information from the analysis depends on a range of factors, including; probe tip dimensions, mode of operation (contact, tapping, etc.), structural integrity of the surface material (potential movement/flex of analysis substrate), and contamination of probe tip by surface material, in addition to others [53].

#### 2.3.2.3. In situ monitoring

Superhydrophobic degradation can be examined directly with WCA measurements, however, testing must be paused during this analysis (in addition to the using other analysis techniques mentioned in this Section 2.3.2) [56]. In situ monitoring of surface roughness is cannot be carried out easily, unless examining large surface features (e.g. using optical microscopy) [57]. Therefore, in situ monitoring is most valuable when examining reversible degradation. A commonly used example is the examination of surface reflectivity of a wetted surface [58]. The presence of air trapped at the water-surface interface notably produce mirror-like effects due to increased reflection of light from the water-air interface, when these materials are submerged in water (**Figure 8**). The monitoring the level of reflected light can be used to gauge the amount of trapped air, and its resultant variation. This testing has been implemented to show air layer stability in a range of conditions, including; submersion endurance, immersion depth testing, and flow measurements. The lifetime of the air layer at the surface upon submersion, has been shown to be highly dependent on both the test conditions (i.e. water flow, or applied pressure) and superhydrophobic surface morphology [59].



**Figure 8.** Analysis of recoverable (and non-recoverable) degradation *via* the use of surface reflectivity to monitor the surface plastron caused by superhydrophobic surfaces (A). The illustration (B) shows the distribution of micro/ nanobubbles arranged across a superhydrophobic surface when submerged in water [59].

As mentioned in Section 2.3.1, water sheer can be used to induce superhydrophobic degradation [35]. Controlled water sheer (through the use of rheometry), has been used as a method for progressive monitoring of surface degradation under water sheer [34]. These techniques utilise the slip-length phenomenon demonstrated by superhydrophobic surfaces. Whereby, slip-length is gauged by monitoring the apparent viscosity of water on a superhydrophobic surface (measured by rheometry), which is lower than expected. The magnitude in the lowering of viscosity is directly proportional to the superhydrophobicity of the surface, and the amount of air trapped at the interface. As sheer stress is applied, both physical and reversible degradation occurs, which consequently reduces the measured slip-length. This measurement is carried out while the sheer stress testing is conducted.

## 3. Real world survivability

The potential application environments for superhydrophobic technologies are extremely diverse [1–3]. As a result, the requirements that ensure the long-term stability of these materials can be focus on a range of different priorities. This section highlights potential application environments, the associated expected tolerances, and the introduction of the associated engineering challenges.

#### 3.1. Application environments

The potential applications areas of superhydrophobic materials, and the expected operational conditions, stem from their numerous functional properties (self-cleaning, antibiofouling, drag-reduction, oil-water separation, etc.) [1–3]. These areas can be classified with respect to environmental tolerances; (i) high (broad-spectrum), (ii) low, and (iii) high (application specific challenges). The environmental stimuli able to influence surface degradation include; fluid flow (water/air), physical (solid) contact, chemical/biological exposure, and environmental changes (pressure, temperature, etc.). These expected tolerance classifications are briefly summarised below.

#### 3.1.1. Broad-spectrum high tolerance environments

This covers a wide range of potential applications, but includes those that require; manual handling, abrasive interaction, sheering water flow, and multi-environment resilience [60]. Currently, no commercially available superhydrophobic products exhibit a generally high environmental tolerance. An example application would be the superhydrophobic treatment of textiles, which requires resilience to handling, abrasion, varied environmental exposure, etc. [61]. Additionally, for superhydrophobic textiles, the loss of functionality when laundered (i.e. water sheer and chemical exposure) would also be a concern [62]. As a result, currently all commercial superhydrophobic fabric treatments are marketed as temporary, requiring reapplication after prolonged wearing, or after laundering [63]. The use of superhydrophobic surfaces in extreme environments would prove hugely beneficial. Aerospace surfaces are an example of a highly challenging, yet highly relevant operational environment, this includes;

high fluid sheer, rapid temperature change, and airborne particle impact [64, 65]. Affording self-cleaning, anti-fogging, and anti-icing properties in these applications would be highly desired, however this currently exceeds technological capabilities.

#### 3.1.2. Low tolerance environments

The current standard of commercial superhydrophobic technology already enables application in low tolerance areas [63]. As described above, the temporary treatment of textiles can be readily achieved. However, superhydrophobicity cannot be maintained by these treatments under garment tolerances over long periods. These types of coating, as well as many other surface treatments reported in the literature, have been shown to resist low intensity stimuli (e.g. water flow, or adhesive testing) [63, 66]. Surfaces that do not experience physical interactions (surface-solid contact) would be an area for potential application. An example would include the internal surface of liquid carrying pipes (e.g. water drainage pipes), omitting any high sheer forces, and any application specific challenges (described below) [67].

#### 3.1.3. Application specific challenges

Surface degradation via physical action, or fluid shear, are commonly considered as target forces to resist [27, 28, 34]. However, there are a range of degradation sources specific to particular applications. Surface chemistry variation can be accompanied by tremendous changes in surface wettability. This commonly occurs via two main mechanisms; (i) surface reactions to remove and/or alter hydrophobic chemistry, or (ii) the addition of surface material to mask effective surface chemistry [18, 19]. The former can occur upon exposure to harsh chemicals or other degradation route (e.g. highly basic conditions, or photocatalytic degradation), but can also degrade readily under ambient conditions over time [9, 44, 68]. Therefore, a thorough consideration of superhydrophobic resilience would include the stability of surface functionalisation, the compatibility between the surface coating and underlying material, in addition to the effect of any reactive species present within the local environment. Surface fouling is often accompanied by an associated reduction in surface hydrophobicity [18]. Biofouling in particular is a rapidly escalating process, whereby any initial fouling can encourage further biological surface attachment. Fouling prevention has been shown possible with respect to specific surface contamination sources. For example, there are many literature examples of the removal of particulates, or dyes from the surface [69]. However, the design of general fouling prevention is not facile, as it depends on a multitude of factors (surface morphology/ chemistry, contamination source, and contaminant delivery method). This is evident when considering the biofouling process, which is a multifaceted mechanism (Figure 9) [70]. The primary fouling prevention target are small molecules that are able to contaminate the surface, conditioning it for microbial attachment. Antifouling in subsequent biofouling focuses on preventing the attachment of microbial species.

#### 3.2. Expected tolerances

The expected resilience of a surface can be considered in three categories; (i) physical degradation, (ii) reversible degradation, and (iii) chemical degradation.



**Figure 9.** The attachment of bacteria to superhydrophobic surfaces is shown to preferentially occur at the tops of surface protrusions. This is caused by superhydrophobic wetting mechanisms, which leaves these areas as the only viable attachment points. This has been demonstrated in bacterial attachment assays (upper), and shown by the illustration (lower) [71].

Physical degradation can occur *via* a range of mechanisms (Section 2.3.1), and the challenge of optimising physical resilience is a multifaceted consideration. However, there are some key principles in surface engineering that can be targeted. The morphology of superhydrophobic surfaces can be imagined as an array of surface protrusions [10]. Physical degradation of these features can occur *via* compression/destruction, or removal, which is dependent on both the structural integrity of individual surface features, and their attachment to the underlying substrate [10, 11]. The real-world applicability of superhydrophobic materials requires the survival of nano/microstructured features. A key consideration for surface design is the exact forces associated with a particular application. Furthermore, considering whether a given design route can offer the required resilience. The surface pressures applied during heavy-duty manual handling processes can range from 100 to 400 kPa [72]. The pressure applied to individual surface features is expected to be higher than this, due to an uneven morphology caused by surface roughness.

The conditions required for reversible degradation can be predicted for highly ordered surface structures, as the hydrodynamic factors that dictate air entrapment at a surface are well established [73, 74]. Most materials aimed commercialisation are made up of randomised surface features, and provide an array of trapped air environments. Therefore, practical testing of these surfaces is the only reliable method for assessing trapped air stability [31]. Generally, critical pressure is used to classify the hydrodynamic pressure required to remove trapped air. Critical pressure is the pressure required for conversion of Cassie-Baxter to Wenzel wetting. For superhydrophobic materials this critical pressure is generally greater than 0.5 kPa, however nanosized features can increase this to ~300 kPa and greater [75]. A reason why superhydrophobic leaves may also incorporate nano-roughness in their surface morphologies, is that this allows protection from impact of rain droplets, where the applied pressure range is 10–1000 kPa [75].

Stable surface chemistry can be ensured *via* careful consideration of the hydrophobic surface treatments [16, 17]. Facilitated through the incorporation of strong chemical bonding between the surface coatings and underlying morphology, or the exploitation of strong adhesive forces. There are many examples in the literature that report resilience to a range of chemical environments (e.g. extreme pH or solvent exposure) [76]. As mentioned in Section 3.1, a general approach for chemical/biological fouling prevention is not straightforward. Successful fouling prevention can be carried out if specific contaminants are targeted. Many literature examples examine the removal of particulates that are loosely arranged on the surfaces [69]. In addition, the prevention of bacterial attachment has also been studied, however no comprehensive approach has been reported that relies upon solely superhydrophobic antifouling properties [77]. Many superhydrophobic surfaces with high antifouling properties also incorporate biocidal species within the reported materials [78].

#### 3.3. Engineering challenge

The requirements for truly resilient superhydrophobic surfaces that are able to function in real-world applications are extremely demanding, particularly if a general high tolerance is required. Numerous approaches for resilience have been developed (Section 4), however a multi-faceted research effort is required to probe the extremities of physical possibility with respect to maximising resilience. This investigation incorporates aspects of chemistry, materials science, materials engineering, fluid mechanics, and microbiology, in addition to other relevant areas. The development of real-world materials requires a drive toward the standardised testing and reporting of resilience, this allows for formulation of an effective design approach.

#### 4. Approaches for robustness

#### 4.1. Hardening materials

The structural integrity of superhydrophobic surface morphology is key to the magnitude of their physical resilience [10]. An improvement to the integrity of a structured surface can be made by modifying the composition of the component materials. This has been achieved through using inherently high strength materials to construct a surface (Section 4.1.1), or *via* the utilisation of strengthening modifications (Section 4.1.2–**Figure 10**).

#### 4.1.1. High strength materials

A range of factors determines the strength of a material (e.g. chemical bonds/structure, intra/ intermolecular binding, etc.), this directly affects the materials stress tolerances [82, 83]. As a result, there is a range of candidate materials for engineering resilient superhydrophobic materials. Materials formed by strong compression of superhydrophobic components provide an



**Figure 10.** Approaches for the formulation of robust superhydrophobic materials. Includes; (A) hardening materials (inherent strength, or via physical/chemical strengthening additives), (B) protective surface features, and (C) the strategic design of optimised surface features [79–81].

assembly method, able to greatly increase their physical resilience. The compression of hydrophobic polymer nanoparticle mixtures has been used to form superhydrophobic disks [84]. These are reported to have high robustness, able to withstand cutting, abrasion, and chemical exposure. The materials are compacted, a high surface roughness remains, and maintain an inherently hydrophobic surface chemistry, facilitating superhydrophobicity. The resistance to physical degradation is explained as a result of the fabrication technique, which relies upon pressing pressures of up to 40 MPa, and the highly condensed material that results. However, within this example, the resilience testing carried out does not provide quantifiable resilience data [84].

Electroplating has also been used to fabricate highly robust coatings on to conductive substrates. The electroplating techniques can provide strong underlying connection to the substrate [85, 86]. Highly rough surface features have been reported *via* numerous literature electroplating routes, with superhydrophobicity resulting from the addition of a hydrophobic surface coating [87]. Superhydrophobic surfaces fabricated *via* electrodeposition exhibit a range of surface features, including; nanopillars, nanoflakes, and various crystallite formations (**Figure 10**). An example reporting high resilience utilises zinc/nickel/cobalt composites to generate superhydrophobic materials able to resist prolonged surface abrasion. The physical robustness is explained through the formation of a highly strong composite material, in combination with effective substrate binding [79].

Another example reported to enhance both physical and chemical resilience, is the utilisation of protective surface treatments. Silanisation has been effectively applied to melamine sponges [88]. Whereby the sponge microstructure acts as a roughening template, with hydrophobic silanisation [-(Si(R)-O)<sub>n</sub>-, where  $R = -(CH_2)_{17}CH_3$ ] delivering superhydrophobicity. The sponge is demonstrated as a selective oil absorbent material, with an affinity for a range of

hydrophobic liquids (includes; toluene, chloroform, diesel, and motor oil). Upon absorption of the liquid, it is subsequently removed by applying a compressive force; this deforms the internal microstructure and is a potential cause of degradation. The sponges undergo successive liquid absorption/removal cycles (up to 1000 iterations) without the loss of functionality. The resilience demonstrated by the sponges is explained through the flexibility properties of the melamine sponges, and robust chemistry of the surface protecting chemistry [88].

#### 4.1.2. Strengthening modifications

The modification of materials can be classified by considering the alteration as either a physical, or a chemical, variation to an existing material. In a physical addition, the chemical structure of the original components does not change (e.g. incorporation of carbon nanotubes into polymer matrix) [89]. Chemical additions are therefore associated with a change in the chemical structure of one or more original components (e.g. the doping of semi-conductor structure) [90].

#### 4.1.2.1. Physical addition

The addition of strengthening components into an existing structure operate *via* a combination of two main mechanisms. The components can fortify the superhydrophobic microstructure by cohesive binding, in addition to the impregnated material imparting intrinsic resilience [82, 83]. The exact balance of these factors varies depending on the particular materials combination. A commonly used physical strengthening additive are carbon nanotubes, as they have an intrinsically high structural integrity, and can also contribute additional roughness to the surface microstructure. The incorporation of carbon nanotubes has been shown to increase resilience to applied forces, while improving surface hydrophobicity [89, 91].

#### 4.1.2.2. Chemical addition

The microstructure and resultant resilience of a superhydrophobic material can be directly determined by the chemical structure of the composite materials. Chemically altered components have been utilised throughout the literature as a means to increase surface hydrophobicity, and improved resilience [90]. Porous organic polymers (POPs) are an example of the importance of chemical structure, as some POPs are susceptible to hydrolytic degradation [92]. The protection of these porous polymers can be achieved through the incorporation of hydrophobic species into the polymer, which reduce the chemical degradation—achieving water contact angles of 152°. This is demonstrated to greatly extend the applicability of the reported POP material [92].

#### 4.2. Structuring materials

The architecture of surface morphology can play a significant role in determining a materials resilience (**Figure 10**). This has led to the development of a range of surface design approaches to secure the physical robustness of superhydrophobic materials.

#### 4.2.1. Protective surface features

The dual-scale roughness of many superhydrophobic surfaces can be exploited to generate bulkier protective features (**Figure 10**) [93, 80]. The principle behind this approach is to utilise larger, more resilience morphological features to act as the sacrificial points of contact when handled manually. Two types of surface architecture that utilise this approach include sacrificial points of contact that emanate from the surfaces, and surfaces with inaccessible superhydrophobic divots. The superhydrophobic divot approach has been accomplished *via* laser etching of metals followed by hydrophobic surface treatment. Whereby the non-etched areas act as protective contact points [93]. Eminent structuring has been achieved through a number of fabrication techniques, this includes micromachining, followed by moulding of polypropylene (**Figure 10**). The result was a multi-scale surface roughness generating samples with large features able withstand mechanical compression up to 20 MPa, and abrasive wear tests up to 120 kPa [80].

#### 4.2.2. Optimised surface architectures

The surface microstructure has been shown to play a significant role in increasing the physical strength of surface features. The degradation of surface microstructures can occur in a range of ways (i.e. shearing, mushrooming, and splitting), with the surface architecture influencing the route of degradation [94]. In the fabrication of thin films and coatings, the strength of adhesion to the substrate must also be considered. Many high strength coatings are supported by the inclusion of binding layers to improve adhesion [95, 96]. Many superhydrophobic coatings from the literature incorporate surface treatments to improve substrate binding, this includes; molecular layers (e.g. SAMs), polymer films, and commercial adhesives [56, 97, 98].

Strategically designed surface architectures are highly challenging to formulate, particularly when designing intensely water repelling, as they require dual-scale roughness (i.e. micro/ nanoroughness) [1–3]. Examples of utilising exclusively micrometre-sized structures to ensure robustness have been reported [99]. One approach implements microfabrication to generate a polydimethylsiloxane pillar array (**Figure 10**), further optimised by the addition of a fluoroalkyl film. Whereby substantial micropillars, in combination with targeted geometry prevent physical degradation, and the loss of trapped air [81]. An example that targets both strong substrate binding, and robust surface features, utilises a multi-step coating deposition [100]. The technique ensures strong substrate adhesion (using a solution growth of silica onto glass), whereby surface roughness is generated by depositing three forms of silica (mesoporous thin film, nanoparticle dispersion, and mesoporous nanosheet dispersion), which is then locked into place by a final coating of silica. Hydrophobic surface treatment is then used to generate the final superhydrophobic material, able to with stand abrasive forces [100].

#### 4.2.3. Preventing air loss

The stability of air trapped at a wetted superhydrophobic interface can be assessed experimentally (Section 2.3.2), however cannot be fully predicted, especially if morphological features are distributed arbitrarily [23]. Generally, it is observed that statistically larger volumes of trapped air are more easily removed then smaller volumes [34]. However, a combination of highly water repellent surface chemistries, and strategically designed morphological features, can be used to prevent air loss [81]. High aspect ratio needle structure (nanoneedles) with hydrophobic surface chemistries have been shown to provide a high stability for trapped air, through a combination of intrinsically high WCAs, and a wide range of trapped air environments [101]. Superhydrophobic surfaces fabricated from arrays of holes have also been demonstrated to provide a high stability of trapped air. This approach is able to provide a high proportion of trapped air that is firmly positioned, requiring a high hydrostatic pressure for its removal [102].

#### 4.3. Responsive surface morphologies

This section summarises materials that exhibit and engineered response to physical stimuli, preserving high surface roughness, and/or hydrophobic surface chemistry, thus maintaining superhydrophobicity.

#### 4.3.1. Mobile surface features

High intensity physical abrasion applied to superhydrophobic materials will tend to result in permanent degradation in wetting properties, due to damage of the surface features [26–28]. An approach reported in the literature utilises surface features that are able to be displaced from one position to another on the surface. Where roughening components are repositioned, the degree of the surface roughness is maintained — the result is a transient microstructure (**Figure 11**) [56]. The utilisation of nanomaterials in the fabrication of superhydrophobic materials is widespread throughout the literature [103]. A coating assembled from solely hydrophobic nanoparticles (no binders/adhesives), has an extremely low resilience, and could be completely removed if manually handled [104]. This has led to the inclusion of adhesives and binders to hold the nanoparticle coating to the substrate. Resilience testing has reviled that the adhesive layer also prevents displaced particles from leaving the surface, with the rearrangement causing no change to observed WCAs. Loss of surface material over extensive abrasive repetitions is reported [105].

#### 4.3.2. Regenerative structures/chemistry

The physical/chemical degradation of superhydrophobic materials and the subsequent reduction in surface hydrophobicity, is likely to be a permanent process [10, 46]. This is a result of a loss in surface roughness, and/or a transformation to lower hydrophobicity surface chemistry. Recovery from inflicted damage can be engineered into superhydrophobic materials by the incorporation of regenerative pathways. Self-healing materials have been reported *via* the inclusion of hydrophobic resins within the surface microstructure [107–110]. The leeching of these resins when surface damage occurs shields the exposed area. Although this leeching approach has demonstrated success, many routes do not involve the recovery of surface roughness. As a result, a reduction in WCAs are generally observed when extended abrasion testing is carried out [107–110]. The comprehensive recovery of surface hydrophobicity requires the regeneration of surface roughness. An example that targets this utilises multicomponent mixtures (including; hydrophobic elastomer, and polyhedral oligomeric



**Figure 11.** Surface morphologies engineered to provide reactive resilience, through the use of (A) transient micro/nanostructures, and (B) regenerative surfaces [56, 106].

silsesquioxane) that are able to regenerate surface roughness even when the material is fully abraded. The regeneration is facilitated through strategic selection of the mixture components, and an optimised regeneration protocol (**Figure 11**) [106].

## 5. Conclusions

This chapter has provided a summary of approaches for evaluating and engineering resilience within superhydrophobic materials. The development of superhydrophobic surfaces robust enough to withstand even light manual handling has the potential to tremendously extend their current applicability. There are huge amounts of literature examples asserting varying degrees of resilience, many utilising arbitrary testing methods that provide minimal quantitative resilience information (Section 2.3.1). Although the engineering of superhydrophobic surfaces has made progress toward materials useable under real-world conditions, this advancement would be accelerated by the adoption of standardised resilience testing techniques.

The approaches to assuring resilience to physical/chemical/reversible degradation are well established (Section 4). The development of these principles (i.e. improving; strength,

versatility, air-layer stability, etc.) is a tremendous focus for researchers in this area. Superhydrophobic materials have been shown to have extraordinary potential in many applications (e.g. antibiofouling, self-cleaning, drag-reduction, etc.). Exploring the limitations of micro/nanostructure resilience will be critical in determining the ultimate applicability of superhydrophobic technology.

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### **Conflict of interest**

CRC would like to declare no conflicts of interest.

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