Accepted Manuscript

Recent advances in the mechanical durability of superhydrophobic materials

Athanasios Milionis, Eric Loth, Ilker S. Bayer

PII: S0001-8686(15)00237-7
DOI: doi: 10.1016/j.cis.2015.12.007
Reference: CIS 1610

To appear in: Advances in Colloid and Interface Science

Please cite this article as: Milionis Athanasios, Loth Eric, Bayer Ilker S., Recent advances in the mechanical durability of superhydrophobic materials, Advances in Colloid and Interface Science (2015), doi: 10.1016/j.cis.2015.12.007

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.
Recent advances in the mechanical durability of superhydrophobic materials

Athanasios Milionis\textsuperscript{a,*}, Eric Loth\textsuperscript{a,*} and Ilker S. Bayer\textsuperscript{a,b,*}

\textsuperscript{a}Mechanical and Aerospace Engineering, University of Virginia, 122 Engineer’s Way, Charlottesville, VA 22904, United States
\textsuperscript{b}Smart Materials/Nanophysics, Istituto Italiano di Tecnologia, Via Morego 30, Genoa 16163, Italy

Keywords: Durable superhydrophobicity, wear, textured surfaces, surface wetting, superhydrophobic, abrasion

ABSTRACT

Large majority of superhydrophobic surfaces have very limited mechanical wear robustness and long-term durability. This problem has restricted their utilization in commercial or industrial applications and resulted in extensive research efforts on improving resistance against various types of wear damage. In this review, advances and developments since 2011 in this field will be covered. As such, we summarize progress on fabrication, design and understanding of mechanically durable superhydrophobic surfaces. This includes an overview of recently published diagnostic techniques for probing and demonstrating tribo-mechanical durability against wear and abrasion as well as other effects such as solid/liquid spray or jet impact and underwater resistance. The review is organized in terms of various types of mechanical wear ranging from substrate adhesion, tangential surface abrasion, and dynamic impact to ultrasonic processing underwater. In each of these categories, we highlight the most successful approaches to produce robust surfaces that can maintain their non-wetting state after the wear or abrasive action. Finally, various recommendations for improvement of mechanical wear durability and its quantitative evaluation are discussed along with potential future directions towards more systematic testing methods which will also be acceptable for industry.

Contents

1. Introduction .........................................................................................................................2
   1.1 Wetting parameters .......................................................................................................3
   1.2 Wetting states and transitions ......................................................................................4
   1.3 Categories of superhydrophobic mechanical durability ..............................................5
2. Adhesive durability ..............................................................................................................8
   2.1. Tape peeling ..............................................................................................................8
   2.2. Cross-cut test .............................................................................................................10
   2.3. Recommendations for adhesion .................................................................................11
3. Tangential abrasion durability ............................................................................................11
   3.1. Linear abrasion ..........................................................................................................12
   3.2. Circular abrasion .......................................................................................................16
   3.3. Blade/knife test .........................................................................................................17
3.4. Pencil hardness test ................................................................. 18
3.5. Oscillating steel ball ............................................................... 19
3.6. Oscillating steel ring ............................................................... 19
3.7. Bare finger contact ................................................................. 19
3.8. Recommendations for tangential abrasion .................................. 20

4. Dynamic impact durability .......................................................... 20
4.1. Solid particle impact ............................................................... 20
4.2. Liquid spray/jet/droplet impact .................................................. 23
4.3. Aerodynamic impact ............................................................... 24
4.4. Recommendations dynamic impact ............................................ 25

5 Liquid bath durability ................................................................. 25
5.1 Laundry wear ............................................................................. 26
5.2 Ultrasound treatment ............................................................... 29
5.3 Rotary slurry test ....................................................................... 30

6 Recommendations and future directions for mechanical durability .... 31
6.1 Recommended primary mechanical durability tests (from Chapters 2 & 3) ......................................................... 31
6.2 Recommended secondary mechanical durability tests (from Chapters 4 & 5) ......................................................... 31
6.3 Future Direction to Improve Mechanical durability ....................... 32

Acknowledgements ........................................................................ 32
References ...................................................................................... 32

*Corresponding authors: Tel.: +30 6995014580 (A. M.)

E-mail addresses: am2vy@virginia.edu (A. Milionis), loth@virginia.edu (E. Loth), ilker.bayer@iit.it (I. S. Bayer)

1. Introduction

The discovery of the unique self-cleaning properties of the lotus leaf by Barthlott and Neinhuis [1] during 1997 was the beginning of an intensive research on bio-inspired artificial non-wettable surfaces. In the following years, an enormous number of papers were published regarding different methods to fabricate superhydrophobic surfaces [2]. Usually, when a liquid droplet is placed on such surfaces, it tends to bead up to an almost spherical shape and subsequently roll-off if the surface is slightly tilted. The enormous research interest in superhydrophobic surfaces stems from their potential to be incorporated in a vast number of applications [4-16].

However, the non-wettability of a superhydrophobic surface can be degraded through exposure to a variety of environmental mechanisms including: chemical reactions with solvents or gases, UV exposure, particle or bacteria contamination and mechanical wear. In this review, the focus will be on “mechanical”
durability, i.e. surfaces that are able to retain their non-wettability after repeated cycles of damage by mechanical forces and motions. This is important because mechanical wear is the main degradation mechanism for superhydrophobic surfaces. Furthermore, other types of degradation (UV exposure, particle contamination, chemical degradation, etc.) generally apply to a broader range of surfaces that are not necessary superhydrophobic.

1.1 Wetting parameters

The primary measured physical parameters for evaluating the performance of a superhydrophobic surface include: the apparent contact angle (APCA), the contact angle hysteresis (CAH), the roll-off angle (ROA) and the shedding angle (SHA). The APCA is a measurement of the equilibrium condition when a liquid droplet is placed on a solid substrate and it is defined as the angle between the tangent to the liquid–fluid interface and the tangent to the solid interface at the contact line between the three phases [17]. For extreme non-wettable surfaces this value has to be greater than 150°. In contrast, the other parameters mentioned above (CAH, ROA and SHA) quantify the ability of the liquid to stay adhered on the solid surface. As such, they are a more consistent indicator of non-wettability from a functional perspective. Typically, the values for these parameters are lower than 5° or 10° in the case of superhydrophobic surfaces. The reason for this focus on adhesion parameters is that damaged non-wettable surfaces sometimes still maintain a high APCA accompanied by high water adhesion, which is problematic in terms of applications. For example, mechanical wear can cause the droplets to lose their easy roll-off behavior and become “pinned” on the substrates, a phenomenon described in the literature by various researchers as the “petal effect” [18]. In the following, primary “liquid adhesion to substrate” parameters are defined in more detail.

The roll-off or sliding angle is simply the maximum angle that the surface can be tilted until the water droplet rolls-off or starts sliding. This measurement can be influenced by the volume of the water droplet, since this movement occurs when gravitational forces exceed the static friction forces. As a result, the roll-off (ROA) or sliding angle (SA) decreases as the size of the droplet increases [19]. The contact angle hysteresis of a surface is the difference between the advancing and receding contact angles, i.e. the contact angles measured during an expanding (advancing) or retracting (receding) motion of the three-phase contact line. The greater the difference between these two angles, the greater the adhesion force will be between water and the surface. Finally, the shedding angle (SHA) is defined as the lowest substrate tilt angle that allows the droplets to leave the substrate by bouncing or rolling-off when released from a given height [20]. This measurement method was originally developed by Zimmerman et al. for overcoming imaging problems in the classic contact angle measurement when using textiles, since the
surfaces of the textiles are usually very rough and the boundaries of the water droplets cannot be well distinguished in order to have an accurate measurement. The shedding angle values are influenced by the dispensing height and the size of the droplets.

1.2 Wetting states and transitions

In general, the key element to obtain surfaces with extreme non-wettability is to use hydrophobic materials to fabricate a rough surface with micro and/or nano-scale features [21]. When water droplets are dispensed on surfaces with appropriate combination of chemical (material) and physical (surface texture) properties, air pockets can form at the interface between liquid and solid such that only a small fraction of the liquid surface contacts the solid while the rest is cushioned by air. In this case, the frictional force for tangential motion of the drops along the surface is due only to the small fraction of liquid-solid contact area. This phenomenon is known as the Cassie-Baxter state, named in honor of the two researchers who first reported it in 1944, and it is present in all the surfaces that exhibit extreme non-wettability with high apparent contact angles [22]. In the early stages of non-wetting surface design and analysis, the conception was that the Cassie-Baxter state only occurs when the solid surface is composed of hydrophobic materials. However, recently Li et al. [23] demonstrated that properly textured surfaces having sub-micron scale roughness and uniform surface chemistry (even hydrophilic) can be superhydrophobic with very low contact angle hysteresis. In fact, they demonstrated this concept by etching paper surfaces to create the required hierarchical roughness and afterwards coating them with a hydrophilic diamond like carbon. The result was a non-wetting paper similar to paper substrates coated with fluoropolymer layers. However, in general, if hydrophilic materials are used instead, the most energetically favorable state is the Wenzel, where the water penetrates into the spacing between the rough protrusions resulting in full wetting of the solid phase. Figure 1 shows the difference between Wenzel and Cassie-Baxter type of wetting on a micro-rough surface. Both these two states can exhibit high APCA but in terms of water adhesion a completely opposite behavior is observed. In a Cassie-Baxter state the air entrapment on the solid-liquid contact causes a dramatic reduction in adhesion, since air can be regarded as a very hydrophobic substance, thus the droplets tend to roll-off easily. In the Wenzel state, the penetration of water in the rough asperities of the surface induces pinning effects that dramatically increase the solid-liquid adhesion [24]. Many researchers have reported the presence of hybrid states to explain particular water adhesion behaviors in surfaces with dual-scale roughness, e.g. Cassie-Baxter in the micro-scale and Wenzel in the nano-scale or vice versa, or semi Cassie-Baxter state where the liquid meniscus penetrates partially in the rough features [14,15,25-27] while the motion of the micro-contact line of the droplet can be affected by adding roughness scales [28]. Some of these wetting states are depicted in Figures 1b,d,e.
In general, most superhydrophobic surfaces are very fragile (i.e. they will lose non-wettability if touched or rubbed by human hands) and are not suitable for commercial uses. This mechanical fragility of the surface texture can cause surface defects which lead to collapse of the Cassie-Baxter state. As a result, a subsequent transition to the energetically more favorable Wenzel state occurs, where the liquid now penetrates in the rough asperities inducing strong pinning effects and eventually increased adhesion of the liquid to the substrate and loss of anti-wetting performance. This lack of surface mechanical robustness to retain a state of high non-wettability hinders the possibility of applying such coatings in household products, vehicles, clothing, electronic devices, machinery, aircraft industry, etc. Owing to this, there has been an increased scientific effort recently towards significantly improving the mechanical performance of non-wettable coatings. The first key review article that emphasized the mechanical durability of superhydrophobic coatings was published in 2011 [29]. The present article builds on this work by surveying many new developments that have occurred in the last few years on the subject of mechanical durability for superhydrophobic surfaces. This article also investigates various methods and tests used to investigate durability and aims to recommend a number of primary and secondary tests to evaluate the “durability” of non-wetting surfaces in the most efficient and convincing way.

1.3 Categories of superhydrophobic mechanical durability

The most common strategy for mechanical durability is to employ surfaces that can withstand structural forces while retaining the geometric features [30] associated with the surface topology and the hydrophobic composition associated with the surface chemistry. The primary categories of durability performance of a superhydrophobic coating are: adherence to the substrate, the ability to resist tangential abrasive forces and the ability to resist dynamic impact. In addition, many coatings are desired to withstand dynamic liquid bath conditions. In all these categories, it is desired that the coating maintain its static anti-wetting state and low water adhesion properties. To understand the details of the durability, it is important to understand the mechanisms that can cause a loss in superhydrophobic performance. In general, all these mechanisms are based on the removal of material that reveals a new chemistry or geometric topology. Generally, preserving the geometric topology is the most important aspect for mechanical durability.

The geometric topology of superhydrophobic surface can be quite complex. Since Cassie-Baxter performance requires at least one scale of roughness and is increased if both micro and nano-roughness are employed [30], multiple scales of features may need to be retained for robust durability. However, the micro-features are generally the most important since their role is to sustain the droplet on their upper part of the surface so that substantial air-pockets are formed on the droplet-substrate interface [31]. Generally,
the height of micro-features must exceed a threshold value, which can vary for different types of textures, in order to suspend the liquid surface in air between two neighboring surface peaks, to maintain a Cassie-Baxter state [32]. If the height of micro-features is lower than the threshold value then transition to a Wenzel state will occur and the non-wettability will be lost. Such a height reduction can happen when textured surfaces undergo mechanical wear, i.e. the height of the micro-features progressively decreases until it goes below the threshold for maintaining a Cassie-Baxter state. When this transition to a Wenzel state occurs, the damaged surface cannot perform its function of non-wettability. This degradation is thus related to the loss in surface structural features that maintain a proper surface topography.

Preserving the surface chemistry is the second most important aspect for mechanical durability. Loss of functionality due to a change in the surface chemistry by mechanical wear depends on the degree of coating homogeneity in the bulk. If the coating is chemically homogenous throughout bulk and unless the entire coating is removed (down to the substrate), no loss of chemical uniformity will appear. If the more common top-coat or surface functionalization strategy is used to induce anti-wetting properties, then removal of this thin upper coat is enough to lose the desired surface chemistry. This is a key concern in terms of durability since very thin monolayers or treatments are usually on the molecular to nanoscale level and tend to be removed very easily by the application of even minor mechanical abrasion. In such cases, this minor abrasion gradually uncovers hydrophilic sites from the underlying material that ruin the desired surface properties. This degradation is thus related to a change in surface chemistry, as described schematically in Fig. 2a, while Fig. 2b describes a loss in geometric topology as previously discussed.

An obvious approach to avoid the top-coat problem is to employ homogeneous chemistry by use of hydrophobic bulk materials that even upon minor surface damage will retain their chemistry. It should be noted that there exist a few materials in the literature which are entirely non-wettable and they are not coatings but rather bulk materials. Zhu et al. [33] developed a superhydrophobic bulk material by embossing carbon nanotubes (CNTs) on polytetrafluoroethylene mold under high temperature (390° C) and pressure (256 kPa). Both these materials are hydrophobic but the protruding CNTs provide the necessary hierarchical texture required for superhydrophobicity (Figure 3). The APCAs for water droplets placed on the bulk material surface varied from 159° in the initial state to 152° after 20 abrasion cycles which were performed by rubbing the surface with a sandpaper under a pressure of 5.6 kPa, whereas the corresponding SAs ranged from 3° to 22°. As depicted in Figure 3e, the superhydrophobic property is present also in the inner part of the material since the water droplets maintain a spherical shape also when deposited on a piece cut from the bulk. Another quite similar molding approach was followed by Zhang et al. [34] where they combined TiO₂ nanorods, hydrophobic SiO₂ nanoparticles (NPs), polypropylene (PP) and a small amount of poly(dimethylsiloxane) that acted as a binder to improve the adhesion of the
inorganic SiO$_2$ and TiO$_2$ nanomaterials to the PP matrix. Water droplets exhibited typical spherical shapes with a water APCA about 158°±1° and a low sliding angle 1°±0.5°. One drawback is that non-wettable bulk materials can be very fragile since their cohesive forces are very weak. Additionally, the use of such materials could be much more expensive compared to the application of thin coatings on various surfaces where much less quantity of non-wettable material is required to perform the same function.

While the above discusses how mechanical wear can degrade superhydrophobic performance, it is also possible that that mechanical wear can enhance the anti-wetting performance of a surface (Figure 2c). In particular, a smooth hydrophobic material roughened by abrasion may reveal roughness topography allowing Cassie-Baxter wetting state. For example, Wang et al. [35] prepared superhydrophobic surfaces by abrading with sandpaper poly(tetrafluoroethylene) (PTFE)/room temperature vulcanized silicone rubber composites (RTVSR). The initial surfaces prior to abrasion were relatively flat. The water APCA for pure RTVSR was measured to be 92.7° and the SA 69.5° while after increasing the volume fraction of PTFE up to 30% the water APCA increased to 108.7° and the SA decreased to 6.5°. Interestingly, after abraded with the sandpaper for 2 min with 10 kPa applied pressure, the surface of the composites showed superhydrophobicity with water APCA 165° and SA 7.3°. This was because the sandpaper abrasion induced surface texture to the bulk material that was composed of hydrophobic constituents. Rough surface microstructures were still observed after abraded with sandpaper or cotton fabric for 100 abrasion cycles. The same authors followed a similar concept to prepare superhydrophobic surfaces by PTFE/poly(vinylidene fluoride) composites with various ratios between the two materials by a simple powder mixing and hot pressing method [36]. Jin et al. [37] prepared superomniphobic fluorinated silica aerogels and their surfaces were abraded with a sandpaper. After 100 abrasion cycles the total thickness of the removed material was 660 μm. Unlike in most of the cases, a gradual decrease of the CAH with increasing abrasion cycles was observed. This is probably due to the fact that the surfaces become smoother while maintaining their hierarchical type of texture but in some cases very high surface roughness can lead to the formation of valleys that can entrap liquid droplets. The non-wettability could be preserved after the abrasion due to the nano-porous self-similar aerogel structure that essentially maintained the desired topography even upon abrasion, and in addition by deposition of surfactant in the interior of the aerogel that self-replenished the damaged sites of the surface acting as a self-healing material. At this point, we need to mention that two other possible strategies to maintain non-wettability include self-healing surfaces [38] and easily repairable surfaces [39]. However, these surfaces are not wear resistant or otherwise mechanically durable since their concept of retaining the non-wettability is different and thus they will not be discussed in this review.
Therefore, mechanical durability depends on how the surface geometry and chemistry change. Unfortunately, different superhydrophobic coatings developed by different groups nearly all employ different test conditions and different apparatus to determine resistance to mechanical force. Therefore, an objective comparison of the abrasion resistance of superhydrophobic surfaces has been hampered by the lack of a single, standardized test method to induce wear. Likewise, no single measure has been used for characterizing the effect of wear on the anti-wetting performance. Moreover, this is complicated by the very diverse surface topography modifications used to create a superhydrophobic surface and the different intended applications for these coatings. To address this issue, the following sections will describe the primary modes of mechanical degradation and the different associated testing for each of these modes. The mode aspect is critical to understanding the mechanisms of wear while the testing aspect is closely related to the practical aspect of commercial development. The mode mechanisms discussed herein are discussed in the following chapters: 2) adhesion to substrate, 3) tangential abrasion to surface, 4) normal impact with solid, liquid or gas phase and 5) laundry and liquid baths. Finally, 6) summarizes recommended primary and secondary durability testing as well as future directions for improving the mechanical durability on superhydrophobic surfaces.

2. Adhesive durability

In the coating industries, adhesion testing is often used to determine if the coating will adhere properly to the substrates to which they are applied. Testing the adhesion is probably the first measurement to be conducted in a test series regarding durability evaluation since lack of strong adhesion to the substrate will cause the detachment of the coating in conditions like minor applied mechanical forces or increased humidity. In addition to substrate adhesion, “internal adhesion” of the material is also important, whereby the cohesive forces between the constituents of the coating are investigated. Despite the fact that adhesion is perhaps the most critical test for a coating to have durability, most of the studies on superhydrophobic coatings do not report nor make reference to their adhesion performance. In this section, we will report on simple methods that can be used to evaluate the adhesion to the substrate and the cohesive adhesion for superhydrophobic coatings.

2.1 Tape peeling

Perhaps the simplest and most useful adhesion test is the tape peeling test. Tape peeling is a material removal test that has been used to test the adhesion strength of non-wettable coatings to substrates. Generally, a tape is applied on the surface of the tested material and it is pressed in order to ensure that there is no air entrapment and the entire adhesive surface is in contact with the non-wettable surface. Subsequently the tape is peeled from one end and the surface is examined to see if the substrate is visible.
Although the tape peel test was designed to test overall adhesion to the substrate for coatings, tape removal on superhydrophobic surfaces can also lead to partial destruction of the micro/nano-scale topography and thus the wetting properties are evaluated after each peeling cycle. In that sense, this test evaluates both adhesion to the substrate and cohesive adhesion. Tapes are classified according to the values of adhesion force to a reference substrate, reported as adhesion to steel in N/m. As this parameter (force/distance) increases, the tape peeling test becomes more destructive to the coating under investigation.

Steele et al. [40] used the tape peeling test to evaluate the adhesion strength and superhydrophobicity of polyurethane/organoclay nanocomposite coatings. They tested six different values of tape adhesion strength ranging from 440 to 3850 N/m (adhesion to steel). The tapes were detached from the coatings at 2 mm/s. Increasing tape adhesion strength was found to degrade faster the anti-wetting performance. After 12 tape tests, some coatings lost their wetting performance in terms of reduced static contact angle, and more notably increased roll-off angle. However, one coating was able to maintain superhydrophobic performance with maximum tape adhesion strength 820 N/m. Even at the highest tape adhesion strength (3850 N/m), this coating retained APCA > 140° and CAH < 20°, which is quite similar to its performance before the peel tape testing (APCA > 160° and the CAH < 10°).

Another example is that of Cholewinski et al. [41] who prepared a robust superhydrophobic bilayer coating containing PDMS-functionalized silica particles on top and an epoxy bonding layer at the base. It was fabricated with a facile dip-coating process that embedded micro-scale PDMS-functionalized silica particles with nano-scale roughness into an epoxy layer spin-coated onto a substrate. The APCAs of the coatings remained stable after four tape tests, though no CAH values were reported.

Barthwal et al. [42] developed superominiphobic surfaces on aluminum with a three-step method including etching with an acidic solution, anodization with sulfuric acid, and fluorination. The durability of the surfaces was tested by performing ten tape peeling attempts. The APCA of water remained above 150° while the oil APCA remained above 150° until the 8th cycle and slightly degraded in the last two cycles. Again no CAH values were reported.

Geng and He [43] used the tape peeling test to compare the adhesion to substrate of superhydrophobic silica thin films before and after a chemical vapor deposition (CVD) process which is used to deposit tetraethyl orthosilicate for improving the mechanical robustness. The water APCA (which initially was measured 171°) decreased to 167° after 10 tape peeling tests, 161° after 20 tests, and 157° after 40 tests. However, APCA of water on the coating without CVD treatment decreased to 150° and 135° respectively after 10 tape peel tests, indicating that the coating lost its superhydrophobicity and that the CVD treatment...
significantly improved the coating-to-substrate adhesion. The same test, but only with one cycle, was performed by Deng et al [44] and Xu et al. (2 cycles) [45]. Unfortunately, CAH measurements were again not reported. In general, it is highly recommended to examine CAH after the peel tape testing as superhydrophobic performance tends to be lost first in terms of water adhesion performance rather than static performance, e.g. a droplet on a degraded surface can retain a high contact angle but may get pinned. Another important issue that often is neglected, is the presence of adhesive residues on the tested surfaces during the peel tape test cycles that might alter the surface properties and eventually the contact angle measurements.

2.2 Cross-cut test

To make a more stringent assessment of the ability of a coating to adhere to the substrate, one may induce a standardized damage to the surface before the peel-tape test is applied. In particular, cross-cut tests involve scratching lines on the target region of the film forming a square grid or an X shape prior to the tape adhesion test [4,6,47]. The tape is then placed on this cross-hatching at a 45° angle, and subsequently removed. Depending on the ASTM procedure, the brand of tape, adhesion time and pass grading may differ. Adhesion strength ratings are typically based upon the regions removed after tape peeling, that is, complete removal, removal at scratch lines, no removal, etc. For instance, the standard ASTM D3359 uses the grades 5B, 4B, 3B, 2B, 1B and 0B, where coatings rated 5B exhibit the highest adhesion to a substrate and 0B the poorest adhesion. This test is also able to provide an evaluation of the brittleness of the coatings by observing the damage patterns along the cut lines. Figure 4 shows adhesion tests conducted by our group on various silicone rubbers that exhibit different levels of adhesion to the substrate. An indicative rating chart based in the ASTM D3359 is also provided.

This ASTM D3359 standard was followed by Kumar et al [44] to evaluate the adhesion of organic/inorganic superhydrophobic coatings based on tetraethylorthosilicate (TEOS) and glycidoxypropyltriethoxysilane (Glymo) that were prepared via a sol-gel method. In the coatings to be tested, they introduced FAS and silica fillers to increase the hydrophobicity, whereby the APCA of these coatings increased from 115° to 164° upon decreasing filler size from 1-5 μm to 10-20 nm. The SA for coatings with 15 wt. % loading of 10-20 nm silica was around 2°. These coatings were then subjected to peel-tape testing. Figure 5 shows the images of the cross-cut test performed on the coatings with 10-20 nm fillers at 0, 5 and 15 wt.% loading. From Fig. 5a, it can be seen that the cross hatch squares on the coating with no fillers show no cracking or chipping, and the coating is rated as 5B according to the ASTM D3359 standard. The coatings with increasing filler content progressively show higher removal of coating from the cross hatch squares and chipping around the cut lines, indicating increased brittleness of
the coating. From Figures 5c and 5d, the cross-cut damage of the coatings with 10 and 15 wt. % silica NPs were rated as 2B and 1B respectively according to ASTM D3359. This is an unfortunately common theme in superhydrophobic coatings. Increased resistance to wetting is often associated with decreased durability.

2.3 Recommendations for adhesion

The adhesion test, even if it has been rarely reported compared to other ones, is the first test of durability that should be conducted since lack of adhesion to the substrate will render the coating unsuitable for almost any kind of application. For evaluating the adhesion to the substrate, the authors first recommend the use of the ASTM D3359 standard: peel-tape testing on a cross-hatched surface. There are specific tapes that are suggested for this test but generally the ones with the highest adhesion strength values are the most suitable. This cross-hatch test is straightforward and provides a simple standardized assessment of substrate adhesion.

As second adhesion test we can measure the static and, especially, the water adhesion parameters after tape peeling cycles to evaluate the adhesion of the micro and nano features to the bulk coating. A coating that passes this test (retains superhydrophobic properties) can be expected to have significant internal adhesion. However, it can be difficult to interpret a test failure since it is not easy to discern which of the two mechanisms degrades the wetting properties for increasing tape peeling cycles: partial adhesive deposition of the tape material to the surface (addition which changes the surface chemistry) and the partial destruction of the surface (removal of micro or nano features which changes the surface geometry and/or chemistry). Therefore such a tape peeling test should be performed as secondary test to evaluate mechanical adhesive durability.

For improving the adhesion to the substrates some general recommended rules are: (1) Introducing surface roughness to the substrate by sandblasting or etching so that the applied coating can “lock” better to the substrate. (2) Cleaning the substrate very well prior to coating application by acid treatments (e.g. piranha solution), various solvents or O₂ plasma. (3) Ensure that the substrate is completely dry prior to coating application. (4) Ensure chemical compatibility of the coating with the substrate by appropriate selection of materials or primers. (5) Post-thermal curing can also help sometimes to improve the adhesion to the substrate.

3. Tangential abrasion durability

Rubbing between two solid surfaces is a common condition that can occur in everyday use of non-wettable materials and therefore this mode of wear is important for characterizing mechanical durability.
Generally, abrasion resistance is most directly and commonly measured using linear shear abrasion with a solid abradant moving tangentially to the tested surface. In this form, wear arises from the contact point moved parallel to the surface with a force vector that is normal to the material surface. This tangential abrasion has been reported in the literature using many different experimental setups, all of them having in common the basic concept of rubbing or sliding a solid material to the surface under investigation. This induces mechanical wear and subsequently material removal that eventually leads to alteration of the surface characteristics and loss of the non-wettability.

Different abradant materials have been used throughout the literature to perform tangential abrasion. These materials vary from study to study since authors have used as abradants, e.g. rough sandpapers of different grades, aluminum, A4 paper sheets, poly(dimethylsiloxane) (PDMS), glass, brushes, wipes, etc. Wu et al. prepared superhydrophobic polyester textiles by a dip-coating approach and later they tested their mechanical durability by abrading them linearly with different types of sandpaper [48]. Due to the difference in the physicochemical characteristics of these two materials (hardness, surface roughness, and chemical affinity) they observed very different degradation rates of the non-wettability of their samples. Furthermore, Wang et al. obtained completely different non-wettability when they abraded their superhydrophobic surfaces by sandpapers of different grades [35]. Interestingly, they were able to obtain superhydrophobicity only when they used sandpaper of grade in the range 280–400#. For all the other grades used, outside these limits, their surfaces did not exhibit superhydrophobic property. These important observations lead to the conclusion that a mechanical test is heavily influenced by factors such as the surface roughness of the abradant surface, or its chemical composition and Young’s modulus. Unfortunately, there are many other influential parameters that vary from study to study when using hand-applied sandpaper wear. These include the applied pressure on the abradant surface of the surface, the amount of contact between the two surfaces, type of motion and the relative speed between the surfaces, etc. Thus, in order to evaluate the mechanical durability of a sample surface across different studies and coatings, a testing method that allows carefully specified pressure, contact area, motion and speed is needed. Such methods are discussed below in order of recommendation.

3.1 Linear Abrasion

The simplest motion is that of a linear abraser which moves back and forth over the same line of contact. As a result, linear abrasion setups are the most common and widely accepted method to quantitatively test the mechanical durability of non-wettable surfaces. Figure 6a depicts a typical experimental setup for performing a linear abrasion test and Figure 6b a Taber linear abraser that it is used by many different research groups to conduct such tests. Usually these experimental setups consist of a horizontal arm
holding a vertical cylinder that reciprocates in a linear direction while the speed and the length can be adjusted. The bottom end of the cylinder can be fitted with various types of abradant materials like cloth, sandpapers, rubbers, papers or hard aluminum oxide which produce different type of mechanical wear. The sample to be tested is mounted and aligned parallel and in contact with the bottom part of the cylinder. The pressure applied on the surface to be tested can be adjusted by adding or removing weight on the vertical cylinder. Alternatively, the surface to be tested is fixed at the bottom part of a solid structure of known weight and it performs a linear reciprocating motion on the substrate which in this case is the abradant material. Figure 6c depicts four different abradants from Taber. The selection of abradant is very important since they can produce very different types of wear. For example the cloths or rubbers tend to smoothen (flatten) the surface while the vitrified abradants or sandpapers tend to produce coarse abrasive action, thus roughening the surface. There is no general rule regarding which of these abradants is more catastrophic to the surface. As we mentioned in the section 1.3, some vitrified abradants that increase the surface roughness might enhance the superhydrophobicity as well (bulk hydrophobic materials) but for other surfaces that have very fine surface features (like patterned surfaces with lithography) this type of coarse abrasion will be destructive. The key performance features that can be measured in such a linear abraser test include the number of cycles to loss of superhydrophobic properties (static and adhesion phenomena) as well as the number of cycles to the loss of the coating (exposing the substrate below).

Figure 6d shows a graph of the ROAs of a superhydrophobic surface against the number of abrasion cycles by using three different abradants. The tested surface is superhydrophobic nanocomposite developed by our research group. It is evident that each abradant produced very different wear effects on the surface since the number of abrasion cycles required for loss of superhydrophobicity was significantly altered. As noted above, when measuring the durability of superhydrophobic surface there are different types of failure. First is the increase of the water adhesion via an increase of the CAH, ROA, SHA or SA which we consider to be the most important. This can happen either due to loss of surface texture, loss of the chemical functionalization or due to complete coating removal. The second is the decrease of the static contact angle which in terms of application does not have significant importance. A very common case is that during a linear abrasion test, a sudden drop in the CAH might be observed but the APCA will maintain very high values for many more abrasion cycles. Many researchers claim that their surfaces maintain for hundreds or thousands abrasion cycles the superhydrophobicity but this is not necessarily true from a water adhesion point of view which is the most critical parameter from an application standpoint.
Wu et al. [49] used a similar apparatus as in Figure 4a in order to test the durability of superhydrophobic cotton fabric obtained by radiation-induced graft polymerization of lauryl methacrylate and n-hexyl methacrylate. Through the steam ironing process, the superhydrophobicity could be regenerated even after the yarns were ruptured during the abrasion test under a load pressure of 44.8 kPa and crocking cloth used as abradant material. The treated cotton fabric could ultimately withstand at least 24,000 cycles of abrasion with periodic steam ironing. However, the term superhydrophobic was used considering only the APCA since no hysteresis values were reported in this study. Textile surfaces will be analyzed more extensively in one of the following sections since they behave very differently in terms of durability compared with non-fibrous materials.

Tang et al. [50] prepared superomniphobic (repelling extremely a wide variety of liquids) coatings by spray-casting dispersions of polyurethane and MoS$_2$ NPs. After the spraying process the surfaces were functionalized by gas-phase silanization with a fluorosilane. The abradant material was stainless steel that was roughened with a sandpaper prior to the abrasion test. The applied pressure on the surface was 0.7 MPa and the water APCA and CAH were measured as a function of the rubbing distance (i.e. the total distance that the abradant covered on the tested surface by rubbing it) and not abrasion cycles like in other studies. The coatings were able to preserve high contact angles (>150°) for up to 100 m rubbing distance but the CAH increased significantly with the first 10 m of rubbing distance. This result is a very good example to emphasize the importance of presenting both static contact angles and water adhesion values when mechanical abrasion tests are performed, since the surfaces might appear extremely non-wettable statically but (which is also the most practical aspect) their water adhesion properties might degrade faster. Wang et al. [51] also expressed the durability of their fluorinated copper oxide superhydrophobic surfaces in terms of rubbing distance. The APCA and the SA degraded immediately with just a few centimeters rubbing distance on an 800 mesh abrasive paper. After 80 cm rubbing distance the water drops remained pinned on the surfaces even at 90° tilt angle.

Steele et al. [52] prepared laser-textured titanium surfaces that were rendered superhydrophobic by applying a subsequent fluoropolymer coating. Titanium was selected as the material for surface texturing due its inherent outstanding mechanical durability. In this study, they investigated harsh applied pressure conditions ranging from 108.4 to 433.7 kPa. This surface was able to survive 200 abrasion cycles before it was destroyed and the APCA decreased gradually. For higher applied pressure, the reduction of the APCA was faster. However, the CAH degraded (increased) much faster even only after 10 abrasion cycles. The effect of the wear mechanism from the abradant material was also described in detail. The primary abrasive wear mechanism was found to be the fatigue by repeated plowing, but there was also
contribution by the small particles detached from the abradant material during abrasion that caused small striations on the textured titanium substrates.

Milionis et al. [53] have also investigated the effect of applied linear abrasion pressure on superhydrophobic biodegradable starch-based thermoplastic nanocomposites. Five different pressure values ranging from 1115 Pa to 2123 Pa were applied on the surface of the coatings and the water APCAs and ROAs were recorded for up to 17 abrasion cycles. A solid smooth plastic disk with Rockwell hardness of M70 (R-scale; ISO 2039-2) similar to polycarbonate was used as an abradant. Again it was observed that increasing the applied pressure on the surfaces gradually decreased the APCAs, a phenomenon that was more intense for the highest pressure used (2123 Pa) since the APCAs dropped below 150° after 10 abrasion cycles. However, the increasing trend of the roll-off angles against the number of abrasion cycles was much more evident, especially for applied pressures equal or greater than 1717 Pa.

Zhu et al. [54] tested the mechanical durability of superhydrophobic surfaces prepared by molding ultra-high molecular weight polyethylene and functionalizing the surface with silver and perfluorodecanethiol. The abradant used was sandpaper (1500 mesh) and the applied pressure was 10 kPa. The resulting surface was able to withstand 10 abrasion cycles under these conditions before eventually starting losing the superhydrophobicity due to decrease in the fluorine concentration on the surface. Zhou et al. [55] used the same experimental apparatus to evaluate the mechanical performance of cotton fabric that was rendered superhydrophobic by incorporation of polyaniline and fluorinated alkylsilane via a facile vapor phase deposition process. The applied pressure was 3.68 kPa. The authors demonstrated that their surface could maintain water APCAs greater than 150° for 600 abrasion cycles but they did not mention anything about hysteresis values. Cho et al. [56] prepared superhydrophobic aluminum surfaces with micro- and nanorough hierarchical structures by a 3-step approach. First, the formation of nanostructured aluminum hydroxide was carried out in a NaOH solution. Subsequently, a micro-rough surface texture was obtained by sandblasting the aluminum sheet with sand particles and finally the surface was hydrophobized with a fluorosilane. The authors used a similar experimental setup to carry out the mechanical durability tests but with a slightly different approach. Instead of reporting the total number of abrasion cycles until their surface would lose its properties, they performed only one abrasion cycle but they increased every time the weight (or the pressure) applied on the surfaces until eventually they would see loss of superhydrophobicity. Their surfaces were able to withstand up to 100 g with this technique (or otherwise 500 Pa, considering the surface area of their specimens).
Chen et al. [57] developed self-repairing superhydrophobic organic/inorganic coatings comprising polystyrene, fluorinated poly(methylsiloxane), fluorinated alkylsilane, modified silica NPs and photocatalytic titania NPs that showed self-repairing ability after mechanical damage with the application of UV light. To evaluate the influence of mechanical wear of the superhydrophobic coating, the surface was abraded using a piece of sandpaper under 10 and 20 kPa pressure. The results showed that the surface was still superhydrophobic although a slight decrease in the APCA was observed (from 155° to 150°) after 10 cycles of abrasion under 10 kPa pressure. Nevertheless, when the surface was abraded under 20 kPa pressure, the water contact angle (WCA) declined considerably from 155° to 139° and the SA rose to 70°. However, after UV exposure the samples fully recovered their superhydrophobicity.

Tenjimbayashi and Shiratori [58] developed superhydrophobic coatings by mixing SiO$_2$ NPs and ethyl alpha cyanoacrylate polymer in acetone and subsequently spraying them while at the same time the distance between spray source and substrate was continuously changing. The change in the distance between spray and substrate was found to be the key for improving the durability. The durability of the coatings was tested for different applied pressures (10 cycles) with cellulose fiber as abradant. The coatings retained their superhydrophobicity after abrasion testing at 40 kPa. Coatings consisting of only NPs lost their superhydrophobicity upon testing. The same group prepared transparent superhydrophobic surfaces by modifying polyester meshes with a fluorinated silane and SiO$_2$ NPs [59]. Figures 7a,b,c show scanning electron microscopy (SEM) images of the surface after 100 cycles of linear abrasion with 10 kPa pressure and cellulose textile as abradant. The samples maintained good level of non-wettability with SA less than 25° and APCA greater than 150° and they could also be used for oil-water separation. In this graph it is clear the difference in the degradation of the water adhesion versus the contact angle. For the first abrasion cycles there is a clear gradual increasing trend for the SAs while the APCAs remain quite stable throughout the whole linear abrasion experiment. This confirms the importance of focusing more in the water adhesion measurements.

Zhang et al. [60] used an emulsion mixture to fabricate micro/nano-porous PTFE. The surfaces maintained SA < 20° for 16 cycles rubbing against sandpaper (pressure 2.7 kPa) while the APCAs remained above 140°. Finally, other abradants that have been less commonly used include wipes [61] and brushes [62]. Generally these types of abradants provide a more delicate type of abrasion.

3.2 Circular Abrasion

Circular abrasion is based on the same concept as linear abrasion and it uses the same experimental apparatus with the only difference being the type of movement that the abradant material performs. In this case the abradant material has the shape of a disk and it performs a rotational motion. For example, the
Martindale method is a common circular abrasion test that is used mainly for evaluating textiles (see also section 5.1). A disadvantage of circular abrasion, compared to the linear abrasion, is that different parts of the abradant material move with different speeds. As a result, this type of testing is not as commonly used, though the setup is easier to implement.

Kondrashov and Ruhe [63] studied the effect on the mechanical durability of different hierarchical superhydrophobic surfaces with micrometer sized cone and nanoscale grass structures produced by reactive ion etching and subsequent deposition of a fluorinated film. Their setup for testing the mechanical durability consisted of a rheometer where a metal disk (2 cm diameter) was brought into contact with the tested surfaces and performed a rotational motion for 30 s (10 rotations/min) (Figure 8). Different forces were applied vertically ranging from 1 to 20 N. The density of the structures varied across the sample and the contact area of the load with the micro- and nanostructures changed with time as some breaking of the micro- and nanostructures occurred. Therefore, it was not possible to calculate the area in contact with the abradant. It was found that the most durable surfaces were the ones with the tallest and densest micrometer sized cone structures that were able to maintain their superhydrophobic characteristics even for 20 N applied force. On the contrary, the nanoscale grass surfaces with no microscale roughness were found to be significantly less durable.

Raimundo et al. fabricated aluminum alloy surfaces with omniphobic behavior [64]. Functional, hybrid organic–inorganic coatings were obtained by a classic sol–gel route, followed by a controlled dip-coating of the substrate in order to achieve surface nanostructures. The surfaces showed good non-wettability with APCA higher than 170° and CAH lower than 5° with water, as well APCA about 145° with low-surface tension liquids. The mechanical performance of the surfaces was tested by applying loads as low as 4 N for a short time (30 s) by an abrasive felt disk (diameter of 6 cm) rotating on the test sample at a speed of 60 rpm. The samples retained their anti-wetting characteristic after the aforementioned test was performed.

3.3 Blade/knife test

There are also occasions when surfaces could come into contact with sharper objects (e.g. knives, pens, forks, etc.) that induce much more severe damage. Driven by this problem, a few studies have been published where non-wettable surfaces undergo blade tests, which are practically linear abrasion tests but instead of a flat abradant material the rubbing is performed by a sharp blade.

Wang et al. [65] used both blade and circular abrasion tests and plotted the wetting characteristics of their samples against the number of abrasion cycles. Superomniphobic, surface-treated polyester fabrics were
fabricated by a 2-step dip-coating procedure. The blade scratching test was performed on a custom-made setup (Figure 9a). The coated fabric sample was placed on a flat smooth plate. A flat blade was mounted vertically on a frame with the blade edge in close contact with the top surface of the fabric sample. A 0.8 kg weight was loaded on the blade, which was adequate load to cut the fabric. The blade was then dragged linearly with 100 drags of the blade being a “cycle”. Only APCA values were reported for the blade test. After 100 scratches were performed the APCA was slightly reduced to 150° for water, while for hexadecane was reduced to 120° and ethanol completely wetted the fabric (Figure 9b). Interestingly, after heat treatment at 140 ºC for 30 min, the treated fabric recovered its extreme non-wetting properties for all liquids (Figure 9c). For the circular abrasion tests, a polyester abradant was used under 12 kPa pressure. The APCA of water remained above 150° even after 20000 abrasion cycles. The SA suffered a larger impact from abrasion testing than the APCA. After 20000 cycles of abrasion, the SA for water increased from 2.8° and 18.5°. As it can be seen from the Figures 9d,e, depicting SEM images before and after 100 blade scratches, the fibers suffer severe damage on their surface. Jin et al. [36] also used the blade test in their surface-treated aerogels. After performing scratches on their samples with the knife, severe abrasion was observed at macroscale. However, the nanoscale roughness features remained similar to that in the original aerogel surface. This demonstrates that the developed silica aerogel had a nanoscale topography that was tolerant to wear. The underlying layers of the material that were exposed upon mechanical damage, exhibited similar nanoscale topography and as a consequence the extreme non-wettability could be maintained.

3.4 Pencil hardness test

Another mechanical durability test is the pencil hardness test. According to this method, a pencil with quantified hardness is dragged on the surface to be tested (Figure 10). Generally, the pencil is held in a carriage that is 45° and is pressed firmly on the surface while moving along it at a constant speed. The maximum pencil hardness that the surface can withstand before the pencil leaves a permanent mark is associated with its mechanical durability. The pencil hardness scale ranges from 9B for the softest pencil up to 9H for the hardest (Figure 10). A good performance for a durable superhydrophobic coating is at least 2H.

Geng and He [43] used the pencil hardness to test the durability of their TEOS-treated silica coatings. Only APCA values were measured for the coatings that reached 171° for water and 152° for ethylene glycol. The pencil hardness test was carried out by holding the pencil firmly against the film at a 45° angle and performing a 6.5 mm stroke at a speed of 0.5 mm/s. The coatings could withstand pencils with
hardness up to 4H without being destroyed. Figure 10 shows the morphology of the surfaces after performing scratches with increasing pencil hardness.

Simovich et al. [66] developed a durable and superhydrophobic coating through encapsulating nylon micrometer sized rods in a hydrophobic silica shell. The resultant coating structure resembled a network of highly entangled micrometer sized rods that gave rise to both surface roughness and hydrophobicity, resulting in contact angles greater than 155°. The embedded nylon polymer within the micrometer sized rods imparted significant mechanical durability to the surface, resulting in a coating hardness of 2H using the pencil hardness test.

Hydrophobic nanosilica and nanofluoric particles were mixed with a fluoropolyurethane resin in various concentrations to fabricate superhydrophobic coatings that had APCA ranging from 140° to 148° and CAH from 5° to 12° [67]. The hardness of coatings was found to increase by raising the NP concentrations. By using the appropriate ratios between the two types of particles and the polymer, the maximum pencil hardness that the coatings could withstand was found to be 3H.

3.5. Oscillating steel ball

Another experimental setup that has been used in the literature by Hensel et al. [68] to evaluate the mechanical durability of their omniphobic polymer membranes is the oscillating steel ball. A steel ball with a diameter of 1.5 mm was brought in contact with the sample surface and pressed with a normal load that was stepwise increased until the surface features were damaged. Shear stress was generated by lateral oscillation of the probe: 10 cycles with a speed of 0.05 cm/s and a maximal displacement of 1 mm (Figure 11). The mechanical durability of the membranes was compared with pillar-patterned surfaces. The membranes resisted loads of 200 to 500 mN depending on the comb (the hexagonal structure) wall width (Figure 11a). In contrast, the mechanical stability of the pillar structures was much lower compared to the membranes and were able to withstand forces ranging from 1 to 75 mN depending on the pillar diameter (Figure 11b). A similar setup has been used by Cao et al. [69] to evaluate the mechanical durability of superhydrophobic sol-gel films on aluminum.

3.6 Oscillating steel ring

Instead of an oscillating ball as described in the previous section, an alternative abradant material is an oscillating ring. In particular, Groten and Ruhe [70] used an experimental setup comprising a steel ring (diameter 2 cm, thickness 1.5 mm) that was pressed on the tested surfaces with a force perpendicular to the surface plane. The surfaces under investigation were silicon pillars with micro- and nano-roughness. To create shear stress, the ring was oscillated for 30 s on the tested surfaces at a frequency of 20 Hz and a
maximal displacement of 4 mm. Parallel alignment of the ring to the tested surface was assured. Whenever force was applied, the ring was automatically (self-) aligned to the surface plane. The force applied on the surfaces ranged from 1 to 20 N. It was found that adding micro-rough pillar structures improved the mechanical performance of the surfaces as they were able to retain better antiwetting characteristic at higher shear forces. However, the surfaces that had only nano-roughness were the only ones that presented CAH values lower than 10° and eventually were destroyed by the abrasion test.

3.7 Bare finger contact

Bare finger touch has also been reported in various tests. This is a qualitative test that is performed on non-wettable surfaces to better mimic human handling and it serves mostly as a demonstration that a superhydrophobic material can be suitable for commercial use rather than be part of a quantitative analysis. The natural and artificial non-wettable surfaces are often fragile to hand touch. A bare finger touch on a surface can also cause performance-degrading material addition, e.g. the touch can add salt and oil contaminant to surface, especially if this surface does not repel organic compounds, i.e. is not oleophobic. Natural secretions of sweat from the eccrine glands that are present in epidermal ridges are easily deposited on surfaces (such as glass or metal or plastics) by just touching them. Consequently, touching a non-wettable surface with a finger can alter its characteristics both physically (by destroying the surface texture) and chemically (by leaving natural secretions), thus degrading its inherent properties. Such qualitative tests have been performed in various studies in the literature [54,62,71-76]. Figure 12 shows the rubbing effect with the finger on coated superhydrophobic wood panels.

3.8 Recommendations for tangential abrasion

The linear abrasion test is currently the most popular durability evaluation method. Therefore, it is a good reference test and is recommended as the primary test for evaluating the mechanical durability of a superhydrophobic surface against wear. However, it important to focus on the water adhesion of the surface against the number of abrasion cycles, thus to measure parameters like CAH, ROA, SA or SHA. Furthermore, it is important to test the surfaces with different abradants in order to examine the different types of wear that might occur on a surface. For instance, a three-abradant set consisting of a textile (smooth, deformable), a rubber (smooth, resilient) and a vitrified (sandpaper) material can provide a comprehensive overview of the surface’s response on various abrasive actions. Based on the various papers that have investigated wear durability of superhydrophobic surfaces, it is recommended to employ a downward pressure of at least 10 kPa. Under such conditions, the surface should withstand tens or even hundreds of abrasion cycles to be considered robust. The pencil hardness or the blade test can be
performed as secondary tests if the type of application envisioned may include contact with sharp objects. The bare finger rubbing is recommended if the surface is going to be handled repeatedly by people.

4. Dynamic impact durability

Surface durability can also be tested under collisions with solid, liquid or gas phases. In these tests the surfaces are usually placed either horizontally or with a 45° tilt. The surface topography can be significantly altered by these collisions so that superhydrophobic performance of the surface can be totally removed/destroyed. In this section, we will present approaches to evaluate how sensitive is a non-wettable surface to normal impacts and material removal as well as methods that have been reported towards making impact-resistant superhydrophobic surfaces.

4.1 Solid particle impact

Solid particle impact is a common test that is performed to evaluate the mechanical robustness of surface finishes. In this test, sand is typically used which is a mixture of micrometer-sized oxide particles with the silicon dioxide being the most dominant. This test can provide information whether a coating is suitable for use in outdoor applications where eventually it has to withstand harsh weather conditions and contamination/degradation of the anti-wetting properties by embedded particles on the surface that can disrupt the surface chemistry by their presence or can cause partial destruction of the surface texture due to the impacts. It is also a common test in aerospace applications (e.g. for helicopters) where they have to withstand very severe particle collisions during their take-off and landing. A typical experimental setup is depicted in Figure 13. The coating under investigation is tilted usually 45°, so that re-deposition of the particles 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, the kinetic energy of the particles increases and eventually the probability of damaged surface is higher. The impact energy \( W_s \) of a solid particle is given by:

\[
W_s = m_s gh = \frac{4\pi}{3} \rho R_s^3 gh
\]

Here, \( \rho \) is the average density of the particles, \( g \) the acceleration of gravity, and \( R \), the mean radius of the particles. Xu et al. used a similar setup (delivering height 20 cm and 50 s exposure time) to test the
durability of their superhydrophobic surfaces which maintained their properties after the test (Figure 13a,b) [45].

Deng et al. [44] prepared transparent superhydrophobic surfaces composed of hydrophobically surface modified silica shells on glass slides. The surfaces showed APCA of 160° and SA of 5°. Sand grains were impacted on the superhydrophobic surfaces and the minimal height at which the porous silica particles burst was determined. Bursting leads to an increase of the sliding angle and finally to loss of superhydrophobicity. If 100 to 300 μm sized sand grains impacted on a superhydrophobic surface the shells remained intact for impact heights, \( h \), up to 30 cm. After the sand abrasion, the surface remained superhydrophobic, i.e. water droplets placed on the surface would bounce and slide-off easily. For \( h \) significantly larger than 30 cm, fractured shells were found. The same research group fabricated superomniphobic surfaces consisting of silica shells and carbon particles (candle soot) and the same sand impact test was performed [77]. The APCA and ROA for water were measured to be 165°±1° and 1°±1° respectively. The silica shells were not sufficiently robust to completely resist sand impact and caves formed underneath the impacted area. However, zooming into the caves revealed almost unaltered submicrometer morphology. Owing to the coating’s self-similarity, the surface kept its superhydrophobicity until the layer was removed after an extended impact. The mechanical stability increased with the thickness of the silica shell, but at the expense of the coating’s transparency. The surface retained its superhydrophobicity for 5 min of sand abrasion from a height of 25 cm (2 m/s).

Tang et al. [78] used a brush-coating approach to fabricate superhydrophobic (APCA 152.5°) nanocomposite surfaces by combining calcium carbonate NPs with either acrylate copolymer or epoxy resin. Sand grains with a diameter of ~200 μm impinged on the surface from a height of 15 cm. After sand abrasion for 5 min, the wettability of the surface was re-characterized. The APCA for the acrylate copolymer based nanocomposite decreased slightly to 150° while for the epoxy-based to 146°. No CAH values were reported.

Zhang et al. [79] prepared polypropylene (PP)/high density polyethylene (HPDE) composite films by a laminating exfoliation method. The treatments performed resulted in the formation of a rough surface. By varying the ratios between the two polymers they were able to achieve superhydrophobicity. Silica particles with diameters of 100 μm to 300 μm impacting the polymer film surface at a velocity of 2.8 m/s (40 cm) for 30 seconds (10 g of silica particles, impacting area 3 cm × 3 cm) did not destroy the superhydrophobicity of the film. Both the APCA and ROA for water remained unaltered.

By spraying polystyrene/SiO₂ core/shell NPs as a coating skeleton and PDMS as a hydrophobic interconnection between the coating and the substrate, lasting and self-healing superhydrophobic surfaces
were fabricated by Xue et al [80]. The sample was abraded for varying time by impinging the coating surface with 50 g of 300 to 1000 μm diameter sand grains from a height of 40 cm at 45°. It was found that an increase in sand abrasion time resulted in a gradual reduction in the APCAs and an increase in the CAH. However, the thicker samples were able to retain APCAs greater than 160° and CAH lower than 10° after 10 sand abrasion cycles. After 15 cycles, the superhydrophobicity in terms of CAH was lost since the value measured was 22.5° while the APCA was still high (158.1°).

Geng and He [43], apart from the pencil test described in section 3.4 used additionally a sand impact setup to test their coatings. In the sand abrasion test, 40 g sand grains with diameters of 100–300 μm were used to impact the coating surface from a height of 30 cm in 1 min. Subsequently, the coating was cleaned with water. The water and ethylene glycol APCAs before and after sand abrasion test showed approximately the same values.

Zhang et al. [81] performed also sand impact tests on their superhydrophobic aluminum alloys. Approximately 10 g sea sand particles were dropped onto the 45° tilted substrate surface for 1 min from a height of 30 cm from the substrate. The samples maintained superhydrophobicity (APCA > 150° and ROA < 10°) after five cycles. Finally a slight variation of this test was followed according to ASTM standards by Boinovich et al [82,83]. The difference was attributed to the fact that the sample was oscillating back and forth as the particles were impacting the surface.

4.2 Liquid spray/jet/droplet impact

Another mechanical impact test which is useful to evaluate the performance of non-wettable surfaces is the liquid impact test. The liquid phase can be in the form of sprayed micro-droplets, regular size drops or jet. Such test can mimic exposure to raindrop impacts commonly encountered in outdoor coating applications. During heavy rain in the thunderstorm, the rain droplets have the maximum diameter of 4–5 mm and could reach a maximum speed \( v = 7–9 \text{ m/s} \) when impacting a rigid surface on the ground with a frequency of \( 3.88 \times 10^5 \text{ drops/m}^2\text{h} \) [81]. A typical 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. Again by increasing the dispensing height, the impact of the ejected liquid on the surface becomes more destructive. In some cases, non-wettable surfaces are not damaged by drop or jet impacts but gradually a loss of their non-wettability is observed due to a Cassie to Wenzel transition. Specifically, 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 height because of the high instantaneous pressure exerted on the surface.
Davis et al. [84,85] have used a water-fed, spray setup to replicate prolonged, high-impact rain. A schematic and a photograph of this setup are depicted in Figures 14a and 14b respectively. High-flux and high-speed 1 mm drops traveling at 25 m/s were produced (more than 105 droplet impacts at Weber numbers exceeding 104), which is equivalent to decades of rainfall impacting a moving surface. The pressure of the impacted droplets was also very high (312 kPa). Polyurethane/fluoroacrylic/organoclay superhydrophobic nanocomposites were found to still exhibit high degree of non-wettability (APCAs > 140° and SAs < 40°) after this harsh test. Figures 14c-h show that there was only minor degradation of the surface topology. The effect of the inclination of the substrate during the impact was also examined and was found that the samples retained slightly better non-wettability when there was a 40° tilt compared to the vertical impact.

Xiong et al. [86] followed a two-step approach including spray-deposition and UV photopolymerization of thiol-ene resins containing hydrophobic silica NPs. The perfluorinated thiols provided a multiscale topography and low-energy surface that endowed the surface with superomniphobicity for increasing particle concentration. Water drops were repeatedly impinged on the surface of the films from a height of 2.5 and 20 cm. For drops released from \( h = 2.5 \) cm (impact velocity of 0.7 m/s), the superomniphobic films did not show any sign of water drop penetration even after extended testing (the experiment was ended after 7600 impact events) indicating a robust superhydrophobic wetting state. For drops released from \( h = 20 \) cm (impact velocity of 1.98 m/s), drop penetration and adhesion to film were observed after 4160 drop impact events, when the superhydrophobic properties of the coating started to degrade. Additionally, a linear abrasion test was performed with sandpaper as abradant and 254 Pa applied pressure. After 200 cycles the water ROA increased to 14° while maintaining APCAs above 150°.

Huang and Lin [87] developed superhydrophobic transparent coatings by following a low temperature (80° C) sol-gel process. The results showed that the coating had water APCA exceeding 160° and SA lower than 10°. The coatings kept their superhydrophobicity even after 20,000 water drop impacts (6 h). Geng and He performed also a water drop impact test on their superomniphobic surfaces [43]. In this test, about 4500 water droplets (ca. 22 mL) were dropped from a height of 50 cm above the coating. The velocity at which the water droplets impacted the surface was 1m/s. The water and ethylene glycol APCAs remained unchanged after the water-drop impact test.

Finally, Zhang et al. [81] performed a water jet test to evaluate the robustness of their superhydrophobic aluminum alloys. A representative schematic of this setup is given in Figure 15. The samples were fixed on a substrate tilted at 45° and placed 5 cm below a water pipe (inner diameter 4 mm), and then jetted for 10 min at different pressures (10–100 kPa). The pressure 25 kPa was selected because according to the
authors’ calculations it corresponds to a heavy thunderstorm. The water APCA remained greater than 150° up to 75 kPa for 10 min. However, ROAs increased significantly when the water jetting pressure was greater than 25 kPa. However, in the thunderstorm condition of 25 kPa the coatings retained their superhydrophobicity. Therefore, the films were water jetted at 25 kPa repeatedly up to five times to investigate the cyclic durability. The surface remained superhydrophobic after water jetting up to three cycles. After five cycles of water jetting water APCAs still exceeded 150°, although ROA increased to ~19°.

4.3 Aerodynamic impact

Aerodynamic exposure is not a very common test for the degradation of non-wettable surfaces. However, exposure to high-speed gas flows should be considered for surfaces that target aerospace applications or outdoor surfaces in regions affected by strong winds.

Nahum et al. [88] prepared stable superhydrophobic coatings by UV exposure using SiO₂ NPs of various diameters grafted with photo-reactive benzophenone (BPh) groups and methylated fumed silica (SiO₂@BPh) NPs in combination with urethane acrylate base layer and fluorosilane top layer. They tested their surfaces under severe air drag conditions. The air drag test was devised using an air gun with air velocity of 300 km/hr. An anemometer was placed at the end of the sample to measure the velocity of air passing along the sample. The APCAs and SAs were measured before and after the air drag test. FC294, FC156, and FC65 were designated as the coatings containing SiO₂@BPh NPs of 294, 156, and 65 nm, respectively. As could be concluded the contact angle measurements showed insignificant changes in all coatings before and after air drag test. However, an increase in sliding angles was observed after air drag due to aerodynamic ablation (material removal). Both FC294 and FC156 kept their superhydrophobicity demonstrating SA smaller than 10° after the air drag test while FC65 exhibited SA above 30°. These results might be explained by the detachment of the non-bonded hydrophobic methylated fumed silica exposing the hydrophilic SiO₂@BPh NPs to the surface. As a result, an increase in contact area between the water drops and polymer substrate was obtained on moving from Cassie to Wenzel state. SEM images (Figure 16A,B) showed a slight decrease in surface roughness for FC294 and FC156 containing formulations which explain the slight increase in SA. However, a close look at FC294 containing coating (Figure 16D) confirmed that surface roughness was retained and the increase in sliding angle was a consequence of the loss of non-bonded methylated fumed silica in some areas. In FC65 containing coating (Figure 16C), cracks could be noticed on the surface that led to the increase in SA.

4.4 Recommendations for dynamic impact
If the superhydrophobic surfaces are intended to be used outdoors, the tests described in this section may be of significant importance. Solid particle impact tests are the harshest ones and they should be performed if the superhydrophobic surfaces will be exposed to dusty environments. Based on what has been reported so far, recommended conditions for durability testing include releasing particles above the coating with the following specifications: particle diameters of approximately 200 μm, release heights of 20 to 50 cm, and exposure time of 5 min with 40-50 g total mass of released particles. After performing these tests, if the surfaces still exhibit low CAH, SA or SHA, they can be considered mechanically durable superhydrophobic materials. Regarding liquid impact, the conditions that have been used are much more variable and it is difficult to provide a single and unified methodology. However, reasonable limits for a superhydrophobic surface to be considered durable can include: (a) impact of several thousands of drops delivered at 1 m/s impact velocity or more and (b): spray/jet impact at a minimum pressure of 25 kPa with an exposure time of at least 30 min. Finally, aerodynamic impact is more specialized for coatings that target automotive and aerospace applications. While there is no standardization, testing superhydrophobic surfaces with air velocity of 300 km/h for several hours has been proposed [88].

5. Liquid bath durability

The mechanical durability of superhydrophobic surfaces has been also evaluated in configurations where the sample is immersed in a liquid. The abrasion of the surface is performed either by the application of laundry (particularly in the case of textiles), ultrasounds or by collisions with particles that are dispersed in the liquid (rotary slurry). These tests additionally examine the resistance of the superhydrophobic surfaces in water absorption. Even if a material is non-wettable, this does not necessarily mean it will not absorb water gradually by time when it is immersed in a water bath. The absorption of water might lead to degradation of the non-wettability but also to destruction of the coating.

5.1 Laundry wear

A laundry test is a very common test to evaluate the mechanical performance of non-wettable textiles since it is the main cause of degradation during their practical use. Fabrics during washing undergo mechanical stresses in addition to exposure to chemical agents. The synergistic effect of chemical and physical actions accelerates the detachment of coating layer from fibrous substrates. These tests are simply performed by washing the treated textiles in commercial washing machines for a specific amount of time and then characterizing the wetting properties. In some of the tests also the amount of detergent present in water is mentioned and in some other cases the washing occurs in the presence of steel balls.
which are introduced in the laundry machine to mimic wear effects that occur in real-world laundry. Other factors that can be varied include the water temperature and the duration of the laundry cycle.

Generally, the fibrous nature of textiles promotes mechanical durability since such surfaces are easily deformed and can withstand better the shear abrasion. Thus, non-wettable textiles are currently top performing in the mechanical durability tests and are able to maintain their properties for a much greater number of abrasion cycles than any other surface. However, it should be noted that in many studies CAH values are not reported, but only APCA measurements that are stable even after thousands of abrasion cycles. Thus, one has to be very careful when evaluating experimental data since in terms of application the CAH is a more important parameter than the APCA. Moreover, for textiles it is common to measure the SHA which was introduced specifically to avoid difficulties when measuring APCAs on textile surfaces with conventional goniometers [20]. Usually the test involving laundry cycles is accompanied by subsequent abrasion tests. In fact, laundry tests can also be considered somewhat of an abrasive test due to the fact that during laundry the textiles always rub against each other. In this section, we will present results both from the abrasion and laundry tests in order to be able to compare the outcomes from these two different durability tests on the same fibrous material.

Wang et al. [89] prepared self-healing superhydrophobic and superoleophobic polyester fabrics from fluorinated-decyl polyhedral oligomeric silsesquioxane and hydrolyzed fluorinated alkyl silane (FAS) by a dip-coating method. After 200 cycles of standard laundry machine, the coated fabric was found to still maintain the superhydrophobicity and superoleophobicity in terms of APCAs. The abrasion durability was evaluated by the circular abrasion method using untreated fabric as abradant to simulate actual damage. During the test, pressures of 9 kPa and 12 kPa were employed, which are typically used for evaluating the coated fabrics for apparel and heavy-duty upholstery usages, respectively. The coated fabric could withstand 6000 cycles of abrasion damages without affecting its super-repellent feature. More abrasion cycles led to a decrease in both water and oil non-wettability. No CAH measurements were reported.

The same research group used a different formulation and dip-coating approach to produce superhydrophobic polyester fabrics by surface treatment with FAS modified PDMS/silica NP composite [90]. With increasing laundry cycles, the APCA slightly decreased, while the SA had a little increase. Changes in both APCA and SA were less than 5° after 500 washing cycles. The SEM observation revealed that the coating surface still retained its particulate morphology, even after 500 cycles of repeated washing. The abrasion resistance was evaluated with the same setup and applied pressure values (9 to 12 kPa). The APCA remained at 170° after the first 2000 cycles under both pressure conditions.
Although the APCA reduced with further increasing the abrasion cycles, the coated polyester fabrics could withstand 28000 cycles of abrasion damages without losing their superhydrophobicity. After 28000 abrasion cycles under 12 kPa pressure, water droplets on the fabric surface still showed APCA more than 150° and the nano-scale roughness could still be observed. In comparison to the APCA, the SA was more sensitive to abrasion cycles. After 20000 abrasion cycles, the SA increased slightly above 10°.

An alternative approach was used by the same group for treating similar fabrics [91]. The fabrics were rendered self-cleaning by one-step vapor-phase polymerization of poly(3,4-ethylenedioxythiophene) (PEDOT) in the presence of fluorinated decyl polyhedral oligomeric silsesquioxane (FD-POSS) and FAS. With increasing laundry cycles, the PEDOT/FD-POSS/FAS coated fabric had only a small decrease in both water and hexadecane contact angles. After 500 washing cycles, the superomniphobic property was retained. After 10000 cycles of abrasion (12 kPa), the PEDOT/FD-POSS/FAS coated fabric still retained its superomniphobicity.

Another two-step dip-coating approach was developed by the same group to prepare self-healing superomniphobic polyester fabrics using poly(vinylidene fluoride-co-hexafluoropropylene), FAS, and modified silica NPs [92]. Washing tests were performed at 49° C for 45 min in presence of a detergent (0.15 wt %) and 50 stainless steel balls. After 600 cycles of standard machine laundry, the coated fabric still maintained its superomniphobicity. Both the APCA and SA underwent a slight decrease with the washing cycles. After 600 cycles of washing, silica particles could be clearly observed on the coating’s surface, indicating that the particles were immobilized firmly on the fiber surface. Abrasion tests were also performed (circular abrasion, 12 kPa). After 8000 abrasion cycles, the coated fabric showed APCA values of 165°. Although the SA increased with increasing abrasion cycles, it was still lower than 10° after the fabric was subjected to 8000 abrasion cycles. After 25000 abrasion cycles, the coated fabric still retained its superhydrophobicity. It was also found that the 25000 abrasion cycles led to physical damage to both the fibers and the fabric structure. The superomniphobic polyester fabrics tested with the blade test by the same group (Wang et al.) were also evaluated under laundry and circular abrasion [63]. In the machine laundry process, the coated fabric did not show changes in the APCAs of water after 200 cycles of washing. The SA values increased slightly to 4.5°. After 20000 abrasion cycles nearly no nanoparticles could be observed on the top surface. However, the damaged surface after the abrasion test was healable when the coated fabric was heated at 140° C for 30 min. The same group (Zhao et al.) investigated the surface modification of cotton fabrics [93]. The method included functionalization of silica NPs with highly photo-reactive phenyl azido groups that were utilized as a negatively charged building block for layer-by-layer (LbL) electrostatic assembly to produce a stable silica NP coating. Combined with a FAS post-treatment, the photo-reactive LbL multilayers were used as a coating for superhydrophobic...
modification of cotton fabrics. The superhydrophobic fabric showed reasonable wash durability with CAH remaining lower than 10° after 25 cycles of machine washing, and APCA above 150° after 50 cycles.

Zhang et al. [94] developed robust superhydrophobic wool textiles by simply dip-coating in a nanocomposite solution of fluorine-free organosilanes. Despite the fact that the APCA remained stable after the laundry test, the water SA increased gradually with increasing laundry cycles but remained below 15° after 10 laundry cycles. No obvious change in contact angle (CA) could be detected after 200 abrasion cycles at 5 kPa using A4 paper as the abradant. SHA increased gradually from 3° to 21° with increasing abrasion cycles at 5 kPa. The increase in abrasion pressure to 9 kPa had no evident influence on SHA. Water droplets remained nearly spherical in shape and could still easily roll-off the tilted sample after 200 abrasion cycles. Similar SHA and bouncing of water drops were observed when sandpaper (2000 mesh) was used as the abradant although the wool fabrics were seriously damaged. The authors conducted also tape and other qualitative tests on the surfaces (Figure 17). The same tests were applied also on the superhydrophobic polyester fabrics developed by the same group [48] and the coatings retained their properties for 50 laundry cycles.

Xue et al. [95] fabricated superhydrophobic colorful surfaces through chemical etching of poly(ethylene terephthalate) fiber surfaces, followed by diffusion of FAS into fibers. The laundering durability was evaluated by washing samples at 40 °C in the presence of 10 stainless steel balls and 0.37% soap powder. The APCA remained at 157.3° after 20 cycles, showing a slight decrease from 162.9° which was the value of the as prepared samples prior to the laundry test. SEM images revealed that the surface retained its rough morphology even after 100 cycles of repeated washing. The abrasion resistance was evaluated using linear abrasion with a common nylon fabric as abradant. The APCA remained at 157.7° after the first 1500 cycles, showing a slight decrease from 161.9° on non-abraded sample. SEM observation revealed that the PET fibers were flattened after 3000 abrasion cycles. However, the CA increased to 162.3°. Figure 18 depicts the difference in the effect of washing and abrasion tests on the surface of the fabric.

Zou et al. [96] prepared superhydrophobic cotton fibers from functional diblock copolymers consisting of both poly(glycidyl methacrylate) (PGMA) and poly(2,2,2-trifluoroethyl methacrylate) (PTFEMA) blocks synthesized via sequential atom transfer radical polymerization. The modified cotton fabrics showed APCA of 163° and SA of 3°. Resistance against mechanical damage was evaluated by laundering samples in water with 0.15 wt% detergent. The superhydrophobicity was maintained, with an APCA of 150° and a SA of 10° after the treated fabrics had been laundered for 50 cycles. The mechanical stability of the
samples was also evaluated by linear abrasion with sandpaper at a constant rate under 3.9 kPa. This experiment demonstrated that although the SAs increased to above 10° after the samples were rubbed for 20 cycles, the APCAs remained above 150° even after the samples had been rubbed for 40 cycles.

Liu et al. [97] developed a dip-coating approach for fabricating superhydrophobic polyester textiles with polydopamine@octadecylamine nano-capsules. Laundering durability of the coated fabric was evaluated in pure water and in soap solution by both machine and hand washing. After 20 laundry cycles (for 45 min at 25°C), the coated fabric still maintained its static non-wettability though the APCA underwent a slight decrease with increasing washing cycles showing an APCA of 144° when it was dried at 80 °C for 20 min. After 20 washing cycles, the nano-capsules could be clearly observed on the coating surface, indicating that they were immobilized firmly on the fiber surface. No CAH values were reported for this test. In order to further test the washing durability of the coated fabric, it was washed 5 minutes by hand in an aqueous solution containing soap powder. The coated fabric still retained its hydrophobicity, and liquid droplets could roll off easily from the surface. The change in non-wettability with abrasion cycles was tested by linear abrasion of the fabric surface (10 kPa). With the increase of abrasion cycles (up to 500), the APCAs of water, juice and coffee decreased only slightly (~140°). No CAH values were reported.

5.2 Ultrasound treatment

Ultrasonic processing (ultrasonication) is the application of energy by ultrasonic frequency (> 20 kHz) in liquid media. It can operate at various frequencies above this threshold and it is used in colloidal chemistry, cleaning materials, etc. The application of ultrasonic frequencies can physically damage a fragile surface where there is no good chemical bonding with the substrate. For this reason, it has been used as a test to evaluate the mechanical stability of non-wettable surfaces.

Li et al. [98] fabricated a superhydrophobic coating by a sol–gel process which was made up of, first the surface chemical reaction of (3-Glycidyloxypropyl) trimethoxysilane and SiO₂ particles, and subsequent spray-coating onto the substrate. Further hardening treatment and surface fluorination allowed the SiO₂ coating to exhibit superhydrophobicity and high adhesion to substrates. The ultrasound treatment was used to inspect the adhesive effect of the superhydrophobic coating to substrate. SiO₂ submicron/nanoparticles can fall off with ultrasound treatment and eventually the surface morphology or the wettability of the superhydrophobic coating can vary with ultrasound treatment. In this study, the coatings were treated with ultrasound bath (225 W) and fluorination (10 min), successively. Varying the ultrasound time affected the mass ratio of the silane and SiO₂ particles and their significant impacts on the wettability of the coating. For ultrasound bath 60 min, the change of APCA of the coating after
fluorination still remained 160°. However, keeping on increasing ultrasound time up to 180 min lead to reduction of superhydrophobicity especially at 180 min. Figure 19 shows the SEM images from the surface of the coatings before and after the ultrasonic treatment. It can be clearly identified the partial removal of the particles.

Liu et al. [99] evaluated the mechanical strength of their superhydrophobic Cu surfaces by ultrasonic treatment in water. After ultrasonic processing for one hour, the resultant surface exhibited a mean APCA of 165° while no CAH value was measured. Yoo et al. [100] applied ultrasonic process to their superhydrophobic fabric in water for more than 4 days and the superhydrophobic film remained intact, which confirmed the strong adhesion between the stacked polymer film and the fabric. On the fabric after ultrasonic processing the receding contact angle was found to be 156°. Zou et al. [96] used the ultrasonic processing test for their superhydrophobic cotton fabrics in the presence of tetrahydrofuran (THF) or trifluorotoluene (TFT) to evaluate both physical and chemical stability. It was found that the water APCAs and SAs of the coated fabrics changed only slightly after they had been ultrasonic processed for 100 min in THF or TFT, thus retaining the superhydrophobicity. Finally, Huang and Lin [87] tested their superomniphobic surfaces with ultrasonic processing. After two hours of ultrasonic treatment the surfaces retained their superhydrophobicity but the diiodomethane CAH increased to 94° from 85° which was the value for the as prepared samples while the APCA remained stable.

5.3 Rotary slurry test

Jokinen et al. [101] introduced another novel type of abrasion test including a rotary slurry (Figure 20). The sample to be tested is rotated in slurry and erosion results from direct impacts between the slurry particles and the surface of the sample. The beaker holding the slurry contains stators to prevent the slurry from picking up momentum and flow. The extent of erosion in the slurry test depends on the composition, size, and shape of the eroding particles, their velocity and angle of impact, and the composition and microstructure of the surface being eroded. The set-up comprised a custom sample holder which was connected directly to a motor by a long steel rod. The sample holder was designed to simultaneously hold multiple test pieces. The samples were tilted so that the angle of impact was 73°. The distance of the sample from the rotation axis was 25 mm as measured from the center of the sample. With this device, it was possible to control both the temperature and the rotation rate. In their experiments, the temperature was kept at ambient conditions and the rotation was set at 900 rpm for the main abrasion experiment. The slurry used for the main abrasion experiment consisted of 10% (by weight) suspension of 30 μm alumina particles in water. The slurry was contained in a 500 ml glass beaker. After the rotary slurry test the
wetting properties of the samples were characterized by measuring the apparent contact angles and the sliding angles of water drops.

6 Recommendations and future directions for mechanical durability

Over the last five years, publications regarding the development of mechanically durable superhydrophobic surfaces have exponentially increased. Various techniques have been demonstrated to produce robust materials with self-similar surface and bulk topographies which can repel water after repeated cycles of mechanical wear. Bulk superhydrophobic materials have been fabricated by embossing mixtures of polymers and nanomaterials while robust and wear-resistant surfaces have been developed by superhydrophobic coatings exhibiting surface-wear-similarity due to the uniform chemistry in their entire thickness. Despite substantial scientific progress, to date no single surface was shown to withstand all types of wear required by the stringent industrial requirements and standards for commercialization. The review intends to present what has been developed during the last few years in terms of non-wetting surface durability. As it is seen, there are a wide range of tests done to report and claim that a non-wetting surface is “durable”. However, researchers working on non-wetting materials and coatings applications still do not have a unified and standardized way to report the robustness of their materials. For instance, wear abrasion resistance is not the same as pencil hardness or tape peel test. We believe that the researchers should find ways of conducting tests that are similar to ASTM standards developed for coatings and painting industry. For instance, during wear abrasion testing the downward pressure as well as the type of the abradant is quite important. But variations in these parameters make it difficult to arrive at meaningful comparisons. This review is intended to display this problem and perhaps can shed some light into conducting tests that can be industrially valuable and useful. At the same time, more research is needed to further improve the wear and abrasion related mechanical characteristics of such non-wetting surfaces.

6.1 Recommended primary mechanical durability tests (from Sections 2 & 3)

In order to help the advances in the development of resilient non-wettable coatings, it is important to have evaluation techniques that are standardized, simplified and prioritized. The present review of techniques indicates that some of the above techniques are well suited in this regard, and this allows specific recommendations. Primarily, a coating should have good substrate adhesion determined by tape peel tests based on a cross-cut geometry. This is an important first test and is relatively simple and inexpensive to
implement. In addition, linear abrasion is a well-accepted and straightforward method to evaluate the wear abrasion resistance and hence mechanical durability. For this purpose, measurements related to the increase of water adhesion (e.g. roll-off angle) as a function of wear cycles for a fixed weight and three different abradants (smooth, resilient and vitrified) are highly recommended. Table 1 presents a summary of the recommended primary tests to be conducted when evaluating the wear-resistance of a superhydrophobic surface based on the arguments of Sections 2 and 3.

6.2 Recommended secondary mechanical durability tests (from Sections 4 & 5)

Additional abrasion tests can be employed as secondary tests from the Sections 4 and 5. Sand and/or water/jet impact and underwater tests like immersion in ultrasonic bath and rotary slurry are also good techniques to evaluate the stability of the surfaces for outdoor applications. Table 2 gives a summary of the tests that are more suitable for such outdoor applications. A third category of tests can be recommended but are application specific. Laundry tests for instance can be considered for textiles, pencil hardness or blade test for surfaces that will often encounter contact with sharp objects and wind tunnel or air drag tests for aerospace applications, etc.

6.3 Future direction to improve mechanical durability and its evaluation

As a future direction, the most important aspect that can further improve the adhesion of coatings is the appropriate physical and chemical modification of the substrates prior to the application of a coating. This can be achieved via the use of primers, substrate roughening and cleaning, as well as post-application treatments (thermal or mechanical). In the case of superhydrophobic nanocomposites, careful selection and dispersion of hydrophobic fillers inside the coating bulk is critical for achieving optimum surface-wear-similarity and eventually abrasion resistance. Additionally, the physicochemical characteristics of the polymeric matrix can dramatically influence the material’s resistance to mechanical wear. Flexible, hard, stretchable, porous, fibrous materials will behave completely different during abrasion under different abradants. Flexible, stretchable or fibrous materials for instance can dissipate the forces acting on a surface better due to their chain mobility while hard materials will tend not to deform easily but can be more fragile.

Finally, when evaluating the mechanical durability of superhydrophobic surfaces, it is highly recommended to perform water adhesion measurements (checking whether the droplets stick when the surfaces are tilted) since they are more important for the functionality of a non-wettable surface and are the most likely to be lost due to mechanical wear. It is also important that the researchers evaluate the
mechanical durability with standardized methods so that more direct comparison can be performed with other relevant studies.

Acknowledgements

The authors would like to thank Dr. Yong H. Yeong from the Department of Mechanical and Aerospace Engineering of the University of Virginia for providing the photos for Figure 4.

References


**Table 1.** Recommendations for Primary Mechanical Durability Tests
<table>
<thead>
<tr>
<th>Durability test</th>
<th>Method</th>
<th>Apparatus</th>
<th>Desired Performance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adhesion</td>
<td>ASTM D3359</td>
<td>Blade for scratching and high adhesion strength tape (e.g. 3M™ 250)</td>
<td>5B (all squares should remain intact)</td>
</tr>
<tr>
<td>Abrasion (smoothing, soft/mild abr)</td>
<td>Linear abrasion</td>
<td>Taber CS-5 abradant, crocking cloth or common textiles</td>
<td>Low CAH after 10’s of cycles with applied pressure &gt; 10 kPa</td>
</tr>
<tr>
<td>Abrasion (smoothing, hard/resilient abr)</td>
<td>Linear abrasion</td>
<td>Rubber-type abradant (e.g. Taber CS-10F)</td>
<td>Low CAH after 10’s of cycles with applied pressure &gt; 10 kPa</td>
</tr>
<tr>
<td>Abrasion (scratching, vitrified abr)</td>
<td>Linear abrasion</td>
<td>Vitrified abradant (e.g. Taber H-18 or sandpaper with varying grade)</td>
<td>Low CAH after 10’s of cycles with applied pressure &gt; 10 kPa</td>
</tr>
<tr>
<td>Finger Rub (with and without glove)</td>
<td>Linear rubbing</td>
<td>No apparatus needed</td>
<td>No material removed to</td>
</tr>
</tbody>
</table>

Table 2. Recommendations for Secondary Mechanical Durability Tests

<table>
<thead>
<tr>
<th>Methods</th>
<th>Sample Applications</th>
<th>Apparatus</th>
<th>Desired Performance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sand impact</td>
<td>Outdoor applications in dusty environment</td>
<td>Sand container with regulated particle delivery system</td>
<td>Low CAH after 40-50 gr of particles delivered from &gt; 20 cm height within 5 min</td>
</tr>
<tr>
<td>Drop impact</td>
<td>Outdoor applications in general</td>
<td>Water drop dispenser with adjustable height</td>
<td>Low CAH after thousands of drops impacting with velocity &gt; 1m/s</td>
</tr>
<tr>
<td>Jet/spray impact</td>
<td>Outdoor applications in rainy environment</td>
<td>Jet dispenser or spray nozzles supplied with adjustable pressure</td>
<td>Low CAH with &gt; 25 kPa pressure with exposure time &gt; 30 min</td>
</tr>
<tr>
<td>Ultrasound baths or rotary slurry test</td>
<td>Underwater</td>
<td>Ultrasonic cleaner and particles dispersed in water</td>
<td>Low CAH after several hours of treatment</td>
</tr>
</tbody>
</table>
Figure 1. Top: Wenzel and Cassie-Baxter states on micro-rough surfaces. Bottom: Schematic representation of possible wetting states on a micro/nano-rough hierarchical superhydrophobic surface. (a) Classic Wenzel state. (b) Wenzel state in the microscale and Cassie-Baxter state in the nanoscale. (c) Classic Cassie-Baxter state. (d) Cassie-Baxter state in the microscale and Wenzel state in the nanoscale. (e) Hybrid state. The water can penetrate partially in micro or nanoscale. Different combinations of hybrid states can be designed.
Figure 2. Three different effects of abrasion on a surface. Next to each image it is written the most probable wetting state that may occur. (a) A hydrophobic surface coating on a roughness pattern may get easily worn off, and hydrophilic bulk material will be exposed as a result. (b) If the roughness features are fabricated of hydrophobic material, wear will not introduce hydrophilic pinning sites. (c) A hydrophobic smooth surface can be roughened resulting to a superhydrophobic material.
Figure 3. Field emission scanning electron microscope images of the bulk material at low (a) and high (b) magnification; (c) water droplets exhibit spherical shape on the surface of the bulk material; (d) mirror-like phenomenon can be observed on the bulk material submerged in water and (e) optical image and contact angle profile of the water droplet placed on the abraded bulk material. Reproduced from [33] with permission of The Royal Society of Chemistry.
Figure 4. Top: Adhesion tests conducted to silicone rubbers coated on aluminum substrates with their ratings according to the ASTM D3359. A high adhesive tape is deposited on the coating in 45° angle with the cuts. After 1 min approximately the tape is peeled off and the sample is evaluated. Bottom: Indicative chart with damaged schematics, after the adhesion test, with their corresponding ratings according to the ASTM D3359.
Figure 5. Cross-hatch tape adhesion test for coatings with 10–20 nm silica fillers. (a) No fillers; (b) 5 wt.%; (c) 10 wt.% and (d) 15 wt.% [46].
Figure 6. (a) Typical linear abrasion setup: a rod with a predefined weight (adjusted by the metallic disks) moves linearly across the direction indicated by the red arrow and rubs the tested sample’s surface tangentially. (b) Photograph of the Taber linear abraser. (c) 4 different abradants provided by Taber. The crocking cloth and the CS-5 are softer and deformable, thus they produce more mild type of abrasion, tending gradually to flatten the superhydrophobic surface. The CS-10F is made from a harder rubber material. It again causes flattening of the surface but since it is harder, the degradation of the surface is usually faster. The H-22 is a vitrified abradant that causes coarse abrasion to the tested surfaces, relatively similar to the rubbing/scratching effect of a sandpaper.
Figure 7. SEM images of (a) the superhydrophobic polyester meshes after 100 cycles of abrasion with a pressure of $\sim 10$ kPa and a cellulose textile abradant, (b) a higher magnification of a fiber in (a), and (c) the SiO$_2$ nanoparticles modified with fluorinated silane on a residual layer of (b). (d) Water contact angle and sliding angle of the superhydrophobic surface as a function of abrasion cycles. Note the difference in the trends of the APCAs and the SAs [59]. Copyright 2015 American Chemical Society.
Figure 8. SEM images of various superhydrophobic surfaces before and after performing the rotating wear tests with forces given in figure (a) nanograss surface (NS), (b,c,d) microcone and nanograss combinations. Scale bar: 5 μm (a), 20 μm (b–d). On the right there is a sketch depicting the circular abrasion configuration. Reproduced with permission from [63]. Copyright 2014 American Chemical Society.
Figure 9. (a–c) Photos to show (a) the method of scratching fabric with a sharp blade, (b,c) colored water, hexadecane, and ethanol drops on the coated fabric (b) after the first blade scratching cycle (100 scratches) and (c) after blade scratching and heat treatment at 140 °C. (d,e) SEM images of the coated fabric (d) after blade scratching (100 scratches) and (e) heat treatment [65]. Copyright 2013 American Chemical Society.
Figure 10. Left: SEM images of the coatings treated by TEOS CVD for 3 h after 2H (a and b), 3H (c and d), 4H (e and f) and 5H (g and h) pencil scratching tests. Reproduced from [43] with permission of The Royal Society of Chemistry. Right: Experimental apparatus of the pencil hardness test and the hardness scale.
Figure 11. Wear tests on a) polymer membranes in comparison to b) pillar arrays: Schematic representation of the experimental setup consisting of an oscillating steel ball, pressed onto the structured surfaces. Experimental data on maximum normal loads the surfaces can resist without destruction and SEM images after failure [68].
Figure 12. SEM images of spray-coated wood slides after finger rubbing. Scale bars in image A, B, C, and D are 2 mm, 1 mm, 1 mm, and 1 mm, respectively. Reproduced from [62] with permission of The Royal Society of Chemistry.
Figure 13. Top: sketch of the setup used to determine the stability of the surface against sand impact. Bottom: (a) Photograph of the sand grains abrading the tilted 45-degree superhydrophobic silica coating from an impact height of 20 cm. (b) SEM image of the superhydrophobic silica coating obtained after being abraded by sand grains for about 50 s. Inset: WCA of the abraded coating was about 153.2 ± 2°. Reproduced from [45] with permission of The Royal Society of Chemistry.
Figure 14. (a) Schematic and (b) photo of the spray impact setup used to investigate rain impact resistance of superhydrophobic surfaces. SEM images of surfaces (c) before exposure to rain-sized droplets, (d) after normal-impact exposure, and (e) after 40° exposure; (f–h) are higher magnification images. Reproduced from [84] with permission of The Royal Society of Chemistry.
Figure 15. Experimental setup for the jet or drop impact test.
Figure 16. SEM topography images of A) FC294 after air flow test, B) FC156 after air flow test, C) FC65 after air flow test, and D) magnified image of FC294 after air flow test [88].
Figure 17. Water sliding angle (WSA) changes depending on (a) laundering cycles (30 min each). (b) SEM images of coated wool fabric after 10 cycles of machine wash. Qualitative mechanical stability tests via (c) scratching with a scalpel, (d) adhesion of double side tape, (e) finger press and (f) twisting by hands. Reproduced from [94] with permission of The Royal Society of Chemistry.
Figure 18. SEM images of PFDTS treated PET textiles after (a) 100 cycles of washing and (b) 3000 cycles of abrasion. Reproduced from [95] with permission of The Royal Society of Chemistry.
Figure 19. SEM images of the SiO$_2$ coated surface (a) before and (b) after ultrasound treatment for 180 min [98].
Figure 20. Rotary abrasive slurry test setup [101].
Linear abrasion on superhydrophobic surface using different abradants

Graphical abstract
Highlights

- Summary of advances on mechanical durability of superhydrophobic surfaces since 2011.
- Categorization of types of mechanical wear and their corresponding evaluation techniques.
- List of the most successful fabrication approaches in each category.
- Recommendations for investigating mechanical durability of superhydrophobic materials.