Historical perspective

Fabrication techniques for bioinspired, mechanically-durable, superliquiphobic surfaces for water, oil, and surfactant repellency

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ABSTRACT

Nature provides inspiration for liquid-repellant and low-adhesive surfaces, such as the lotus leaf and pitcher plant. While water-repellency is frequently found in nature, oil-repellency and surfactant-repellency are uncommon to nonexistent. To obtain oil- and surfactant-repellency, hierarchical, re-entrant, bioinspired surface structures along with low surface energy materials are needed. This overview presents wetting literature, common liquids and their composition, and fabrication techniques for superliquiphobic surfaces with repellency toward water, oil, and surfactant-containing liquids. Four techniques for creating such surfaces are explained in detail: nanoparticle/binder, layer-by-layer, nanoparticle-encapsulation, and liquid-impregnation. Static contact and tilt angles with water and hexadecane liquids, morphology, wear, transparency, self-cleaning, anti-smudge, and oil–water separation data are examined to compare the techniques. Data for these techniques are presented showing evidence of re-entrant geometry and the ability for these surfaces to repel surfactant-containing liquids such as shampoo and laundry detergent. The data will provide guidance in implementing superliquiphobic surfaces for self-cleaning, anti-smudge, antifouling, and low-adhesion properties for various applications including plastic packaging and biomedical devices.

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1. Introduction

Liquid-repellent surfaces are of interest and may include self-cleaning, anti-smudge, antifouling, and low-adhesion characteristics. These properties have applications in a large number of industries which include automotive, aerospace, electronics, plastic packaging, and biomedical devices [1]. When the liquid-repellent surfaces are also transparent, additional applications include smart screens for electronic display, camera lenses, window glass, and solar panels. A range of materials are used in these applications which require superliquiphobic1 surfaces. As an example, materials of interest for smart screens in electronic displays include soda-lime silica, polyethylene terephthalate (PET), and polycarbonate (PC). For plastic bottles and caps, materials include high-density polyethylene (HDPE), PET and polypropylene (PP). For automotive applications, materials include glass, PC, polydimethylsiloxane (PDMS), PET, nylon, HDPE, polyurethane, polymethyl methacrylate (PMMA), PP, steel, aluminum, and leather.

Inspiration can be taken from nature in order to create liquid-repellent and low-adhesive surfaces. The lotus leaf (Nelumbo nucifera) [2] and the pitcher plant (Nepenthes) [3] exemplify these characteristics and their water-repellent and slippery surfaces are shown in Fig. 1. In the lotus leaf example, a water droplet on a leaf is shown with a contact angle of ~164°. This superhydrophobicity originates from the hierarchical structure formed by the combination of papillode epidermal cells as the microstructure and 3-D epicuticular wax tubules covering these cells as the nanostructure [2,4].

In contrast to the roughness-induced superhydrophobicity of the lotus leaf, the carnivorous pitcher plant derives its properties from a slippery rim, known as a peristome. The peristome has a microstructure formed with regular ridges of smooth, overlapping epidermal cells. The microstructure can be wet by nectar and rainwater to form a continuous liquid film, resulting in an extremely slippery surface. Insects are unable to adhere to the slick surface, and therefore, they aquaplane across the surface, fall inside the pitcher trap, and become ingested by the plant [3].

By understanding the resourceful designs in nature, mimicking them, and improving upon them, many applications can be found that aid humanity and be of commercial interest. Nature has a limited material toolbox, but by incorporating synthetic materials and better manufacturing processes, the surface properties can be enhanced. Understanding structures found in nature and using them as design inspirations is the field of biomimetics [1,4].

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1 The nomenclature superliquiphobic surfaces implying repellency to range of liquids was coined by Thushan (2016).

1.1. Wettability

The applications of a surface depend on the wetting characteristics of a droplet on the surface. A droplet can be any liquid and is commonly denoted as hydro- for water or oleo- for oil. A suffix of -philic or -ophobic is used when the droplet is attracted or repelled, respectively. Therefore, four states can be obtained: hydrophilic or oleophilic for wetting with a water or oil droplet and hydrophobic and oleophobic for repelling with a water or oil droplet, respectively. When the contact angle (CA) is <10° in a -philic state or >150° in a -ophobic state, the prefix super- is added. These wetting states and their possible applications are shown in Fig. 2 [1].

The wetting of a droplet on a solid surface is dependent upon surface chemistry and surface roughness. On a flat surface with a low surface energy, the maximum achievable CA with a water droplet is ~120° [5]. In order to increase the CA, roughness-induced superhydrophobicity can be utilized [1,6]. For self-cleaning, anti-smudge, antifouling, and low-adhesion, another property of interest is contact angle hysteresis (CAH), which is the difference between advancing and receding contact angles. CAH can be shown to be related to the energy dissipation of a droplet flowing along a surface. Low CAH results in a droplet rolling along a surface at a very low tilt angle (TA), which facilitates particle removal for self-cleaning [1].

On a rough surface, two wetting states have been observed: the Wenzel regime and the Cassie-Baxter regime. In the Wenzel state, liquid fully penetrates the roughness features, which creates complete wetting of the solid interface [7]. In the Cassie-Baxter state, the liquid droplet sits on top of the roughness asperities with air pockets trapped in between, which creates a composite solid-air-liquid interface [8]. The Cassie-Baxter state leads to higher CA with a given surface roughness and is preferred for liquid-repellent surfaces. The high liquid-air fractional contact area also leads to low CAH, which is important for droplets to easily roll off a surface at a low TA to facilitate self-cleaning.

While superhydrophobicity is common in nature, superoleophobocity is uncommon and more difficult to accomplish, as the surface tensions of oils are much lower than that of water as shown in Table 1 [9,10]. Certain species of leaf hopper display high CA for diiodomethane and ethylene glycol [11] and springtails show repellency to olive oil [12]. However, surfaces from nature with repellency to liquids <30 mN/m have not yet been found.

Fluorinated components help repel low surface tension liquids such as oils by reducing adhesion forces. Oil is non-polar and therefore only interacts with another molecule through a London dispersion force, which is a temporary attractive force due to a pair of induced dipoles. Polarizability depends on the mobility of electrons and therefore quantifies the ability of a molecule to form instantaneous dipoles. Fluorine is commonly chosen to create low surface energy materials due to its low
polarizability. In addition, fluorine is highly electronegative, which measures the tendency of an atom to attract bonding electrons to itself. Fluorine only requires one more electron in its 2p electron shell to create a stable electron configuration. The low polarizability and high electronegativity of fluorine leads to weak London dispersion, cohesive, and adhesive forces. Consequently, fluorinated materials are good choices for creating materials with a low surface energy [10].

Fluorinated materials are combined with re-entrant geometries for improved repellency. Re-entrant geometries are shapes that have overhang structures where the surface features become narrower at the base. Re-entrant curvatures can be inverse trapezoidal, spherical, etc. and lead to higher CA than non-re-entrant geometries [6,10]. These geometries are necessary for repelling low surface tension liquids, and particularly surfactant-containing liquids such as shampoos and laundry detergents due to their low surface tension components and active groups [13,14]. Common ingredients in shampoos and laundry detergents are shown in Figs. 3 and 4, respectively. Both liquids contain surfactants that act as detergents, wetting agents, and foaming agents. Surfactants are molecules that can lower the interfacial tension between phases. They typically comprise a hydrophilic head group and a long hydrophobic tail. Common anionic surfactants feature a sulfate head group with a sodium counter-ion. Both examples of shampoo and laundry detergent contain a mix of anionic, amphoteric, and non-ionic surfactants. This mixing of ionic and amphoteric surfactants is common in formulations for these types of products [15]. The anionic surfactants are typically the main surfactant for cleaning purposes, while the amphoteric surfactant serves as a foaming agent. All surfactants have the potential to lower the surface tension of the liquid, as well as adsorb at the interface of any solid with which the liquid comes into contact. These components typically have surface tension values of 25–60 mN/m, depending on concentration with higher surface tensions in the product if the surfactant is heavily diluted [16,17]. The surface tensions of surfactants are on the same order as oils. However, a surfactant has polar head groups that are highly active and adhere to surfaces stronger than oils. These liquids readily coat the inside of plastic bottles, leading to wasted product and issues with recyclability. Plastic bottles are typically made of high density polyethylene (~70%), polyethylene terephthalate (~25%), and polypropylene (~5%). Bottle caps are typically made of polypropylene. Creating surfaces repellent to surfactant-containing liquids is important for the consumer packaging industry.

1.2. Re-entrant geometry

A schematic explaining re-entrant geometries is shown in Fig. 5. In the Cassie-Baxter state, previously explained, air pockets are formed due to surface roughness (Fig. 5a) and results in a higher CA than the complete wetting in the Wenzel state. For the geometry shown in Fig. 5a, the ability to achieve the Cassie-Baxter state relies on the fact that the CA of the liquid on the corresponding flat surface (θ_{flat}) is ≥ 90°. The θ_{flat} CA is the angle formed by the surface and the tangent of
the solid-liquid interface. The surface tension force is directed along the surface and acts in the direction opposite to the tangent of the solid-liquid interface. As shown in Fig. 5b, a non-re-entrant surface has a flat \( \theta_{\text{CA}} \approx 90^\circ \) with a surface tension force directed straight down. This geometry is not sustainable and results in full wetting of the surface by the liquid.

However, a high \( \theta_{\text{CA}} \) can be achieved, even if the \( \theta_{\text{CA}} \) of a liquid on the flat surface is small, by creating re-entrant structures. Re-entrant geometries are shapes that have overhang structures where the surface features become narrower at the base. For example, Fig. 5c shows a re-entrant surface with inverse trapezoidal features where the combination of the re-entrant angle (\( \alpha \)) and \( \theta_{\text{flat}} \) is \( \geq 90^\circ \). This geometry supports a favorable shape for the liquid–vapor interface with the surface tension force pointing upward along the trapezoidal features. In this scenario, the liquid does not fully wet the surface, but has vapor pockets and a composite interface with a low liquid-solid contact fraction [10]. If the combination of angles (\( \alpha + \theta_{\text{flat}} \)) is still \( < 90^\circ \), then the liquid will wet the re-entrant geometry as seen in Fig. 5d with a surface tension force pointed downward.

Structures with re-entrant curvature (spherical, cylindrical, oval, etc.) as shown in Fig. 5e are able to support high droplet \( \theta_{\text{CA}} \) for various liquids with flat \( \theta_{\text{CA}} < 90^\circ \) since it is possible to draw multiple tangents of a corresponding flat surface, as demonstrated in Fig. 5f. Therefore, liquids with various flat \( \theta_{\text{CA}} \) can wet the re-entrant curvature to different extents to achieve a favorable liquid–vapor interface shape with the surface tension force directed upwards [10].

1.3. Objective

This paper covers strategies and fabrication techniques for liquid repellent surfaces in a comprehensive manner. The work is split into five sections. In Section 1, background literature has been presented on biomimetics, wetting, re-entrant geometry, and common liquids and their composition. In Section 2, fabrication techniques for repellency of water, oil, and surfactant-containing liquids will be reviewed and compared. In Section 3, experimental procedures for four fabrication techniques that
have been shown to repel oils and surfactant-containing liquids will be explained in detail. The characterization methods for these samples will also be discussed. Section 4 will discuss data for these four techniques using static contact and tilt angles, morphology, and wear. Additional data will be presented showing evidence of re-entrant geometry and the ability for these surfaces to repel surfactant-containing liquids and other related properties. Section 5 will present a summary of the techniques and future outlook.

2. Literature review

A number of fabrication techniques have been advanced in the literature to obtain superhydrophobicity and superoleophobicity [1,10,18–20]. In this section, selected techniques that have been used to create superoleophobic surfaces will be discussed. Different studies claim superoleophobicity using a variety of oils. Various oils are shown in Table 1 where edible oils generally have surface tensions \( N \approx 30 \) mN/m and alkanes-based oils generally have surface tensions of 20–30 mN/m. Studies that solely investigate repellency using diiodomethane (50.80 mN/m) and/or ethylene glycol (47.70 mN/m) are less likely to be repellent to other lower surface tension oils. A more appropriate choice for oil-repellency testing is hexadecane (27 mN/m).

In order to achieve superoleophobicity, combinations of roughness and fluorination methods are commonly used as shown in Fig. 6. Roughness methods include etching, micropatterning, combining nanoparticles and polymer, and encapsulating nanoparticles in a substrate. Fluorination methods include using fluoropolymer, fluorosilane or fluorothiol, fluoroplasma, or fluorosurfactant.

The etching roughness method has been demonstrated on metals such as aluminum, copper, steel, titanium, and zinc using acid-etching and/or electrochemical-etching [21–23]. Etching on various polymers including polystyrene and PMMA has been completed using plasma treatment [24]. Etching is advantageous in that it typically treats an entire surface, regardless of geometries, and is an aggressive process. However, it can be difficult to control and only suitable for small-scale experiments, making it unsuitable for scale-up. Micropatterning allows for accurate replication of features with complex and possible re-entrant geometries. It has been successfully used to create flower-shaped structures [25], inverse-trapezoidal pillars [26], and mushroom-like pillars [27]. The nanoparticle + polymer and nanoparticle-encapsulation roughness methods are explained in Sections 2.1 and 2.3, respectively.

The fluoropolymer fluorination method has been applied to many different forms of roughness. This technique is straightforward, but if the fluoropolymer coating is too thick, the surface roughness features are compromised and durability is poor. In contrast, a thin, self-assembled fluorinated layer can be formed from a deposition of fluorosilane or fluorothiol. The fluorosilane method typically requires –OH surface groups to form a covalently bonded layer. Because silanes are sensitive to moisture and may require a chemically activated

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Fig. 4. Major ingredients in laundry detergent (Tide®, Procter and Gamble) with their structural formula and role in the product.

Fig. 5. Liquid interacting with various surface geometries. (a) Liquid droplet sitting on roughness asperities with air pockets trapped in between, known as the Cassie-Baxter wetting state, (b–d) \( \theta_{\text{flat}} \) angles < 90° on non-re-entrant and re-entrant geometries, liquid does not fully wet structure if \( \theta_{\text{flat}} + \alpha \geq 90° \) thanks to favorable shape of the liquid–vapor interface, (e) geometry with re-entrant curvature supporting a \( \theta_{\text{flat}} \) angle of 70°, (f) geometry with re-entrant curvature supporting various \( \theta_{\text{flat}} \) angles of ≤90°. (Adapted from Ref. [10]).

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Techniques for creating superoleophobic surfaces

2.1. Nanoparticle + polymer technique

The nanoparticle + polymer technique involves using a mixture of nanoparticles and polymer in order to create a coating. The nanoparticles create a nanoscale, rough structure for superoleophobicity, and the polymer is used as a binder to hold the nanoparticles and adhere to the substrate. In addition, roughening of the substrate via etching or micropatterning can also be carried out in order to add microscale roughness. Lastly, a low-surface energy coating is generally applied in order to repel the low surface tension of oils. The idea of hierarchical roughness is similar to the hierarchical roughness found in the lotus leaf. However, by using synthetic materials and better manufacturing processes, not only can superhydrophobicity be obtained, but superoleophobicity as well.

Using a binder of fluorinated acrylic copolymer and nanoparticles of various composition and size, superoleophobicity has been obtained. TiO₂ nanoparticles (20–50 nm) spray coated on a Si wafer resulted in ethylene glycol CA of 144° [29], ZnO nanoparticles (50 nm) spray coated on glass resulted in hexadecane CA of 154° [30]. SiO₂ nanoparticles have been spin coated on glass for ethylene glycol CA of 165° using 30–50 nm nanoparticles [31], spray coated on glass for hexadecane CA of 147° using 55 nm nanoparticles [32], and dip coated on polyethylene terephthalate (PET) for hexadecane CA of 153° using 55 nm nanoparticles [33].

SiO₂ is often used for the nanoparticle material, and other polymers have been combined with it for superoleophobicity. These binders have included 1H,1H,2H,2H-perfluorodecytriethoxysilane for xylene CA of 141° [34], heptadecafluoro-1,1,2,2-tetrahydrodecyltrimethoxysilane for hexadecane CA of 137° [35], and trichloro(1H,1H,2H,2H-perfluoroctyl)silane for diiodomethane CA of 141° [36]. Milionis et al. [37] used an acrylic fluorochemical binder with 5-15 nm diameter SiO₂ nanoparticles for hexadecane CA of 159°. Martin and Bhushan [38] obtained hexadecane CA of 156° using 10 nm diameter nanoparticles combined with methylphenyl silicone resin.

In these techniques, the size of the nanoparticle and particle-to-binder (P–B) ratio are of importance. Smaller diameter nanoparticles result in more scales of roughness especially when combined with a rough substrate. When nanoparticles and polymer agglomerate, they can form structures with rough surfaces and using smaller diameter nanoparticles results in rougher structures with more air pockets. In addition, when transparency is of interest, smaller diameter nanoparticles lead to greater visible light transmittance. The P–B ratio affects the wettability and durability of a surface. When P–B ratio is optimized, a surface will have its ideal CA and TA characteristics. When the P–B ratio is too low, there will not be enough roughness. When the P–B ratio is too high, the CA will decrease due to too many particles leading to Wenzel roughness properties [32] or the CA will remain constant due to no additional air pocket formation [33]. At too low or too high of a P–B ratio, a droplet will become pinned leading to a high TA [32].

2.2. Layer-by-layer technique

The layer-by-layer technique involves layers of oppositely charged species deposited separately in order to create a multi-layer coating held together via electrostatic interactions. Many different charged species can be used in each layer, which allows for a highly flexible coating with many applications in areas such as bioactive coatings [39], anti-reflective coatings [40,41], and chemical sensors [42]. In addition, the layer-by-layer technique was used for superhydrophilicity. Because the components are typically water-soluble polymers, these coatings are typically hydrophilic and oleophobic. Several superhydrophilic layer-by-layer coatings have used poly(sodium 4-styrene sulfonate), polydiallyldimethylammonium chloride (PDDA), and silica nanoparticles. Using these components, Liu and He [43] created an anti-reflective coating using 30 bilayers of PDDA and nanoparticles. Du et al. [44] created highly transparent coatings with >90% visible light transmittance. Lee and Ahn [45] used these materials to coat microchannels for capillary-driven bioassays.

By changing the top layer also known as the functional layer, Brown and Bhushan [46] obtained all quadrants of the wettability landscape (Fig. 2) using PDDA and 7 nm diameter silica nanoparticles. The initial layers of PDDA and nanoparticles result in superhydrophilic and superoleophobic properties. However, with further treatment with a silane, superhydrophobic and superoleophobic properties were obtained; with a fluorosilane, superhydrophobic and superoleophobic properties were obtained; and with a fluorosurfactant, superhydrophilic and superoleophobic properties were obtained. For the first time, this single,
facile fabrication method with its flexible functional layer resulted in all four possibilities of water and oil repellency and affinity [46].

2.3. Nanoparticle-encapsulation technique

The nanoparticle-encapsulation technique involves embedding nanoparticles into a surface. Different nanoparticles have been embedded into a surface for anti-bacterial properties [47,48], increased durability [49], and catalytic capability [50]. In order to obtain liquid repellency, embedded nanoparticles need to form nanoparticle agglomerates with re-entrant geometries.

Initially, superhydrophobic, polycarbonate (PC) surfaces were created without nanoparticles via solvent-induced phase transformation. When PC was immersed in acetone, crystallization of the polymer formed hierarchical structures that exhibited advancing water CA of 152° [51]. By adding SiO2 nanoparticles during the immersion process, re-entrant geometries were obtained. The nanoparticles agglomerated forming micron-sized clusters and acted as nucleation sites for polymer crystallization. After ultraviolet (UV) activation and fluorosilane deposition, a superoleophobic surface was demonstrated with water CA of 165° and hexadecane CA of 154° [13].

Another method for nanoparticle-encapsulation involves recrystallization of polypropylene (PP). Initially, superhydrophobic PP was created by solvent casting a PP film from a mixture of good (xylene) and bad (methyl ethyl ketone) solvents [52]. Good solvents dissolve the polymer, and bad solvents precipitate the polymer. Polypropylene can also be dipped into a xylene-nanoparticle mixture for superhydrophobicity [53]. A xylene-nanoparticle-PP mixture spin coated onto a PP substrate results in a nanocomposite polymer surface. With subsequent UV activation and fluorosilane deposition, superoleophobicity is obtained with water CA of 172° and hexadecane CA of 159° [14].

2.4. Liquid-impregnation technique

The liquid-impregnation technique involves adding a non-volatile liquid layer to a porous surface. This impregnated liquid has a surface tension lower than the liquid trying to be repelled. In order to ensure the impregnated, lubricating liquid remains on the surface and is not also removed, a porous surface topography is typically created. The repellency of the surface is dependent upon the miscibility of the liquids and the properties of the liquid layer. This technique takes inspiration from the pitcher plant due to its peristome that becomes extremely slippery when wet by nectar and rainwater.

It is important to choose a lubricating liquid that is immiscible with the liquid being repelled. If the two liquids are miscible, then the liquid being repelled could adhere to the surface or become embedded in the pores. When the liquids are immiscible, the pores and lubricating liquid form a flat surface for liquid-liquid contact with the liquid being repelled. This surface results in the repelled droplet sliding on the lubricating film at a low TA.

In order to combine the low-surface tension, fluorinated, lubricating liquid with the porous structure, the chemistry of the porous structure typically needs to be modified. An untreated, porous structure likely has a much higher surface energy than the lubricating liquid. Therefore, when they are combined, there is little interaction between the surface and liquid. Trying to repel a liquid droplet with a higher surface tension would likely displace the lubricating liquid. In order to keep the lubricating liquid adhered to the structure, the chemistry of the porous structure can be modified to more closely match the fluorinating liquid by adding a fluorosilane coating [54,55]. In this case, the lubricating liquid will not be displaced because it has a more favorable attraction with the porous surface than the liquid being repelled.

Various liquid-impregnated surfaces have been created using different methods for creating a porous structure. An early work used Teflon nanofibers or epoxy-molded nanoposts as the porous surface [54]. Although it made for a good model surface, its composition, fragility, and cost made it unsuitable for certain real world applications. Other porous structures were created using electrodeposition of highly textured polypropylene nanostructures on aluminum [56] and nanotextured alumina gel films [57], but did not show repellency to oils. Vogel et al. [58] showed repellency to olive oil using a nanostructured film created using colloidal templating. However, it required glass or other oxide substrates to form strong, covalent bonds, limiting its application to specific substrates.

Another technique involves spray coating wax to form a porous layer [59]. In this method, the liquid is impregnated in a subsequent spraying step. The durability of the wax coating remains questionable. A porous structure is more fragile than its solid counterpart, but still must have long-term durability. If the durability is compromised, the repellency of the liquids of interest becomes threatened.

A durable structure has been created using porous PP created using a solvent-nonsolvent polymer solution [55]. After coupling the structure with fluorosilane and impregnating the lubricating liquid, the liquid-impregnated surface repelled water, hexadecane, shampoo, and laundry detergent. In addition, the structure showed wear-resistance to abrasive wear via a pin-on-flat test.

3. Fabrication techniques

In this section, first the experimental procedures for creating four types of superoleophobic samples will be reviewed. Next, surface activation methods and its background will be discussed. Lastly, the methods of characterizing the samples will be presented.

3.1. Four superoleophobic techniques

Four different techniques that show repellency to water, oil, and surfactant-containing liquids will be presented. Expanded schematics of the fabrication methods are shown in Fig. 7. The nanoparticle/binder technique falls under the spectrum of nanoparticle + polymer. It uses a combination of high hardness nanoparticles and durable resin as a binder in order to create hierarchical, re-entrant roughness with a simple manufacturing method of spray coating. The layer-by-layer technique uses charged components where each component is kept separate and deposited individually in order to create a highly functional coating. The nanoparticle-encapsulation technique uses solvent-induced swelling and subsequent crystallization of the surface to create highly durable, rough surfaces. The liquid-impregnation technique uses an immiscible liquid immobilized on a porous surface for long-term repellency stability.

These techniques are presented on two substrates: glass for nanoparticle/binder and layer-by-layer, and PP for nanoparticle-encapsulation and liquid-impregnation. However, these techniques are not limited to these substrates and similar coating properties were achieved on different substrates by following similar coating procedures. Additional substrates for each technique can be found in Table 2 and include additional polymers such as polycarbonate (PC), polydimethylsiloxane (PDMS), polyethylene terephthalate (PET), nylon 6/6, polyurethane (PU), poly(methyl methacrylate) (PMMA), and polyethylene (PE). In order for the layer-by-layer technique to be deposited on PC, PDMS, and PET, the substrate surface needed to be activated using ultraviolet or ultraviolet-ozone treatment, described in Section 3.2. The experimental procedures for fabricating each technique on glass or PP are now presented.

3.1.1. Nanoparticle/binder technique

The nanoparticle/binder method used a coating of hydrophobic SiO2 nanoparticles and methylphenyl silicone resin with subsequent fluorination of the coating by vapor deposition of fluorosilane (Fig. 7a) [38]. Methylphenyl silicone resin was selected because it is known to be durable and offer strong adhesion between the nanoparticles and substrate [60]. Hydrophobic, 10 nm SiO2 nanoparticles were selected...
because they have high hardness for wear-resistance and high visible transmittance for transparency [61].

For the coating mixture, 150–600 mg of hydrophobic silica nanoparticles (10 nm diameter, Aerosil RX300) were dispersed in 30 mL of 40% tetrahydrofuran (THF, HPLC Grade, Fisher Scientific) and 60% isopropyl alcohol (IPA, Certified ACS, Fisher Scientific) by volume. This mixture was sonicated using an ultrasonic homogenizer (20 kHz frequency at 35% amplitude, Branson Sonifer 450A) for 15 min. Then, 150 mg of methylphenyl silicone resin (SR355S, Momentive Performance Materials) was added for a particle-to-binder ratio of 1.0–4.0. A particle-to-binder ratio of 2.5 was found to be optimal using CA and TA measurements. The mixture was then sonicated for an additional 15 min to form the final mixture.

For the coating fabrication procedure, first glass slides (Fisher Scientific) were cut to dimensions of 25 by 10 mm and used as substrates. Next, the glass substrates were cleaned in IPA with bath sonication (45 kHz frequency, Model FS5, Fisher Scientific) for 15 min. Then, substrates were rinsed with DI water and allowed to dry. After drying, 1 mL of the coating mixture was deposited via spray gun (Paasche®) from 10 cm away with compressed air at 210 kPa. The sample was transferred to an oven operating at 70 °C for 5 min to remove the remaining solvent. Next, the sample was irradiated using ultraviolet-ozone treatment with the samples placed 2 cm underneath the lamp source for 60 min. Lastly, one drop of trichloro(1H,1H,2H,2H-perfluorooctyl)silane (448,931, Sigma Aldrich) was vapor deposited on the sample using a closed container. The sample was attached to the top of the container via double-sided sticky tape with the surface facing down, and the drop was placed on the bottom of the container. This setup allowed the fluorosilane gas to uniformly coat the sample, and a vapor deposition time of 30 min was used [38].

3.1.2. Layer-by-layer technique

The layer-by-layer technique used components of polydiallyldimethylammonium chloride (PDDA) and hydrophilic, 7 nm SiO₂ nanoparticles (Fig. 7b) [28,46,62]. Polyelectrolyte, PDDA was chosen as the polymer base layer as it has a high cationic charge density and has been known to bind strongly to glass substrates [44, 45] and SiO₂ nanoparticles. The specific molecular weight range (100,000–200,000) was chosen to balance mechanical properties and ease of deposition (viscosity). Hydrophilic SiO₂ nanoparticles were used to enhance the roughness of the coating and the negatively charged surface silanol groups would ensure good adhesion to the positively charged PDDA layers [28,46,62]. Additionally, SiO₂ nanoparticles
are known to have high hardness for wear-resistance and high visible transmittance for transparency [61]. It should be noted that for non-active substrates, they can be activated using UV or plasma treatment.

Glass slides (Fisher Scientific) were cut to dimensions of 25 by 10 mm and used as substrates. PDDA (409,014, Sigma Aldrich) was dissolved in distilled water (DS Waters of America Inc.) at various concentrations. Silica nanoparticles (7 nm diameter, Aerosil 380, Evonik Industries) were dispersed in acetone (Certified ACS, Fisher Scientific) using an ultrasonic homogenizer (20 kHz frequency at 35% amplitude, Branson Sonifier 450A) at various concentrations. First, a PDDA layer was created by submerging the glass substrate in a PDDA solution (52 mg/mL) for 15 min. After removal, any excess was removed from the surface via bursts of compressed air from a spray gun (Paasche). The spray gun operated with compressed air at 210 kPa and was held 10 cm from the glass substrate at all times. Second, the SiO2 nanoparticle solution (15 mg/mL, 3 mL) was spray coated. Third, a second PDDA layer was deposited (8 mg/mL, 1 mL). After all the layers were deposited, the sample was transferred to an oven operating at 70 °C for 1 h. Finally, the functional layer was deposited onto the sample. For superhydrophobic/superoleophobic (top right quadrant, Fig. 2) coatings, chemical vapor deposition under atmospheric conditions was used. One drop of trichloro(1H,1H,2H,2H-perfluorooctyl)silane (448931, Sigma Aldrich) was deposited next to the samples, which were then covered, and left for 6 h to produce a vapor deposited fluorosilane coating [28,46,62].

In addition, other quadrants of the wettability landscape could be obtained by changing the functional layer. By not adding a functional layer, the superhydrophobic/superoleophobic (bottom left quadrant, Fig. 2) state could be obtained. By adding a silane treatment using methyltrichlorosilane (M85301, Sigma Aldrich) using the previously discussed chemical vapor deposition of a fluorosilane coating [14]. Hydrophilic, 7 nm SiO2 nanoparticles were used to enhance the roughness of the coating because they have been shown to be susceptible to irreversible aggregation, resulting in non-spherical, micrometer-sized clusters [63]. Additionally, SiO2 nanoparticles are known to have high hardness for wear-resistance, which will aid in the creation of a mechanically durable coating [61].

3.1.3. Nanoparticle-encapsulation technique

The nanoparticle-encapsulation technique creates polymer-nanoparticle composite surfaces with re-entrant geometries [Fig. 7c] [14]. Hydrophilic, 7 nm SiO2 nanoparticles were used to enhance the roughness of the coating because they have been shown to be susceptible to irreversible aggregation, resulting in non-spherical, micrometer-sized clusters [63]. Additionally, SiO2 nanoparticles are known to have high hardness for wear-resistance, which will aid in the creation of a mechanically durable coating [61].

A polypropylene (PP) sheet (ASTM D4101-0112, SPI) was cut to dimensions of 25 by 10 mm and used as substrates. Hydrophilic, 7 nm SiO2 nanoparticles (NP, Aerosil 380, Evonik Industries) were dispersed in xylene (Mallinckrodt), known to dissolve PP, using an ultrasonic homogenizer (20 kHz frequency at 35% amplitude, Branson Sonifier 450A) at various concentrations. Polypropylene (0.6 g) was then added to the mixture. The xylene–NP–PP mixture was heated to a temperature of 135 °C in a glass flask fitted with a water-cooled condenser to prevent solvent evaporation. Then, the mixture (1 mL) was added to the PP surface via spin coating and the surface was allowed to dry in air. To activate the polymer surface for silane attachment, samples were irradiated with ultraviolet light for at least 12 h. Samples were fluorinated via chemical vapor deposition of a fluorosilane (to lower surface energy), which was required in order to ensure preferential wetting by the lubricating liquid. One drop of trichloro(1H,1H,2H,2H-perfluorooctyl)silane (448931, Sigma Aldrich) was deposited next to the samples, which were then covered, and left for 2 h to produce a vapor deposited fluorosilane coating [14].

3.1.4. Liquid-impregnation technique

The liquid-impregnation technique creates a porous polypropylene (PP) layer using a xylene-cyclohexanone-polypropylene mixture (Fig. 7d). The porous layer is treated with fluorosilane and impregnated with an immiscible liquid. This technique was created for long-term stability of repellency toward water, oils, and surfactant-containing liquids [55].

A PP sheet (ASTM D4101-0112, SPI) was cut to dimensions of 15 by 15 mm and used as substrates. 0.2 g of PP was dissolved in 10 mL xylene (Mallinckrodt) heated to 135 °C in a glass flask fitted with a water-cooled condenser to prevent solvent evaporation. Once the polymer was fully dissolved, 4 mL cyclohexanone (Sigma Aldrich) was added and the mixture was stirred for 1 h. Then, a droplet of the solution was added to the PP surface and the surface was dried in an oven at 70 °C for 1 h. To activate the polymer surface for silane attachment, samples were irradiated using ultraviolet treatment for at least 12 h. Samples were fluorinated via chemical vapor deposition of a fluorosilane (to lower surface energy), which was required in order to ensure preferential wetting by the lubricating liquid. One drop of trichloro(1H,1H,2H,2H-perfluorooctyl)silane (448931, Sigma Aldrich) was deposited next to the samples, which were then covered, and left for 2 h. The sample was then dipped into the impregnating liquid, in this instance a perfluoropolyether (Krytox GPL 102, Dupont) with a chemical structure of F-(CF2CF2)n-CF2CF3 where n = 10–60, a surface tension of 16–20 mN/m, and a viscosity of 38 cSt [55].

3.2. Surface activation

Surfaces are commonly chemically activated via plasma or ultraviolet (UV) treatment in order to modify the surface functionality [64,65]. After activation, surfaces typically have a higher surface energy and improved adhesion for additional coatings. Plasma treatment is an effective surface treatment due to its aggressive nature. However, there are some disadvantages. It can be difficult to control and can require conditions not typically suitable for scale-up. Another possible option is UV treatment, which is a milder activation that can be applied in ambient environments and is more suitable for scale-up [65]. Various polymer surfaces have been activated using UV including PC [66,67], PP [68,69], PET [68,70] and PDMS [38,71–73]. Coating surfaces have been activated using UV [(10,13,14)] and UVO [38] in order to deposit fluorosilane coatings.

UV treatment can be broken up into two forms: ultraviolet and ultraviolet-ozone (UVO) treatment. These two treatments are commonly used to activate surfaces in order to apply a coating with improved adhesion to the treated surface. The techniques presented in this overview used UV or UVO treatments in order to modify the surface functionality. The UV exposure was generated from a compact germicidal lamp (15 W, Model CFL15/UV/MED, LSE Lighting) with the maximum energy output at the 254 nm wavelength. The UVO exposure was generated from a U-shaped, ozone-producing, ultraviolet lamp (18.4 W, Model G18T5VH-U, Atlantic Ultraviolet Co.) connected to an electronic ballast (120 v, Model 10-0137, Atlantic Ultraviolet Co.). It is expected that this lamp outputs a total of 5.8 W of 254 nm light, 0.4 W of 185 nm light, and 1.6 g/h of ozone in ambient conditions.

Also in this section, UV and UVO processes are discussed and are shown schematically in Fig. 8. These treatments are photo-sensitized oxidation processes in which organic molecules in the surface layer are excited and/or dissociated by the absorption of UV radiation [38, 71,74].

The UV method uses irradiation at 254 nm, whereas the UVO method uses a combination of 185 and 254 nm wavelengths. In the presence of 185 nm light, molecular oxygen can be dissociated into atomic oxygen, and atomic and molecular oxygen can be synthesized into ozone. In the presence of 254 nm light, ozone is decomposed into atomic and molecular oxygen [65,67,74]. These chemical reactions are shown in Fig. 8a [38].

The UV and UVO surface activation processes are shown in Fig. 8b. In the UV process, 254 nm light breaks up organic bonds in the surface layer, which causes the surface to attempt to return to a stable
Irradiation using 185 and 254 nm (UVO) light

Surface activation process through

Ultraviolet (254 nm)  Ultraviolet-ozone (185 + 254 nm)

Organic molecule Excited and/or dissociated molecule

Ozone is continuously synthesized/ decomposed

Desorbing volatile molecule (CO₂, H₂O, N₂, etc.)

Atomic oxygen breaks with excited and/or dissociated molecules

Bonds create desorbing, volatile molecules

Desorbed sites bond with oxygen to form polar groups

Chemically active, hydrophilic surface

Fig. 8. (a) Irradiation using 185 nm and 254 nm (UVO) light. A wavelength of 185 nm decomposes molecular oxygen into atomic oxygen and also synthesizes ozone. In the presence of 254 nm ultraviolet light, ozone decomposes into atomic and molecular oxygen. (b) Comparison of ultraviolet and ultraviolet-ozone surface activation processes. In the UV process, 254 nm light breaks up organic molecules at the surface, and these excited and/or dissociated molecular sites attempt to return to a chemically stable condition by reacting with oxygen molecules. After oxidation, polar groups are formed, which leads to a chemically active, hydrophilic surface. In the UVO process, the combination of 185 and 254 nm light causes ozone to be continuously synthesized and decomposed. Due to the irradiation, surface molecules are excited and/or dissociated, and therefore, react with atomic oxygen to form desorbing volatile molecules. These volatile molecules desorb from the surface. The desorbed sites bond with oxygen to form polar groups, which leads to a chemically active, hydrophilic surface [38].

3.3. Characterization of samples

In this section, characterization methods for the samples are described. These methods include contact and tilt angle measurements, scanning electron microscope imaging, coating thickness, repellency of surfactant-containing liquids, wear, self-cleaning, anti-smudge, anti-fogging, anti-icing, and oil–water separation.

3.3.1. Contact angle and tilt angle

Contact and tilt angle data were measured using a standard automated goniometer (Model 290, Ramé-Hart Inc.) using 5 µL DI water and hexadecane (99%, Alfa Aesar) droplets deposited onto the samples using a microsyringe. Contact angle was measured by taking a static profile image of the liquid-air interface and analyzing it using DROPimage software. Tilt angle refers to the angle when the droplet just began to roll off the sample surface. All angles were averaged over at least five measurements on different areas of the sample and reported as ±Δ.

3.3.2. Scanning electron microscope imaging

Top down, scanning electron microscope (Philips/FEI Sirion) images were taken to determine the topography of the techniques. To image the re-entrant geometry, SEM images were taken at a 70–75° angle. Samples were mounted with conductive tape and gold-coated prior to imaging.

3.3.3. Coating thickness

The coating thickness was measured using a step technique. One half of the substrate was covered with a glass slide using double-sided sticky tape before coating and then removed after the coating procedure resulting in a step. A scanning area of 100 by 100 µm² including the step was imaged using a D3000 Atomic Force Microscopy (AFM) with a Nanoscope IV controller (Bruker Instruments) to obtain the coating thickness. A Si, n-type (Si₃N₄) tip (resonant frequency f = 66 kHz, spring constant k = 3 N/m, AppNano) was used. The coating thickness was measured in contact mode for the nanoparticle/binder technique and tapping mode for the layer-by-layer technique.

3.3.4. Surfactant-containing liquid repellency

To test the repellency of surfaces towards surfactant-containing liquids, droplets of shampoo (Head and Shoulders®, Procter and Gamble Co.) and/or laundry detergent (Tide®, Procter and Gamble Co.) were placed onto surfaces tilted at ~25° for the lotus-inspired techniques and ~45° for the pitcher plant-inspired technique. The resulting surface–liquid interaction was photographed. The shampoo primarily contains sodium laurel sulfate and sodium laureth sulfamate, while the laundry detergent primarily contains sodium alcoholethoxy sulfate and sodium alkylbenzene sulfonate surfactants. At high concentrations, these surfactants typically have surface tensions on the order of 25 mN/m. In the products listed, depending upon concentration, the surface tensions will likely be in the range of 25–60 mN/m with values closer to the higher end [16,17].

3.3.5. Wear experiment

The mechanical durability of the surface was examined using an established macroscale wear test of a ball-on-flat tribometer [61]. A 3 mm diameter sapphire ball was fixed in a stationary holder. A load of 10 mN was applied normal to the surface, and the tribometer was put into a reciprocating motion for 100–200 cycles. Stroke length was 6 mm with an average linear speed of 1 mm/s. The surface was imaged before and after the experiment using an optical microscope with camera (Nikon Optihot-2).

Contact pressure for the tribometer wear experiment was calculated based on Hertz analysis [61]. An elastic modulus of 390 GPa and Poisson’s ratio of 0.23 were used for the sapphire ball [75]. For the nanoparticle/binder technique, an elastic modulus of 0.5 GPa and Poisson’s
were obtained using a Si, n-type (Si3N4) tip (resonant frequency 1 cm in height. The removal of particles by the water droplets was on the sample mounted on a 45° tilted stage for 30 min. Chamber (0.3 m diameter and 0.6 m high) by blowing 1 g of SiC powder and Poisson's ratio of 0.2 for the borosilicate ball[77], the mean contact pressure was calculated as 4.87 MPa using Hertz analysis[46]. This resulted in mean contact pressures of 8.6 MPa. Due to the inclusion of SiO2 nanoparticles in the nanoparticle/binder, layer-by-layer, and nanoparticle-encapsulation techniques, the elastic modulus of the final coating is expected to be higher, so an underestimated pressure will be obtained with the selected modulus.

With the nanoparticle/binder and layer-by-layer techniques, hexadecane TA was recorded before and after the wear test to determine if the coating was still repellent. Hexadecane droplets were placed on tilted samples both above the wear scar and directly on the wear scar. In both cases, the TA at which the droplet could roll across the scar was recorded. These results are not presented in this overview, but showed that the surfaces still repelled hexadecane droplets [38,46, 62].

For the layer-by-layer technique, microscale wear was examined through an AFM wear experiment. The nanoparticle/binder and nanoparticle-encapsulation techniques were too rough to be imaged by AFM and therefore AFM wear experiments were not performed. However, similar microscale durability is expected due to similar hardness of nanoparticles. For the AFM wear experiment, the surface was worn using a 30 μm diameter borosilicate ball mounted on a rectangular cantilever with nominal spring constant of 7.4 N/m (resonant frequency \( f = 150 \text{ kHz}, \text{All-In-One} \)). Areas of 50 by 50 μm² were worn for 1 cycle at a load of 10 μm so as to be later imaged within the scanning limits of the AFM. To analyze the change in morphology of the surface before and after the wear experiment, height scans of 100 by 100 μm² in area were obtained using a Si, n-type (Si3N4) tip (resonant frequency \( f = 66 \text{ kHz}, \text{spring constant} k = 3 \text{ N/m, AppNano} \) operating in tapping mode. Root mean square (RMS) roughness values before and after wear experiments were obtained. Using an elastic modulus of 70 GPa and Poisson’s ratio of 0.2 for the borosilicate ball [77], the mean contact pressure was calculated as 4.87 MPa using Hertz analysis [46].

### 3.3.6. Self-cleaning

The self-cleaning characteristics were examined by contaminating the sample with silicon carbide and comparing the removal of particles by water droplets before and after the experiment. Silicon carbide (SiC, Sigma Aldrich) particles of size 10–15 μm were dispersed in a glass chamber (0.3 m diameter and 0.6 m high) by blowing 1 g of SiC powder for 10 s at 300 kPa. After dispersion, the particles were allowed to settle on the sample mounted on a 45° tilted stage for 30 min.

The contaminated sample was then secured to a 10° stage and water droplets (total volume of 5 mL) were dropped onto the surface from 1 cm in height. The removal of particles by the water droplets was compared before and after tests. The ability for the water droplets to remove particles was quantified using image analysis software (SPIP 5.1.11, Image Metrology A/S, Horsholm, Denmark).

### 3.3.7. Anti-smudge

The anti-smudge characteristics of the surfaces were examined by placing coated samples over boiling water for 5 s. The steam condensed on the coatings and was then photographed to determine the resulting transparency.

### 3.3.8. Anti-fogging

The anti-fog characteristics of the surfaces were examined by placing coated samples in a freezer set at −18 °C for 2 h. The samples were tilted 10° and droplets of supercooled water (−18 °C) were then dropped onto the samples from a height of 5 cm.

### 3.3.9. Anti-icing

The anti-icing characteristics of the surfaces were examined by placing coated samples in a freezer at −18 °C for 2 h. The samples were tilted 10° and droplets of supercooled water (−18 °C) were then dropped onto the samples from a height of 5 cm.

### 3.3.10. Oil–water separation

Superhydrophobic/superoleophilic and superhydrophilic/superoleophobic coatings were found to be suitable for oil–water separation. The stainless steel meshes (#400) were first cleaned with acetone and IPA until they were found to be hydrophilic, then the coatings were deposited onto the meshes via spray coating. The coated meshes were then placed on top of beakers. Agitated mixtures of hexadecane and water were then poured onto the coated meshes. In

**Table 3**

Comparison of static contact angles and tilt angles for water and hexadecane droplets on the four superoleophobic techniques.

<table>
<thead>
<tr>
<th>Technique</th>
<th>Contact angle (°) / Tilt angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glass substrate</td>
<td></td>
</tr>
<tr>
<td>Untreated</td>
<td>22 ± 2 / n/a</td>
</tr>
<tr>
<td>Nanoparticle/binder</td>
<td>156 ± 2 / 2 ± 1</td>
</tr>
<tr>
<td>Layer-by-layer[46]</td>
<td>163 ± 1 / 2 ± 1</td>
</tr>
<tr>
<td>Polypropylene substrate</td>
<td></td>
</tr>
<tr>
<td>Untreated[14]</td>
<td>96 ± 1 / n/a</td>
</tr>
<tr>
<td>Nanoparticle-encapsulation[14]</td>
<td>172 ± 1 / 1 ± 1</td>
</tr>
<tr>
<td>Liquid-impregnation[55]</td>
<td>115 ± 2 / 2 ± 1</td>
</tr>
</tbody>
</table>

**Fig. 9.** Hexadecane contact angles and tilt angles for the four superoleophobic techniques compared to untreated glass and polypropylene substrates. Layer-by-layer image adapted from Ref. [46]; nanoparticle-encapsulation image adapted from Ref. [14]; and liquid-impregnation image adapted from Ref. [53].

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separate experiments, the meshes were inclined at an angle and the oil-water mixtures were poured over them. To improve contrast, Oil Red O and Blue 1 were used as oil and water dispersible dyes respectively. The use of dyes was not found to have any effect on the performance of the coating.

4. Discussion of data

The wettability, surface morphology, repellency of surfactant-containing liquids, mechanical durability, transparency, self-cleaning, anti-smudge, and antifouling, and other properties for each of the four techniques, nanoparticle/binder coatings on glass, layer-by-layer coatings on glass, nanoparticle-encapsulated polypropylene (PP) surfaces, and liquid-impregnated PP surfaces will now be reported and comparisons drawn between them.

4.1. Wettability

The CA and TA data using water and hexadecane droplets for the four superoleophobic techniques is presented in Table 3. The table presents data on untreated glass and untreated PP as well as the data for techniques deposited on these substrates. Untreated glass substrates

![Top- and tilt-view SEM images](image-url)

**Fig. 10.** SEM images of the four superoleophobic techniques. The top-down view (shown at two magnifications) shows the microstructure. The nanoparticle/binder, layer-by-layer, and nanoparticle-encapsulation techniques show agglomerates of nanoparticles that form micron-sized structures. The liquid-impregnation technique shows pores which can be filled by a lubricating liquid. The tilt view shows re-entrant geometries for the nanoparticle/binder, layer-by-layer, and nanoparticle-encapsulation techniques. The liquid impregnation technique does not require re-entrant geometries in order to repel oils and therefore does not have re-entrant geometries. Nanoparticle-encapsulation images adapted from Ref. [14] and liquid impregnation images adapted from Ref. [55].

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display CA for water and hexadecane of 22 ± 2° and 12 ± 2° respectively, Table 3. For the nanoparticle/binder and layer-by-layer coatings on glass substrates, the hexadecane CA were found to be >150°, Fig. 9. In addition, the hexadecane TA were <5° on both samples, Table 3. Therefore, both could be considered to be superoleophobic, in addition to superhydrophobic (high CA and low TA for water, Table 3) [62].

Untreated PP substrates were found to be slightly hydrophobic with water CA of 96 ± 1° but oleophilic with hexadecane CA of 35 ± 2°, Table 3. After treatment with the xylene–NP–PP mixture followed by drying in air, UV activation, and fluorosilane treatment, the surface becomes superhydrophobic and superoleophobic with CA of 172 ± 1° and 159 ± 1° for water and hexadecane respectively, Table 3 and Fig. 9 [13]. Low hexadecane TA of 4 ± 1° were also found on the fluorinated PP–NP composite surface. In all three of these cases, these high CA and low TA are a product of a composite interface with the droplet resting partially on pockets of trapped air.

Finally, pitcher plant-inspired, liquid-impregnated surfaces comprising porous PP dipped into a lubricating liquid were found to exhibit water CA of 115 ± 2° and hexadecane CA of 70 ± 2°, Table 3 and Fig. 9 [55]. These numbers do not seem as impressive as the static CA found on the lotus-inspired surfaces. However, due to the presence of the lubricating liquid, the surface displays very low TA of 2 ± 1° and 4 ± 2° for water and hexadecane respectively, Table 3. Because the low TA are a product of the homogeneity of the liquid–solid interface, the surface tension of the liquid being repelled has little effect on the repellency of the surface. This is in contrast to lotus-inspired superoleophobic surfaces, where decreasing the surface tension of the oil being repelled results in an increase in the TA [28,62].
4.2. Surface morphology

In order to achieve superoleophobicity, specific surface topographies are required. Re-entrant geometries, where local CA of $<90^\circ$ can be supported as demonstrated in Fig. 5, must be incorporated into the coating or surface treatment. In the case of the nanoparticle/binder and layer-by-layer coatings on glass, hierarchical, re-entrant geometries are found as discrete, micron-sized agglomerates as seen in Fig. 10. For nanoparticle-encapsulated PP surfaces, the rough surface contains a hierarchical surface morphology with re-entrant, overhanging geometry, Fig. 10. In both cases, once fluorinated, these re-entrant structures enable the formation of a favorable liquid-vapor interface for lower surface tension liquids and therefore result in high CA for hexadecane. Previous work has also demonstrated that these coatings remained repellent towards lower surface tension liquids such as octane (Table 1), though an increase in TA was observed with decreasing surface tension [28,62].

It is believed that the re-entrant structures are formed due to nanoparticle agglomeration. The small diameter of a nanoparticle leads to a very high surface-to-volume ratio. Since surface energy is inversely proportional to particle diameter, surface energy is a significant contributor to nanoparticle properties. The large surface energy would promote nanoparticle agglomeration and, in order to minimize the surface energy, these agglomerates would form tightly packed and quasi-spherical shapes [38,78]. In addition, smaller particles form agglomerates with a rougher surface that are more likely to give the re-entrant structure. A larger particle is less likely to form agglomerates and more likely to become partially embedded in the surface leading to hemispheres or spherical caps [38].

For the liquid-impregnated surfaces, a porous structure is required to help hold the lubricating liquid in place to ensure continued repellency. When cast, the presence of the nonsolvent leads to separation into two phases, one polymer-rich and the other polymer-poor [52]. This phase separation results in the crystallization of the polymer into the porous structure observed after solvent evaporation and drying, Fig. 10.

4.3. Repellency of surfactant-containing liquids

Oil repellency is now a fairly common property to find in coatings and surface modification techniques, and there are many methods capable of producing superoleophobic surfaces. A new challenge is creating surfaces that repel surfactant-containing liquids. Such surfaces could find use in many applications including consumer goods packaging, where repellency of surfactant-containing liquids is important in the packaging of shampoos and laundry detergents. Surfactant-containing liquids readily coat the inside of plastic bottles, leading to wasted product and issues with recyclability. To determine the applicability of the four different techniques in real-world applications such as consumer packaging, their repellency against shampoo and laundry detergent was tested. For the nanoparticle/binder and layer-by-layer coatings,

![Shampoo on tilted polypropylene and nanoparticle-encapsulated surfaces](image)

**Fig. 13.** Photographs demonstrating repellency of shampoo (a surfactant-containing liquid) by comparing shampoo droplets deposited on untreated polypropylene and nanoparticle-encapsulated surfaces. (Adapted from Ref. [14]).

![Surfactant-containing liquids on tilted polypropylene and liquid-impregnated surfaces](image)

**Fig. 14.** Photographs demonstrating repellency of surfactant-containing liquids by comparing shampoo and laundry detergent droplets deposited on untreated polypropylene and liquid-impregnated surfaces. (Adapted from Ref. [55]).

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droplets of shampoo and laundry detergent were found to roll or slide from the surface with no noticeable contamination, Figs. 11 and 12. This is in contrast to the untreated glass substrates where both shampoo and laundry detergent were found to spread and foul the surface.

For the nanoparticle-encapsulated surfaces, shampoo was found to slide across the surface, Fig. 13. However, it was found that laundry detergent was not repelled and contaminated the sample surface. This difference is probably due to the different viscosities of the two surfactant-containing liquids. The laundry detergent is less viscous and so is potentially more readily able to wet the solid surface and collapse the liquid-air interface of the Cassie-Baxter state. Additionally, the surfactant concentration of the laundry detergent may be higher than that of the shampoo, resulting in a lower surface tension liquid that was more likely to spread over the re-entrant geometry found on the nanoparticle-encapsulated surfaces.

For the liquid-impregnated samples, both surfactant-containing liquids were able to slide over with no contamination, Fig. 14. In the case of shampoo, the highly viscous liquid slid from the surface in the shape of a droplet with a pronounced trailing edge. For the laundry detergent, the liquid was found to spread more due to its lower viscosity. Though the main bulk of the liquid quickly vacated the surface, a thin film of detergent briefly remained before slowly dewetting the surface and leaving the sample clean. It was found that these pitcher plant-inspired samples required more tilting than the lotus-inspired surfaces due to the lower contact angles of the droplets and so a slower sliding action on the former compared to the rolling action on the latter. Despite this, both liquids were successfully repelled by the liquid-impregnated surface [55].

4.4. Comparing repellency for the four techniques

The four techniques reported here are capable of repelling both water and hexadecane with very high CA and low TA for both liquids. The lotus leaf inspires three techniques: nanoparticle/binder coatings, layer-by-layer coatings, and nanoparticle-encapsulated surfaces. These surfaces achieve liquid repellency by featuring surface topographic features that are able to trap air between the substrate and liquid, reducing the solid–liquid interface and therefore increasing droplet CA and reducing TA. However, liquids on such surfaces occupy a metastable state that may be collapsed either over time or by some external action (i.e. applied pressure, vibration, etc.). If this happens, the composite air–solid–liquid interface underneath the droplet fails and the droplet fully wets the surface and the surface loses liquid repellency. This dependency on a metastable state could prove troublesome for applications where long-term contact with the liquid being repelled is required.

Repelling surfactant-containing liquids can also prove challenging for lotus-inspired surfaces. As reported above, the three techniques demonstrate some repellency towards both shampoo and laundry detergent (the nanoparticle-encapsulated surface was only repellent towards shampoo), with droplets of the liquids rolling or sliding over the treated surfaces. However, if a droplet of either liquid is allowed to rest on these surfaces for a significant period of time, surfactant molecules may attach to the surface at the liquid–solid interface. These surfactant molecules may alter the surface chemistry of the solid surface,
leading to a decrease in the local (flat) CA and a collapsing of the composite interface between the droplet and the surface. The surfactant can also remain on the surface after the liquid is removed, which may lead to a permanent loss of repellency.

Pitcher plant-inspired, liquid-impregnated surfaces are repellent due to a lubricating liquid layer that preferentially wets a porous surface structure. Because of the smooth liquid–liquid interface, the liquid being repelled is able to slide over the lubricating liquid with low TA. As long as the lubricating liquid and the liquid being repelled are immiscible and the lubricating liquid remains within the porous structure, these liquid-impregnated surfaces can effectively repel liquids regardless of their surface tension, unlike lotus-inspired surfaces where repellency decreases with decreasing surface tension [28,62]. Furthermore, because this repellency does not rely on metastable states, these liquid-impregnated surfaces may possibly remain repellent for longer than the lotus-inspired surfaces. Additionally, since the lubricating liquid preferentially wets the porous structure, the liquid being repelled remains on top of this liquid layer and has little contact with the solid surface below. This means that surfactant-containing liquids may be repelled with low risk of contamination of the solid surface by surfactant. Finally, the ability to change the lubricating liquid depending upon the application improves the flexibility of this method. For instance, for consumer packaging applications, a food-safe lubricating liquid would be desirable.

When comparing the two different types of surface, it is important to note that, in the case of the lotus-inspired samples, if shampoo is left on the superoleophobic surfaces for a significant amount of time, there is some reduction in the repellent nature of the material. The superoleophobic material reported here could therefore find use in applications where extended contact with the fouling product is minimal.

Fig. 17. Optical micrographs of contaminated coatings before and after self-cleaning test. Glass samples include untreated, nanoparticle/binder, and layer-by-layer. Polypropylene samples include untreated and nanoparticle-encapsulation. Dark spots on coatings indicate silicon carbide particle contaminants. Image analysis suggests >90% removal of particles on the techniques. Layer-by-layer images adapted from Ref. [46].

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(such as bottle cap or single-use applications). However, for shampoo-repellent applications where surfaces are in constant contact with shampoo such as in the inside of a typical consumer bottle, liquid-impregnated surfaces could be more suitable. The surfactant-containing liquid has little contact with the substrate and therefore is less likely to adhere and alter the surface energy. Furthermore, liquid-impregnated surfaces should display greater stability compared to traditional liquid-repellent surfaces whose repellency relies on metastable states and trapped air. Liquid-impregnated surface treatments as reported here would therefore be more suited for applications where the contaminant liquid is in contact with the surface for long periods of time or is subject to vibration, both of which could result in the collapse of the Cassie-Baxter regime in traditional liquid-repellent surfaces.

4.5. Mechanical durability

The mechanical durability of the samples produced by the four techniques was investigated through tribometer and AFM wear experiments and the resulting optical images are displayed in Fig. 15. These experiments show the surface resistance of the coatings to wear and abrasion. AFM wear is solely presented for the layer-by-layer technique because the nanoparticle/binder and nanoparticle-encapsulation techniques were too rough to be imaged by AFM. However, similar micro-scale durability is expected due to similar nanoparticle hardness. For the tribometer wear experiments, a portion of the wear track is shown, Fig. 15a. In the case of the nanoparticle/binder and layer-by-layer coatings on glass, the wear experiments were carried out with a load of 10 mN for 100 cycles. After the wear experiment, there is some noticeable burnishing to the coatings; however, damage to the coatings is minimal in both cases. Higher magnification images confirmed that the nanoparticle/binder and layer-by-layer composite coating morphology is similar before and after the wear test and there is no removal of the coating from the substrate [38,46]. It is likely that the hard SiO2 nanoparticles used in both techniques help improve the durability of both the coatings. In the case of the layer-by-layer technique, the oppositely charged PDDA binder layers anchor the negatively charged particles to the glass substrate via an electrostatic bond. In contrast, the nanoparticle/binder technique uses the resin binder to adhere the coating to the substrate.

In the case of the nanoparticle-encapsulated surfaces, there was no noticeable wear scar, even after 200 cycles, Fig. 15a. It is believed that these surfaces are significantly more durable than many current examples of superoleophobic surfaces. Other surfaces typically rely on poorly adhered coatings, delicate surface structures, or the studies report either poor mechanical properties or fail to report any durability data. Finally, for the liquid-impregnated samples, the images confirm that the surface features are not completely destroyed with minimal burnishing of the surface in the wear location. While not as durable as the nanoparticle-encapsulated samples, it is believed that these surfaces are significantly more durable than many other examples of liquid-impregnated surfaces, which typically rely on poorly adhered wax coatings [59] or delicate surface structures [54]. The durability of the porous layer is required since it ensures the lubricating liquid remains in place, impregnated within the pores. The porous structures required for this liquid repellency technique may be susceptible to higher contact stress than more typical oil-repellent surfaces and so it is crucial that mechanical durability is reported.

For the AFM wear experiment on the layer-by-layer technique, a wear region of 50 by 50 μm² is shown in the center of a 100 by 100 μm² scan area, Fig. 15b. The layer-by-layer coating survived the AFM wear experiment with no observable defects [46]. Similar microscale durability is expected for the other nanoparticle techniques due to their incorporation of hard nanoparticles. However, AFM wear experiments were not performed due to the surface being too rough to image.

4.6. Transparency

Many applications of oil-repellent surfaces rely on the transparency of the coating. Text remains legible when it is placed behind the nanoparticle/binder and layer-by-layer coatings, suggesting that the coatings display characteristics of transparency, Fig. 16. Further improvement in transparency, potentially by decreasing the thickness of the nanoparticle layer, may be possible in the future. In the examples of the nanoparticle-encapsulation and liquid-impregnation techniques reported here, PP, a translucent material, is used as the substrate. If these techniques are used on transparent substrates, there will likely be a loss of transparency.

4.7. Self-cleaning, anti-smudge, and antifouling

The water- and oil-repellent properties of these surfaces make them suitable for self-cleaning, anti-smudge, and antifouling applications. When contaminated with silicon carbide, the vast majority of the contaminants can be removed in a self-cleaning test where water droplets roll across the repellent surfaces, collecting particles in the process, Fig. 17. After the self-cleaning test, >90% of the particles are removed from these surfaces. Dark spots on coatings and cloth indicate silicon carbide particle contaminants.

Anti-smudge test on contaminated glass and nanoparticle/binder surfaces

Before Untreated glass Glass surface Cloth
Fig. 18. Optical micrographs of contaminated surface and oil-impregnated microfiber cloth before and after anti-smudge test on untreated glass and the nanoparticle/binder surfaces. Dark spots on coatings and cloth indicate silicon carbide particle contaminants.
on the superhydrophobic coatings. On the untreated glass and polypropylene samples, the majority of the contaminants remain after the self-cleaning test. These coatings are self-cleaning due to their high water CA and low CAH. Water droplets deposited onto these samples are able to roll over the coating with little impediment, collecting less hydrophobic contaminants as they go [13,46,62]. The liquid-impregnation technique does not exhibit the self-cleaning action because it does not have high water CA and so water droplets do not roll over the surface collecting contaminants.

For anti-smudge, the surfaces were contaminated in a similar way and a hexadecane-soaked cloth was used to wipe the surfaces [79]. The anti-smudge data for the nanoparticle/binder, the layer-by-layer, and nanoparticle-encapsulation are shown in Figs. 18–20. For the oil-repellent surfaces, the particles were transferred to the cloth with no observable particles remaining on the surfaces. However, on the untreated samples, many particles remained on the sample and oil was transferred from the cloth to the sample. Similar to the self-cleaning experiments with water, the anti-smudge property relies on a high CA and low CAH for the oil. The oil in the cloth is able to collect oleophilic contaminants from the surface of the coating without sticking to the surface [13,28,46,62]. Because the liquid impregnation technique does not exhibit high hexadecane CA, the hexadecane-soaked cloth is likely to transfer oil to the surface making it less suitable for anti-smudge applications.

Finally, the oil-repellent coatings could be used for anti-biofouling, where superoleophobicity and nanostructuring can contribute to reducing microorganism attachment [80].

4.8. Other properties

All the techniques here are capable of producing a water- and oil-repellent surface. If other properties on the wettability landscape (Fig. 2) are desirable, the layer-by-layer technique offers additional flexibility to result in coatings that exhibit all four possible combinations of liquid repellency and affinity. The coating is comprised of several discrete layers, which are deposited individually. The final (top) layer in the coating contains the desired surface chemistry and can be easily swapped to produce a different functionality as shown in Fig. 21. In the case of the superhydrophilic/superoleophilic coating, no additional functional layer is added, leaving the high surface tension polymer

![Anti-smudge test on contaminated glass and layer-by-layer surfaces](image1)

![Anti-smudge test on contaminated polypropylene and nanoparticle-encapsulated surfaces](image2)

**Fig. 19.** Optical micrographs of contaminated surface and oil-impregnated microfiber cloth before and after anti-smudge test on untreated glass and the layer-by-layer surfaces. Dark spots on coatings and cloth indicate silicon carbide particle contaminants. Layer-by-layer images adapted from Ref. [46].

**Fig. 20.** Optical micrographs of contaminated surface and oil-impregnated microfiber cloth before and after anti-smudge test on untreated polypropylene and the nanoparticle-encapsulated surfaces. Dark spots on coatings and cloth indicate silicon carbide particle contaminants.
layer exposed. For superhydrophobic/superoleophilic coatings, a non-fluorinated silane is used to repel water but not oils, which have lower surface tensions (Table 1). For superhydrophobic/superoleophobic coatings, a fluorinated silane is used to repel both water and oils. Finally, for superhydrophilic/superoleophobic coatings, a fluorosurfactant is used to yield the desired “flip-flop” of surface properties required [46]. In all cases, the inclusion of a nanoparticle layer enhances the surface properties of the functional layer to result in super-philic/super-phobic surfaces. Water and hexadecane droplet images and CA for all four coatings are shown in Fig. 22. The superhydrophilic/superoleophilic coating was instantly wet by both water and oil. The superhydrophobic/superoleophilic coating was wet by oil whilst repelling water. The superhydrophobic/superoleophobic coating repelled both liquids. Finally, the superhydrophilic/superoleophobic coating repelled oil, but was wet by water. Table 4 provides a summary of all CA and TA data [46].

![Schematic of four layer-by-layer composite coatings](image)

**Fig. 21.** Chemical composition and charge of each layer for the four layer-by-layer composite coatings. Each layer is deposited separately. The functional layer is deposited last and provides the desired surface chemistry. (Adapted from Ref. [46]).

![Liquids on layer-by-layer composite coatings showing wettability landscape](image)

**Fig. 22.** Water and hexadecane droplets deposited on the four layer-by-layer composite coatings to show adaptability of the technique and its flexibility in achieving the four regimes of the wetting landscape. (Adapted from Ref. [46]).

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The oil repellency of the superhydrophilic/superoleophobic coating, in addition to wetting by water, is due to the fluorosurfactant containing a low surface tension fluorinated tail and a high surface tension head group complexed with a hydrophilic polyelectrolyte. During spray coating, the polar head group forms an electrostatic complex with the polyelectrolyte layer below and the fluorinated tails orient themselves at the air interface. Large, bulky oil molecules are trapped at this fluorinated interface while smaller water molecules can more easily penetrate down through the thin layer (ca. 30 nm) to the hydrophilic region where the surfactant head group complexes with the polyelectrolyte layer. The result is a “flip-flop” of surface properties and a coating that repels oils but is wet by water [46].

The flexibility of this technique allows one to select the surface properties most suitable for the application in mind. For instance, anti-fogging surfaces rely on substrates that have high wettability to water. To examine the anti-fogging properties, all four coatings were placed directly above a source of boiling water for 5 s. The samples were then photographed to assess their transparency, shown in Fig. 23. Both the superhydrophilic coatings were found to retain their transparency with text remaining visible through the condensed water layer. In contrast, on the superhydrophobic coatings, the formation of discrete droplets of water results in samples that are completely opaque.

For the superhydrophilic/superoleophobic coating, the speed of the water penetration through the low surface tension fluorinated tail groups to the high surface tension head groups is crucial for the condensed droplets to spread out and form a continuous water layer and thereby maintain transparency [46]. Previously developed coatings would not be suitable for anti-fogging applications because the rate of water penetration is too low (takes 5–30 min for surface to become superhydrophilic) [81–84].

Another example of selecting the correct surface properties for a given application is anti-icing. For anti-icing experiments, all four coatings were placed in a freezer set at −18 °C for 2 h. The samples were tilted and droplets of supercooled water were deposited onto them, as shown in Fig. 24. For the superhydrophilic coatings, the droplets spread out and froze on the sample surface. For the superhydrophobic coatings, droplets rolled off the surface to freeze on the bottom of the freezer. This occurs because the water droplets are in the Cassie-Baxter state. The formation of a composite interface minimizes the contact with the cooled substrate and ensures a low hysteresis so droplets can roll from the tilted surface [46].

Finally, superhydrophilic/superoleophobic coatings exhibit a different response to water and oil and therefore are suitable for use in oil-water separation. The use of hydrophilic/oleophobic coatings is preferable over alternative configurations where the surface is hydrophobic/oleophilic, because surface contamination by oil and other oil-based contaminants is common, and the porous material must then be cleaned or replaced, resulting in a drop in the separation efficiency. It is therefore preferable for the water phase to be allowed to pass through the

<table>
<thead>
<tr>
<th>Coating</th>
<th>Contact angle (°) / Tilt angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Superhydrophilic/superoleophilic</td>
<td>~0 / n/a</td>
</tr>
<tr>
<td>Superhydrophobic/superoleophilic</td>
<td>161 ± 1 / 2 ± 1 / 0 / n/a</td>
</tr>
<tr>
<td>Superhydrophobic/superoleophobic</td>
<td>163 ± 1 / 2 ± 1 / 157 ± 1 / 4 ± 1</td>
</tr>
<tr>
<td>Superhydrophilic/superoleophobic</td>
<td>&lt;5 / n/a</td>
</tr>
</tbody>
</table>

Data taken from [46].

Table 4
Comparison of static contact angles and tilt angles for water and hexadecane droplets on the layer-by-layer composite coatings.

a Same as layer-by-layer in Table 3.

Anti-icing properties of layer-by-layer technique

![Anti-icing properties of layer-by-layer technique](image)

**Fig. 23.** Photographs of the four layer-by-layer coatings after exposure to water vapor to show anti-fogging properties. The hydrophilic coatings maintain transparency due to the formation of a thin water film on the surface. The hydrophobic coatings become opaque due to the formation of discrete water droplets on the surface. (Adapted from Ref. [46]).

**Fig. 24.** Photographs of the four layer-by-layer coatings after freezing and deposition of supercooled water to show anti-icing properties. The water immediately froze upon contact with the hydrophilic coatings whereas the droplets were able to roll off the hydrophobic coatings before freezing. (Adapted from Ref. [46]).
mesh and the oil phase be repelled. Additionally, water is denser than oil and tends to sink to the bottom of a mixture meaning hydrophobic/oleophilic materials are not suitable for certain applications, such as gravity-driven separation.

Agitated oil–water mixtures were poured onto a superhydrophilic/superoleophobic-coated mesh suspended over beakers, as shown in Fig. 25. The water component passed through the mesh while the oil remaining on top, rolling across the top of the mesh to be collected in a separate beaker. This tilted setup is only possible due to the fast penetration by water. There was no degradation of oil–water separation after sitting in ambient for over a year. Previously developed coatings would not be suitable for this method of oil–water separation because the rate of water penetration is too low (takes 5–30 min for surface to become superhydrophilic) [81–84].

It should be noted that by using fluorosurfactant in place of fluorosilane, the nanoparticle/binder technique can also be used for oil–water separation. The benefit of the nanoparticle/binder technique is that it requires fewer manufacturing steps than the layer-by-layer technique, although surface activation for the fluorosilane layer is needed. In the layer-by-layer technique, electrostatic attraction between the top polyelectrolyte layer and the fluorosurfactant may provide greater durability.

5. Summary and outlook

Four different fabrication techniques have been developed for superliquiphobic surfaces repellent to water, oil, and surfactant-containing liquids. All four techniques result in surfaces that are extremely repellent to water and hexadecane. The high contact angles and low tilt angles for the nanoparticle/binder, layer-by-layer, and nanoparticle-encapsulation techniques result in self-cleaning and anti-smudge properties. Because the liquid impregnation is only repellent to these liquids at lower contact angles than the other three techniques, it does not exhibit the self-cleaning and anti-smudge properties. In addition, all techniques demonstrate some repellency toward surfactant-containing liquids. The liquid-impregnation method performs well because shampoo and laundry detergent may not foul these surfaces even after extended contact, so long as the lubricating liquid remains within the porous structure. In the other techniques, if a surfactant-containing droplet is allowed to rest on the surface, eventually surfactant molecules can alter the surface chemistry of the solid surface, leading to a decrease in the local contact angle and a collapsing of the composite interface between the droplet and the surface. It should be noted that formation of re-entrant geometry in these techniques allows repulsion of liquids, which is extremely desirable. Further experiments are needed to determine if permanent loss of repellency occurs.

The nanoparticle-encapsulation technique exhibited good wear-resistance. Nanoparticles were directly incorporated into the surface during solvent-induced softening of the polymer material, resulting in durable surface properties. In contrast, the nanoparticle/binder and layer-by-layer techniques are applied as a coating. The robustness and durability of the surface properties achieved from a coating will be dependent upon their adhesion to the substrate. Selecting suitable coating materials and activating the substrate for coating attachment can lead to high wear resistance.

All four techniques can be easily fabricated. However, the nanoparticle/binder and nanoparticle-encapsulation techniques require the fewest steps. The nanoparticle/binder method is a one-step spray technique followed by fluorosilane deposition. Similarly, the nanoparticle-encapsulation technique involves spin coating or immersion followed by fluorosilane deposition. However, both the nanoparticle/binder and nanoparticle-encapsulation methods require surface activation before fluorosilane deposition. In contrast, the layer-by-layer technique does not require surface activation for fluorosilane deposition, but requires three spray steps and possible surface activation on hydrophobic substrates for the first layer. The difficulty in fabricating liquid-impregnated surfaces arises from forming the porous structure, but the subsequent steps of depositing the fluorosilane layer and adding the low-surface tension, lubricating liquid are relatively straightforward.

The nanoparticle/binder and layer-by-layer techniques have the greatest flexibility in terms of substrate applicability and modifying the functionality for various applications. The substrate-independence can be advantageous for applications where multiple base materials are frequently used or where the same properties are sought across different products. In addition, by simply modifying the last step of the coatings, the properties of the coatings can be radically altered. Such an approach could simplify fabrication, with different products receiving the same base coatings with only the final layer differing between products.

By understanding surfaces in nature and improving upon them by incorporating synthetic materials and better manufacturing processes, many different techniques have demonstrated water and oil repellency. By weighing the strengths and limitations of various techniques, the suitability of each for a particular application can be determined. New areas can implement these techniques or use them as a foundation for additional techniques to create surfaces with self-cleaning, anti-smudge, antifouling, and low-adhesion properties. The field of superliquiphobicity continues to grow as more surfaces implement these properties and the number of applications requiring these surfaces increases.

References

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