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Non-fluorinated durable water repellent and stain resistant coating

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Abstract: Fluorinated materials have been broadly used in the industry of water repellent and stain resistance. Because fluorinated materials have low surface tension, and the coatings could easily be manufactured as water-repellent and stain-resistant, fluorinated materials dominate the market for breathable waterproof textiles. However, these materials had substantial health hazards because of the toxicity of fluorinated materials. Moreover, many governments also regulate fluorinated materials for health reasons. As a result, non-fluorinated materials replacing fluorinated materials have become a trend in the industry. As a result, many companies are actively looking for solutions for non-fluorinated water-repellent and stain-resistant materials. This literature review will give a comprehensive understanding of water-repellent properties, materials surfaces, and stain-resistance properties, materials, and surfaces.Moreover, this review would also include reviews of natural water repellent and stain repellent. Furthermore, this review will also talk about the theories behind the materials. Additionally, the fabrication process limitation and future outlook will be discussed in this review.

Keywords: fluorinated materials, stain resistant coating, non-fluorinated durable water repellent

1. Introduction

Water-repelling and stain-repelling materials have become increasingly important in everyday life. For example, the water-repellency and stain resistance of non-stick pans, raincoats, umbrellas, and surface water-repellent sprays are all critical in daily life. Manufacturers favor superhydrophobic surfaces to handle water and stain resistance adequately. In addition, superhydrophobic surfaces' self-cleaning and fouling resistance make them valuable in industrial settings. Most superhydrophobic materials are currently fluorinated because they have low surface energy and surface tension, making them useful

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for various industrial applications [1]. Since fluorinated materials are easy to manufacture and relatively inexpensive, fluorinated materials have been dominant in the waterproof breathable textile market for decades. Substantial market demand is another driving factor that fluorinated materials are broadly used. According to Global Market Insight Research, the waterproof textile market will expand from 1.6 billion dollars in 2019 to 2.5 billion dollars in 2025, growing at a 7.1 percent rate [2]. However, due to toxicity and potential health hazards, people started becoming aware of the harm of using fluorinated materials.

Moreover, more and more research studies reveal that fluorinated materials pose significant health issues. Therefore, government regulation and technology reform stimulate the research and development of non-fluorinated materials for water-repellent and stain resistance. The current stages of non-fluorinated materials are still booming. However, many non-fluorinated materials studies are still in the early stages of research. Indeed, non-fluorinated materials would become the future of water and stain-repellent materials because of their sustainability and toxicity.

1.1. Global regulation
Various perfluoroalkyl substances can adversely affect human health, including reproductive, developmental, and immune effects. Developmental effects include fetal weight loss, cleft palate, systemic edema (edema), delayed bone ossification (sternum and phalanx), and cardiac abnormalities (ventricular septal defect and enlargement of the right atrium). Lau's research observed dose-dependent deleterious effects of PFOS during childbirth in rodents exposed to PFOS. In the highest dose assessed (10 mg/kg) group, newborns became pale, inactive, and dying within 30-60 minutes, and all died shortly after. More than 95 percent of these animals did not survive their first day of life, and only a few pups reached puberty. The surviving pups were also somewhat impaired by long-term exposure to PFOS in utero; the pups were significantly heavier than the controls, and the effects persisted after weaning. This has led to EPA bans on perfluoroalkyl substances and the need for more environmentally friendly and sustainable alternatives, which are gradually being developed to replace different products as international production of C8 is restricted [3].

Due to the high toxicity of fluorocarbon materials, EPA (Environmental Protection Agency), European Unions, China, Japan, and other countries regulated fluorocarbons as a pollutant. According to Enviliance ASIA, after 2019, the Stockholm Convention on Persistent Organic Pollutants (POPs), Perfluorooctanoic acid (PFOA) was listed as Annex A (Elimination) of the Convention [4]. Starting in 2020, China listed PFOA as a priority control substance; especially in 2021, China’s Ministry of Ecology and Environment declared an action plan on the pollutant, which included PFOA. [4]. Singapore, Indonesia, Thailand, and Vietnam exercises similar regulation, including implementing a license for import and export [4]. Meanwhile, as technology reforms, the company is devoting resources to developing non-fluorinated carbon because of tightening policy, environmental concerns, and health issues. The momentum of replacing fluorocarbon has never been motivated in academia and industry. As result, the fluorine-free carbon solutions to water and stain-repellent-related research have been substantially boosted.

1.2. Contact angle
The surfaces that are repellent specifically to water are hydrophobic [5]. The surface tension includes two parameters: contact angle and contact angle hysteresis [6]. The definition of contact angle is the angle that is shaped within the liquid-solid interface [5]. Based on Young’s relation, the definition of surface energy is excessive energy on the material surface [7].

Here the γ refers to the interfacial tension, such as γ_{SV}, γ_{SL}, and γ_{LV}. First, the surfaces can be separated into four types based on the angle θ from Young’s relation. If $\theta \approx 0°$ (Figure 1 a), the surface is super hydrophilic. The surface is hydrophilic if $\theta < 90°$ (Figure 1 b). The surface is hydrophobic if $\theta > 90°$ (Figure 1 c). The surface is superhydrophobic if $\theta > 150°$ (Figure 1 d).

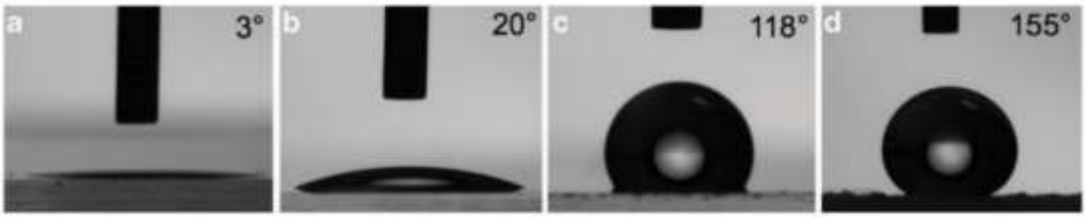

Figure 1. Images of surfaces in that area a. Super hydrophilic, b. hydrophilic, c. hydrophobic, and d. superhydrophobic.[5].

The second one, contact angle hysteresis, represents the differences between receding and advancing contact angles. Physically, the definition of contact angle hysteresis is a calculation of energy consumption as the water droplet moves along a solid's surface.

1.3. Cassie baxter state and wenzel state

In Wenzel State, as Figure 2a shows, the water droplet can completely cover the microstructures on that surface, forming a situation that is "fully wetted." Under such circumstances, the calculation of the apparent angle can be done with the equilibrium of the Wenzel relation [8]:

$$cos\theta^{*} = r \times \, cos\theta \quad (1)$$

The r here symbolizes the roughness of a surface, which is the ratio between the projected surface and the actual surface. Because the transparent surface is more extensive than the projected surface, the numerical value of r is always bigger than 1[8]. θ* is the contact angle between the textured surface and the water droplet. θ is the contact angle between the smooth (or non-textured) surface and the water droplet; when θ>90°, the apparent contact angle will be great due to surface roughness.

If the water does not completely cover the microstructures on the surface (Figure 2b), the Contact angle in this situation can be confirmed with the Cassie equation [9]:

$$cos\theta - f_1 cos\theta_1 + f_2 cos\theta_2 \quad (2)$$

Where f_1 and f_2 are two interfacial area fractions in this equation, and f_1+f_2=1.

The composite interface can be formed using the liquid-air interface and the liquid-solid interface (Figure 2). Under this situation, the Cassie-Baxter equation can be applied [9]:

$$cos\theta^{*} = r_{\varphi}\varphi_s \, cos\theta + \varphi_s - 1 \quad (3)$$

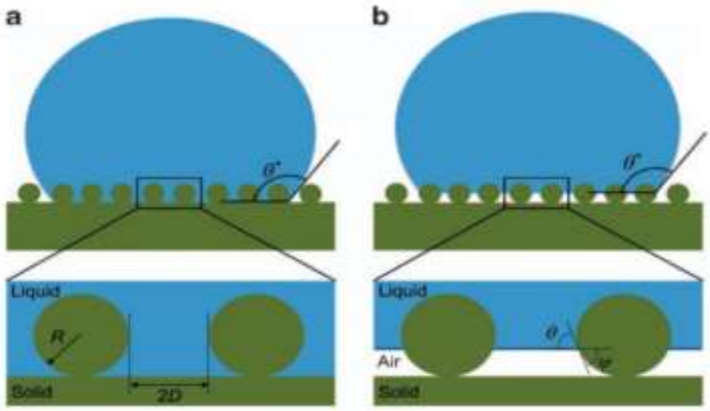

Figure 2. Droplet of liquid on a solid surface. (a) it shows the Wenzel State; (b) it represents the Cassie-Baxter State. [5]

1.4. Fluorinated coatings

It is evident from Young's equation that the contact angle θ is oppositely proportional to the solid surface energy. This suggests that lower surface energy leads to a higher contact angle. The surface energy includes the dispersion force, orientation force, and induction force. The increase in water

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contact angle is caused by the larger size of C-F groups in the carbon skeleton covering the surface [10]. Thus, the surface energy is low when the dispersion force is low so that the surface will be more hydrophobic.

2. Natural water repellent

Many materials are derived from natural materials. For example, the design of the airplane was motivated by birds. The aerodynamics of airplanes are similar to birds' aerodynamics. Water repellent and stain resistance are also motivated by nature. Plants and animal surfaces are equipped with hydrophobic properties, and some of them are even anti-stain surfaces. The secret of hydrophobic properties is that those structures contain multiple-hieratical structures and low surface materials or natural coasting above the surface. The combination of low surface energy materials and hierarchical structure was critical in forming a hydrophobic surface. The properties of hydrophobic surfaces have been discovered through decades of development and studies on natural phenomena. As a result, a human could be able to duplicate the surfaces and materials in order to achieve hydrophobic purposes.

2.1. Lotus leaves

The Lotus effect was discovered in 1997, and the self-cleaning characteristics of *lotus* leave started becoming a classic example of hydrophobic surfaces and self-cleaning [1]. According to research findings by barthlott & Neinhuis, the multiple-hierarchical structure was critical in increasing water-repelling ability through the surfaces of *lotus* leaves [1]. Because of the discovery of contact angles through surfaces and the development of scanning electron microscopy (SEM), researcher future discovered the profound reason for the classic hydrophobic surfaces of *lotus* leaf: large contact angles (164°) and low contact angle hysteresis (3°) [1]. The hierarchical structure created roughness of the surfaces for each scale. Figure 3 demonstrates how a spherical water drop stands on the surface of a *lotus* leaf. Furthermore, from the visual demonstration, the ‘little fingers’ represented the level of the structures on *lotus* surfaces. Due to the large water contact angles, the water drop could perfectly stand as a spherical shape on the surface without wetting the lotus leaf.

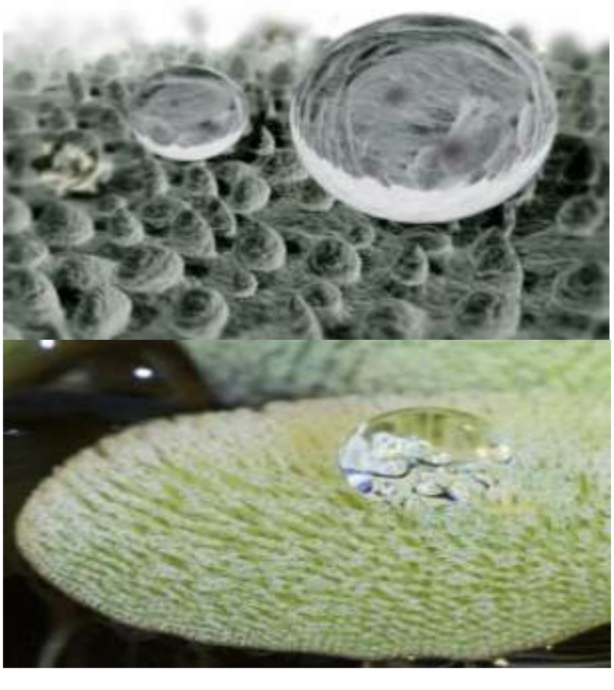

Figure 3. Left Spherical Water Drop on Surface of Lotus Leaf Hierarchical structures [2] (Taken from UNIVERSITÁ DEGLI STUDI DI PARMA) right Spherical Water Drop on Surface of Salvinia Hierarchical structures [3].

2.2. Salvinia

The Salvinia effect was discovered as a phenomenon in skinny air pockets throughout the *Salvinia* surface between the hierarchical structure, which give*s Salvinia* the ability to survive underwater for very long periods [1]. The unique hydrophobic characteristics could also motivate the development of water-repellent surfaces. Figure 3 demonstrated that the water drop could sit on the *Salvinia* leaf as a perfectly spherical shape. This hydrophobic surface was created by a hierarchical structure on *the Salvinia* leaf surface. The wax materials coating the *Salvinia* surface could prevent more wetting [1]. Wax materials are well known for hydrophobicity and low surface energy. Therefore, a combination of low surface energy material coating with hierarchical structure roughness will be the best recipe for forming water-repellent surfaces—many surfaces designed to use water-repellent or hydrophobic surfaces implemented this combination. Most consumer and industrial applications also favored this combination to fabricate the surfaces.

Rose petals, Mosquito eyes, and Sharkskin create hydrophobic surfaces with the different-pattern recipe. In rose petals, periodical patterns are formed on the surfaces with large water contact angles (158°) and sliding angles (7°). Mosquito eyes use similar physics to form a hydrophobic surface. In a mosquito's eye, millions of microstructures like hemispheres form a unique pattern, and each hemisphere has a 101.1 ± 7.6 nm average diameter with an interparticle spacing of 47.6 ± 8.5 nm. The unique patterns on mosquito's eyes not only prevent wetting on the surfaces, but this feature could also provide anti-fogging. Shake skin is another good example of hydrophobic surfaces. However, the functions of shark skins are reducing fluid drag forces and creating an oleophobic surface with low adhesion. To achieve the functions, stick shape structure dermal denticles and riblets adjusted to the same direction of water moving. Riblet could also have shaken to move faster since riblet could alter the total forces with water flow. This could also enhance anti-fouling ability, bioadhesive ability and flow efficiency [1].

3. Nature stain-resistance

The upper side of the *lotus* leaf has super hydrophilicity because of the 3D wax tubules. However, the lower side of the *lotus* leaf does not have the same wax structure, making it hydrophilic. As shown in Figure 4, oil droplets can keep spherical under water. Under the environmental scanning electron microscope and the atomic force microscope, the lower side surface has convex papillae (about 30 µm width and 50 µm length). Each papilla has a nano-groove with a size of 500 nm and a height of 4 µm [11]. By testing, even more than 24 hours, the oil contact angles (OCA) of different oil substances are still greater than 150° [12].

Springtail (*Collembola*) is an essential insect with superoleophobic properties for researchers to study. Many springtails have neatly arranged, approximately circular structures on the cuticle surface at the nanometer size. The surface of the cuticle is composed of more than 50% of glycine, tyrosine, and serine. The upper film above the surface is made of lipids such as steroids and terpenes. Most polar and non-polar liquids can be repelled except for some organic solvents, such as hexane [13].

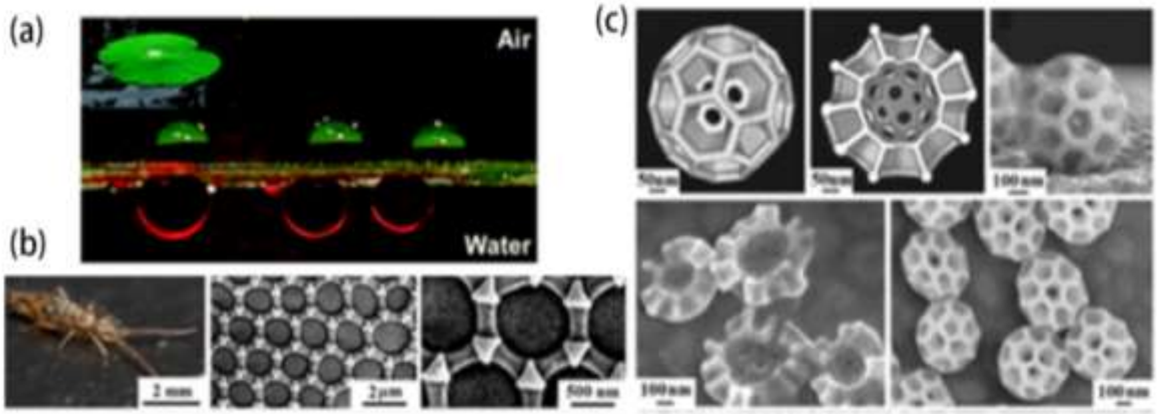

Figure 4. (a) Green spheres: water droplets on the upper side of the *lotus* leaf; Red spheres: oil droplets on the lower side of the *lotus* leaf (dyed by hexane). [12] (b): Images of nanostructures of superoleophobic springtail. (c) Images of superoleophobic bronchoscopes of leafhoppers' surfaces [14,15].

Leafhopper (*Cicadellidae*) is one kind of tiny insect belonging to the Hemiptera. All leafhoppers' members have the same unique structure on their body surfaces: a bronchoscope. Figure 4 (right) shows bronchoscopes have honeycomb-like hollow spherical shapes with Penta-and hexagonal walls. Most of them are between 200-700 nanometers in diameter and are covered on leafhoppers' body surfaces evenly. This specific structure is called re-entrant curvature and is made of protein. Since those protein molecules are polar, bronchoscopes have superoleophobic properties [16]. Through experiments, bronchoscopes can repel water, ethylene, and diiodomethane with a CA between 145° and 175°.

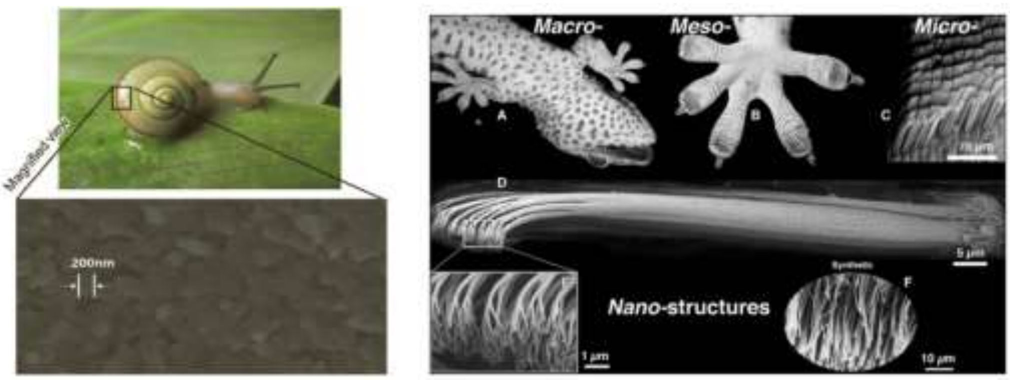

Figure 5. Snail shell in the rainy season (left). Images of the gecko adhesive system under different scales (right). [17,18].

As shown in Figure 4 (right), snails can always keep their shells clean and shiny, even in baiu (a rainy season in Japan). According to Isu's research, the snail shell has a superoleophobic surface [19]. In addition, there are some nano-scale convex-concave structures on shells. The average width is 200nm. This unique structure helps snails form a film that can repel stains and oils.

Geckos (*Gekkonidae*) are creatures that can move freely on vertical walls and ceilings, no matter what the surfaces are. The rationale is that the gecko has a complex but efficient adhesion system. There are millions of tiny hairs called setae on the gecko's toe pad surface [20]. Also, gecko setae are the first well-known adhesive with a self-cleaning property [18]. *Lotus* keeps it clean with the help of water and the hydrophobic surface. However, gecko self-cleaning and stain-repellent systems do not need the assistance of any water or liquids.

4. Synthesis water repellent

The replacement products of PFOA and PFOS are mainly divided into two categories. The first category is C6 and C4 perfluorinated non-octyl carbon compounds, which have lower bioaccumulation and toxicity than C8, but their safety still needs further verification. The second type is a completely fluorine-free waterproofing agent; compared with fluorine water-proofing agent, fluorine-free waterproofing agent is not easy to deposit in the biological body, are easy to degrade, harmless to the human body, and is a safer, environmentally friendly product. Non-fluorine hydrophobic agents without fluorine include long-chain alkane water-proofing agents, silicone water-proofing agents, and biological non-fluorine water-proofing agents.

4.1. PU

Zhang et al. synthesized waterborne polyurethane (WPU) prepolymers. However, their poor water repellency limited their further development. However, if polydimethylsiloxane (PDMS) were introduced into polyurethane for hydrophilic modification, The PU part limits the migration of silicon in the backbone to the surface, which in turn limits the water resistance of the WPU [21]. The oligomer containing the siloxane side chain can be modified, so we choose aminoethyl aminopropyl polydimethylsiloxane (AEAPS) to modify the prepolymer. Because siloxane is located on the side chain of polyurethane, the fluidity and surface enrichment of the siloxane chain are improved. The details are discussed below.

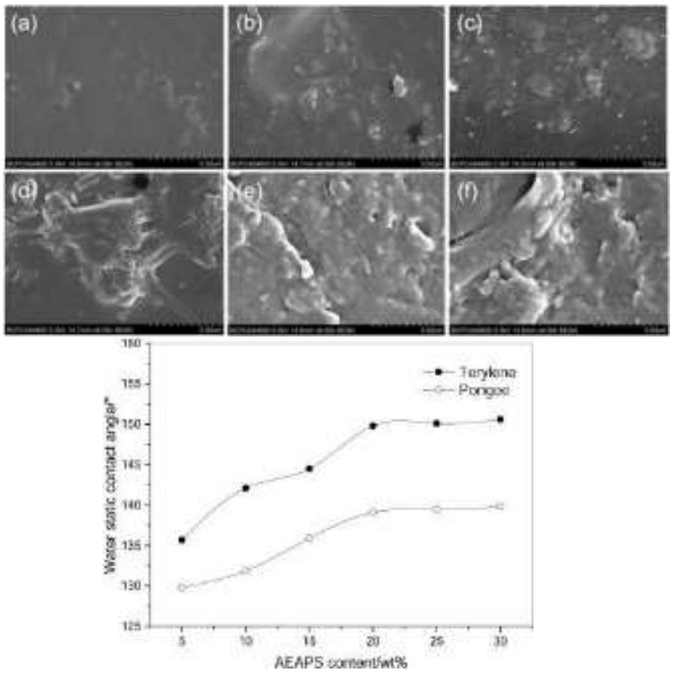

Figure 6. Micrographs of the AEWPU films ((a) AEWPU-5; (b) AEWPU-10; (c) AEWPU-15; (d) AEWPU-20; (e) AEWPU-25; (f) AEWPU-30). (right) Effect of the different contents of the AEWPU on the static contact angle of the fabrics finished with the AEWPU.

The introduction of AEAPS into WPU can effectively improve the hydrophobicity of the films, which the micro-morphology observation can demonstrate. The morphology of different AEAPS (AEAPS content: 5%, 10%, 15%, 20%, 25%, 30%) after introduction into AEWPU is observed. It can be seen from the observation that the surface film of polyurethane becomes rough with the increase of AEAPS content, which may be caused by the poor compatibility of AEAPS and polyurethane. At the same time, when the ratio increases to 25%, the apparent phase separation phenomenon appears. Therefore, it is suggested that the 20% WT ratio with good compatibility should be selected for optimization. The

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change of static contact angle in Figure 6 (right) also confirms this point. With the increase of AEAPS content, the static contact angle of the two fabrics increased significantly. The static contact angle of the polyester fabric AEWPU package increased from 135.7° to 150.6°. The static contact angle of AEWPU composites increased from 129.8° to 139.8°. According to the experimental results, the modification of AEAPS has successfully improved the waterproof performance of WPU. In addition, the optimum dosage of AEAPS is 20% (mass fraction). At the same time, stearic acyl acrylate (SA) and double bond encapsulated waterborne polyurethane (DWPU) were prepared by self-boiling copolymerization and radical copolymerization [22]. As a result, the modification of DWPU by SA is realized. As can be seen from figures 7(a) and 7(b), the water absorption of SAWPU films decreases with the increase of SA content. With the increase of the content, the water contact angle increases gradually. This is because when the SA content increases, the content of long-chain alkanes in the hydrophobic molecules also increases, and more -CH_2CH_3 neatly arranges on the fabric surface, forming an effective hydrophobic layer.

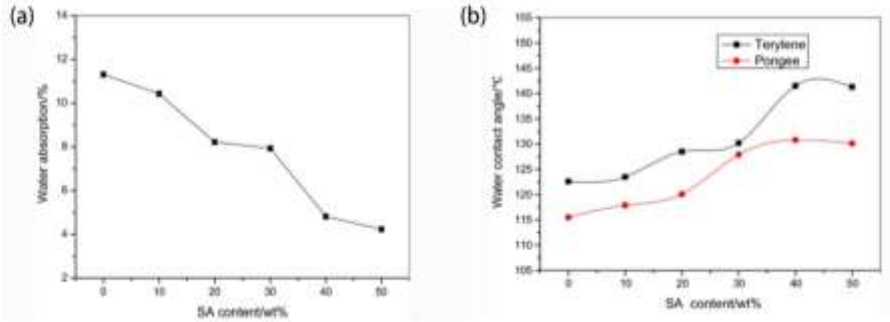

Figure 7. (a)Water absorption of SAWPU films (b) Water contact angle of fabrics treated using SAWPU with different SA content.

4.2. Acrylate

Liu et al. use alkyl ketone dimer to improve the waterproofing performance of SA polymer [23]. Samples 3,4,5 were mixed with different proportions of AKD dimer in the same proportion of SA polymer samples, and their effects on the properties of the polymers were investigated. Alkyl ketone dimer (AKD) contains an active group and a long alkyl chain hydrophobic group, which reacts with the hydroxyl group in the heat setting process to form a chemical bond and improve the waterproof property of the fabric.

Table 1. Effect of AKD dosage on fabric waterproof grade Note: The baking temperature is 180 °C.

Sample Number	Waterproof score	Monomer conversion rate [%]	Contact angle [°]	Solid content [%]
3	70	95.95	129	16.06
4	80	>98	128	22.22
5	80	>98	132	24.36

4.3. Silicone water repellent

When the functional POSS was modified by Zhou, the surface area of the POSS was reduced, and the Surface roughness was increased by synergistic action with the octyl side chain [24]. As a result, when water droplets come into contact with the finished cotton fabric, the air is trapped on the micron/nanometer-sized rough surface, forming a layer of air that maintains the typical Cassie pattern of the finished cotton fabric and has good hydrophobicity.

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4.4. Biological fluorine-free waterproof agent

Rabia uses bio-stearic acid as the main ingredient in its water-repellent [25]. Bio-stearic acid is a kind of harmless waterproof material, but its waterproof performance is poor and needs cross-linking to improve performance. The formulation was optimized by the polymerization of biological stearic acid with succinic acid, and another optimized formulation was obtained by the polymerization of stearic acid with itaconic acid. When these two formulas are applied to cotton fabrics, the treated fabrics have the properties of waterproof grade 4 and oil-repellent grade 1.

5. Synthesis stain-repellent

The synthetic anti-stain surface with superhydrophobicity must be both hydrophobic and oleophobic. Some materials are prepared to have self-cleaning properties. Cotton fabric preparation, new ceramic surface firing techniques, and silicon-based surface coatings are discussed separately. This section solely discusses the stain resistance performance; the durability properties are further discussed in section 6.

5.1. Anti-stain cotton

Preparing low-cost and environmentally friendly superhydrophobic cotton fabric with anti-fouling properties, Studies use PDMS/HDTMS as the main ingredient. By fabrication in HDTMS using a simple immersion technique, cotton fabric receives a water contact angle of 157 ± 5°and a slide angle of 7°. Another method is creating multiple layers of PDMS and ZnO, increasing the surface roughness of cotton fabric and receiving a water contact angle of 160 °.

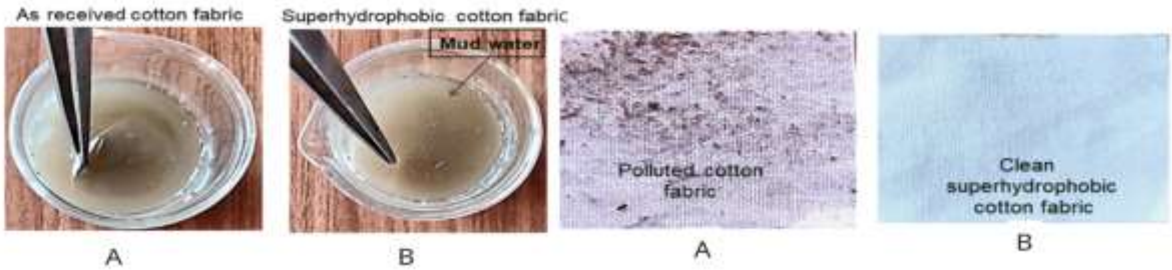

Figure 8. Pictures of raw and treated cotton fabric before and after immersion in the mud water, demonstrating the stain-resistance property of the cotton fabric.

5.2. Anti-stain porcelain surface coated with ZrO2

Treating by nano and micro-sized zirconium dioxide and glass-ceramic frit, the Porose surface of porcelain becomes permanently stain-resistant. Low particle dimensions make it deposit into surface pores, contributing to anti-stain properties. In Figure 9, the surface with original esthetical qualities becomes much smoother from the SEM image.

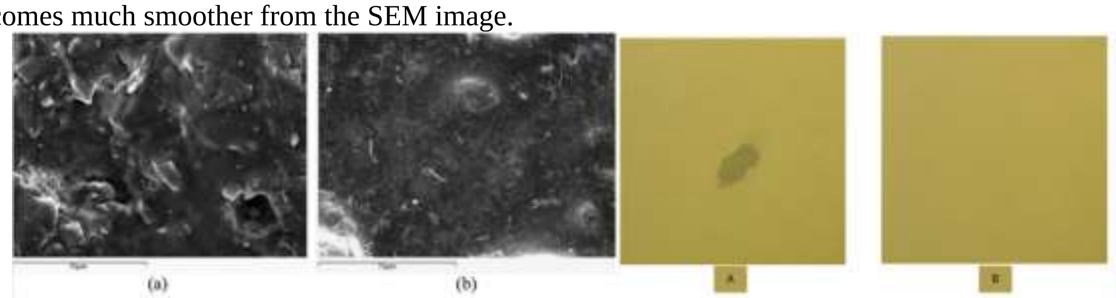

Figure 9. SEM image (a) sample before treatment and (b) after treatment [26] Figure Visual image of bright yellow tile A before and B after the treatment [27].

5.3. MT3 side chain for polyacrylate

To make oleophilic Silicone materials more stain-resistant, Tris-trimethylsilyl(M_3T) units are used as a side chain of polyacrylate. Lowering the surface energy by applying M_3T polyacrylate to fabric, as shown in Figure10(a), Good anti-stain performance has been obtained on the treated substrate with polyacrylate (molecular weight of 80,000 and concentration of 20 wt.%). An increasing ratio of M_3T leads to lower surface energy and better anti-stain performance, as demonstrated in Figure 10(b).

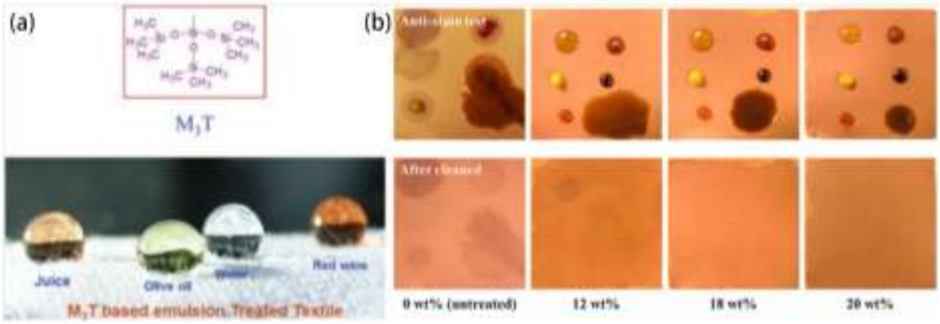

Figure 10. (a)Stain agent on cotton fabric coated by M_3T based emulsion. (b) Anti-stain test with increasing M_3T ratio.

6. Processing and performance

6.1. Processing

In this section, the standard processing of water-repellent and stain-resistance coating will be discussed. Some of the processes are utilized to generate both fluorinated and non-fluorinated coating [28].

6.1.1. Spraying method. The spraying method is widely utilized in various fabrication methods—three significant steps for spraying methods: preparing solution, spraying, and post-treatment. The preparation of solutions can be done within hours (EP, EA, PDMS) or taking more than one day (CNTs/RGO) [29-31]. The amount of coating solution applied to the surface must be carefully designed for the best performance, usually estimated by spraying time, the total thickness of the applied solution, or the spraying interval [28,32]. Post-spraying treatments involve resting for various times at certain temperatures to gain water-repellent and stain-resistance properties [28,32].

6.1.2. Sol-gel coating. The term “sol-gel” was first mentioned by Thomas Graham in his research in 1864 regards silicic acid [33]. Merits of sol-gel involve no solid intermediate present, low-temperature, and wide range of materials applications [34]. The sol-gel process requires a chemical precursor, and metal alkoxides like tetraethyl orthosilicate (TEOS) is mostly used as a network-forming reactant [35-36]. Meanwhile, hexadecyltrimethoxysilane (HDTMS) is widely used in fabric coating [37-38].

6.1.3. Chemical vapor deposition. Chemical vapor deposition (CVD) refers to a process where the solid-phase product is converted from a gaseous precursor flow through a chamber with a heated substrate [39]. Depending on the target product, diffusive and precipitate growth can be applied. Diffusive growth is achieved by CVD on a low coating agent solubility substrate. The coating agent can only form on the surface. Precipitated growth proceeds on substrates with high coating agent solubility. During the process, gaseous coating agent precursors can dissolve into the substrate while forming a coating on the surface. [40] Agent atoms can precipitate to the surface and form a new layer of coating from the opposite direction. Two techniques for graphene coating from carbon atoms are illustrated in Figure 11.

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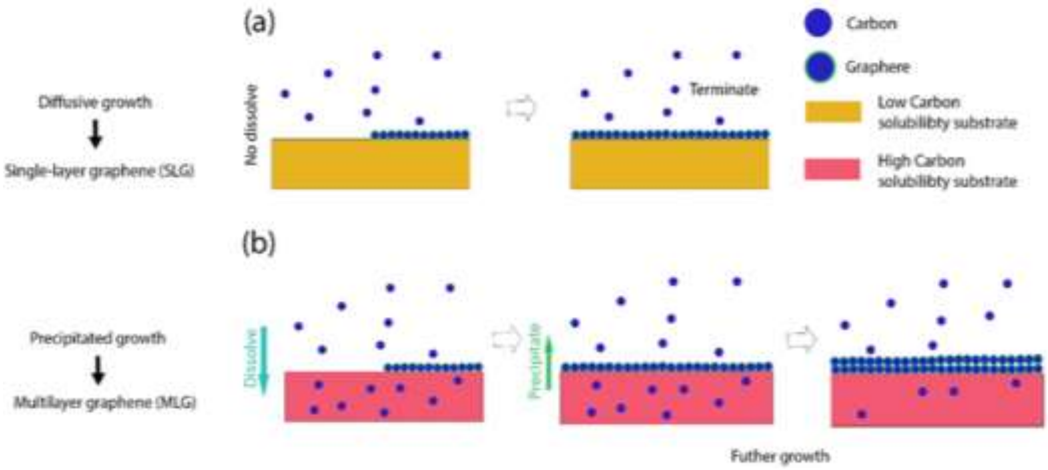

Figure 11. Schematic illustration of (a) diffusive growth and (b) precipitated growth. Precipitation is not necessarily happening after forming the first layer of graphene; the figure uses a simplified demonstration.

6.1.4. Layer by layer. Layer by layer (LbL) includes repetition of a single technique or a combination of various. For example, in the research of Jin's group, a sol-gel reaction was carried out to form the primary structure of silica nanoparticles. A chemical vapor deposition of n-dodecyltrimethoxysilane (DTMS) was applied to achieve a two-level hierarchical structure [36]. Yanji Zhu's group prepares PPS/SR/CNTs composite coatings by repeating the spraying and heating cycle [31]. Sometimes LbL strategy is part of the experiment to find the best ratio and thickness, or particle size for higher water contact angle (WCA) and resistance performance such as corrosive resistance, abrasion resistance, and UV resistance.

6.2. Durability performance

The durability of coatings indicates coatings' ability to remain water-repellent and stain-resistant under various conditions. The durability test evaluates coatings' function under extreme environments, such as anti-icing coating on aircraft. Another purpose is to test the "aging" resistance of the coating, as some abrasion and corrosion tests enable the researchers to simulate the aging process and achieve a reasonable prediction [41].

6.2.1. Chemical stability and corrosive resistance. Chemical stability is usually tested via sequentially immersing the coating in strongly acidic and basic solutions or via commercial standards like ASTM B117 [30-33]. Electrochemical Impedance Spectroscopy (EIS) is typical for evaluating corrosion resistance [28]. EIS can be achieved via a three-electrode setup, and usually, a polarization curve is generated to estimate corrosion current and voltage. Figure 12 (a) demonstrates a three-electrode setup.

Papers with similar testing standards of EIS enable comparison, and data collection of papers with the same electrolyte solution, a counter electrode, and the reference electrode was plotted. As shown in Figure 12 (c), the metal coating (Ni-P/Cu/Ni) has a higher corrosion voltage, indicating they remain stable longer before corrosion starts. At the same time, the silica/CNT matrix can achieve a lower corrosion current, which means they have a lower corrosion rate after the corrosion process starts.

6.2.2. Mechanical durability and abrasion resistance. Mechanical durability for coatings generally refers to the resistance to abrasion. Sandpaper of various grit is often used as the test agent, while Taber linear abraders are also used. Several samples of silica and silica/carbon nanotube matrix coating from different researchers are compared. [29-30,32,42-46]. In Figure 12 (d), samples solely made from silica particles are generally able to resist 10~200 abrasion cycle. Once carbon nanotubes are introduced as matrix, the abrasion durability is dramatically enhanced, partially contributed by the self-lubricate properties and strong structure of carbon nanotubes.

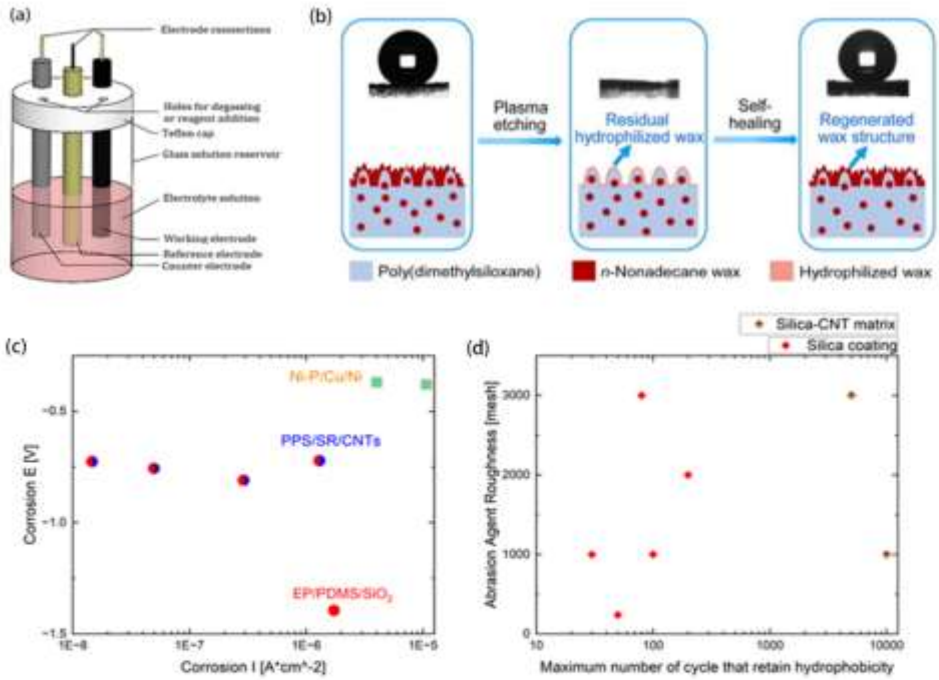

Figure 12. (a) Three-electrode cell configuration for electrochemical characterization. [47] (b) Schematic illustration of self-healing mechanism [48,49] (c) Anti-corrosion performance of various water repellent coating. (d) The abrasion resistance performance of pure silica and silica/carbon nanotube samples. The x-axis is in a log scale.

6.2.3. Tunable wettability and self-healing. Tunable wettability refers to either control of ingredient composition in the processing of coating or the post-treatment of the product coating to achieve various wettability [48,49]. For both, the key is to vary the surface energy of the coating, and usually not reversible. Self-healing, on the other hand, is a heating process of damaged coating that enable extra coating materials stored in the substrate to immigrate to the surface and recover their hydrophobicity, as shown in Figure 12 (b) [50].

7. Discussion and conclusion

Combining low surface tension materials with suitable roughness of the surfaces can lead to the formation of hydrophobic surfaces with various resistance, including abrasion, corrosive, and UV. Most designs of the surfaces are inspired by natural hydrophobic surfaces induced by natural selection. For example, when water droplets lay on the *lotus* surface, the Cassie–Baxter state interface will form, which gives hydrophobic and stain resistance properties. Furthermore, most review usually does not cover fabrication due to drastic variation in processing techniques. Since each of the techniques is unique, and there is currently no standard established for engineering the surfaces, most papers are inclined to use their methods and standards. The lack of uniform standards introduces multiple obstacles to researchers because it is challenging to make a comparison between papers. This current situation urges the establishment of brand-new standards and methods for this boosting field. Therefore, this review added a unique lens of view of surface fabrication and test of resistance. The effort is to provide a comprehensive literature review and understanding of hydrophobic surfaces, their properties, and manufacturing strategies. Major polymers are widely studied among various candidates to fabricate new generations of water-repellent and stain-resistant coating for thin films and fibers. The current challenge of polymers is the deficiency in abrasion resistance, which would affect the product's expected lifespan. Non-fluorinated materials and surfaces are a promising field of study due to less toxicity to humans and the environment and potential cost efficiency. Thus, the research in non-fluorinated hydrophobic surfaces becomes significant in the following decades of development. This literature review could be the stepping stone for future scientists and researchers to develop a systematic, industrialized approach to manufacturing non-fluorinated hydrophobic surfaces and materials.

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