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Designing Non-fluorinated Durable Stain-resistant Textiles

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Abstract: *Though being highly stain-resistant and durable, recently, the harmful effects of fluorinated chemicals on the environment and organisms have gained people's attention. It has now become necessary to find non-fluorinated alternatives with comparable properties. Current research shows that non-fluorinated materials have achieved excellent hydrophobicity, but oleophobicity or stain-resistance is still difficult to reach. In this review, the chemistry of hydrophobic materials, morphology control of textiles, and the enhancement of durability of coatings are respectively discussed and summarized with examples. The combination of these techniques would help develop better repellency. This review also attempts to elucidate and discuss the necessity to consider textile properties according to end-use requirements, the asymmetric wettability design to increase comfort and the possible directions for future research on designing non-fluorinated durable stain-resistant textiles.*

Keywords: *Non-fluorinated, hydrophobic, durability, stain-resistance, repellency, textiles, fabrics, contact angle*

1. Introduction

In recent years, demand for multifunctional textiles which consists of properties such as superhydrophobicity, stain-resistance, antimicrobial and high-durability has increased drastically due to their commercial potential [1]. Textiles with those desirable properties can be widely used in a variety of areas, such as the use of durable water repellency (DWR) in outdoor sports clothing and military uniform under harsh environmental conditions, and in packaging, especially for long-distance transferring that requires stain and liquid repellency and high durability. Even in the field of medicine, using waterproof bioactive garments with antimicrobial property can reduce the risk for infection. For example, waterproof breathable textile is used for orthopaedic orthoses [2]. Many functional textiles have been made using highly fluorinated chemicals, especially per- and polyfluoroalkyl substances (PFASs) that have been manufactured and used since the 1940s. PFASs are well-known for their unique physicochemical characteristics like oleophobicity, hydrophobicity, stain-resistance, as well as temperature resistance and friction reduction. For decades, PFASs have been used in clothing, furniture coatings, cookware, food packaging, and many other common household items [3]. However, there is currently a major ongoing debate over regulating the use of PFAs due to the harmful effects PFASs have imposed on the environment. In the early 2000s, PFASs were proven to be toxic so they are detrimental to both humans and animals as they can accumulate in the bodies of animals and circulate in the food chain. For instance, PFOA and PFOS have a half-life of 3 years [4] in the human body. Moreover, they are mobile and persistent which means they can contaminate our drinking water, leading to a high concentration of the toxic chemicals in the body over time [3]. Due to the regulations and concerns over the use of PFASs, the textile market has started to research more into replacements for PFASs that can provide similar properties [5]. Although efforts have been made to substitute C8 chemistry (8 atoms in the fluorocarbon chain) with C6, evidence has proved it contradictory - these C6 PFASs have shown the same level of persistence and toxicity as the C8 PFAS[6]. Thus, many researchers have shifted their focus onto the fabrication of non-fluorinated textiles as the use of PFAS is phasing out in the industry. Herein, this article explores non-fluorinated textiles, their durability and hydrophobic properties. All liquids, including water and oil, follow the same principle in regards to lowering the surface energy and enhancing roughness to design stain-resistant textiles. Therefore, we reviewed different representative and inspiring methods that could obtain hydrophobic textiles and also could be extended onto the fabrication of stain-resistant textiles. Noting that the selection of the chemistry of hydrophobic materials, morphology control of textiles, and the enhancement of durability of coatings are not mutually exclusive, these properties are respectively discussed in separate sections, so that useful experience can be concluded from different works. Last but not least, we discuss the balance between high performance and comfort, and prospective future directions for designing non-fluorinated durable stain-resistant textiles.

2. Theory

2.1. Surface energy

Atoms or molecules on the surface of liquids or solids have higher energy than the ones in the interior due to lacking neighboring atoms. This excessive energy is characterized quantitatively as surface tension and surface energy [7]. When a liquid droplet is placed on a flat solid surface, the whole system tends to reduce its free energy and interactions between each two of the three interfaces will come into equilibrium to determine the intrinsic contact angle θ_0 (Figure 1), which can be defined by the well-known Young Equation

$$\cos\theta_0=\frac{\gamma_{SA}-\gamma_{SL}}{\gamma_{LA}} \tag{1}$$

where γ_{SA} and γ_{SL} are the surface energy of solid against air and liquid, and γ_{LA} is the surface tension of liquid against air.

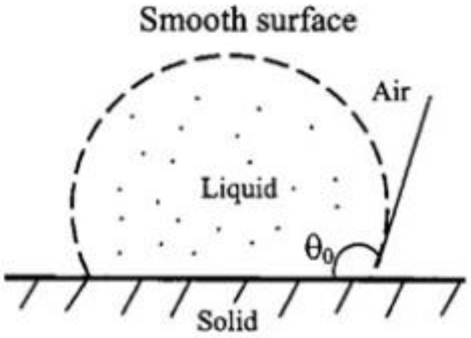

Figure 1. Schematic of liquid droplet in contact with a smooth solid surface (contact angle, θ_0). Reproduced from Bhushan et al., 2011 [7].

If the contact angle is more than 90°, the solid is classified as a hydrophobic material, while superhydrophobicity implies that the contact angle is more than 150°. Therefore, surface energy γ_{SA} should be as low as possible in order to obtain greater hydrophobicity.

When selecting hydrophobic materials, for most cases, moieties with low surface energy are needed. Besides, these moieties need to be densely packed [8]. $-CF_3$ groups have extremely low surface energy (only ~ 6 mN/m for ideal hexagonal packing [9]). Therefore, despite their harmful effects, fluorinated materials still have an irreplaceable role, especially in the fields strictly demanding liquid repellency. Except for $-CF_3$, $-CH_3$ is another group with low surface energy, which still reaches a surface energy of 22mN/m [10]. Most non-fluorinated hydrophobic materials essentially depend on n-alkyl chains that are connected to the fiber backbone through different reactive groups, crosslinkers or different treatments. Linear alkyl chains with a certain length are favorable for crystallization, after which the side chains will be aligned [11], ensuring that the $-CH_3$ groups are densely packed at the top of the coating layer. Otherwise, other groups, such as $-CH_2-$ (with a surface energy of 31 mN/m), will be exposed to the surface [8], increasing the surface energy.

2.2. Surface structural properties

2.2.1. Roughness

Increasing surface roughness is a crucial way to texture superhydrophobic material and extensive studies have also been done around it. Two states were introduced to describe how roughness affects hydrophobicity.

In the Wenzel state [12] (Figure 2a), liquid droplets penetrate the surface texture, wetting the surface completely. The apparent contact angle can be defined by the Wenzel equation

$$\cos \theta^* = r \cos \theta_0 \tag{2}$$

where r is the surface roughness (the ratio of the actual surface area to the projected surface area) and it is always greater than 1. This relation suggests that $\theta^* \ll 90°$ if $\theta_0 < 90°$ while $\theta^* \gg 90°$ if $\theta_0 > 90°$ [13].

However, in the Cassie-Baxter state (Figure 2b), air pockets may be trapped in the cavities of a rough surface, forming a solid-liquid-air interface [14]. The Cassie-Baxter equation gives that

$$\cos\theta^* = f_{SL} \cos\theta_0 - f_{LA} \tag{3}$$

where f_{SL} is the area fraction of the solid-liquid interface and f_{LA} is the area fraction of the liquid–air interface underneath the liquid droplet. Therefore, by forming Cassie-Baxter state, we are able to texture superhydrophobic materials even if $\theta < 90^\circ$ as long as f_{LA} is large enough.

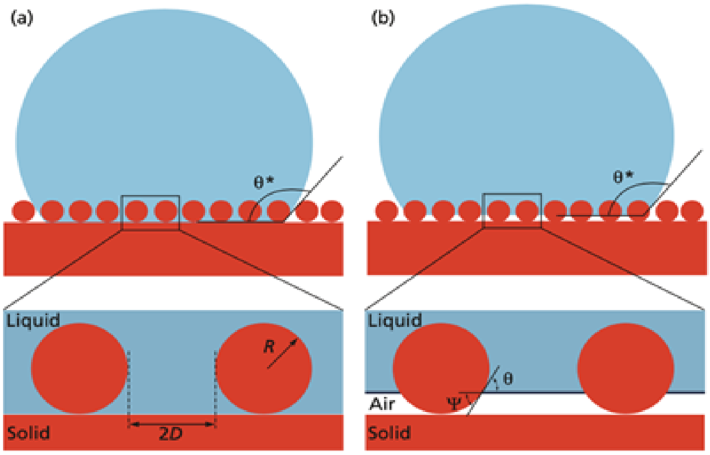

Figure 2. (a) A liquid droplet in the Wenzel state on a rough surface. (b) A liquid droplet in the Cassie-Baxter state on a rough surface. Reproduced from Tuteja et al., 2013 [13].

2.2.2. Hierarchical structure

Scientists have known for a long time that lotus leaves show great stability and perfection of superhydrophobicity as well as self-cleaning property, namely “lotus effect”. This is attributed to its hierarchical structure, consisting of papillae, wax clusters and a high density of wax tubules, demonstrated by SEM images Figure 3 [15].

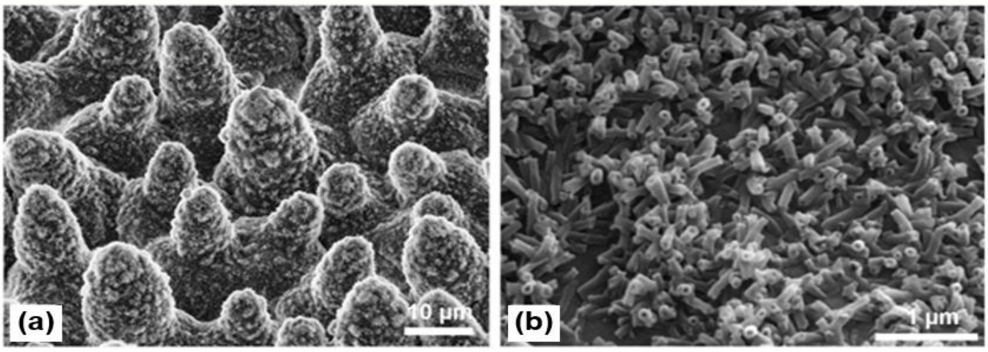

Figure 3. (a) Scanning electron microscopy (SEM) image of the upper leaf side prepared by ‘glycerol substitution’ shows the hierarchical surface structure consisting of papillae, wax clusters and wax tubules. (b) Wax tubules on the upper leaf side. Reproduced from Ensikat et al., 2011 [15].

Inspired by lotus leaves, it is proposed that nanoscale and microscale hierarchical surface structures are crucial to the stable hydrophobicity. The main reason is that hierarchy plays an important role in increasing the apparent contact angle, enlarging the energy difference between the Cassie state and the Wenzel state, reducing the real contact area, and reducing the total length of the triple-phase contact line [16].

Take self-similar hierarchical structure as an example. Simply, hierarchical structures (Figure 4) entrap extra air pockets and therefore f_{LA} would be larger, leading to higher contact angles. Su *et al.* explained this effect in detail and then deduced the explicit expression of the apparent angle

$$\theta_N = arccos\left(\prod_{n=1}^{N} f_n \cos\theta_0 + \prod_{n=1}^{N} f_n\right) \tag{4}$$

where the subscript *n* stands for the level in the hierarchy. This relation suggests that the increase in the structure levels significantly increases the apparent angle [16].

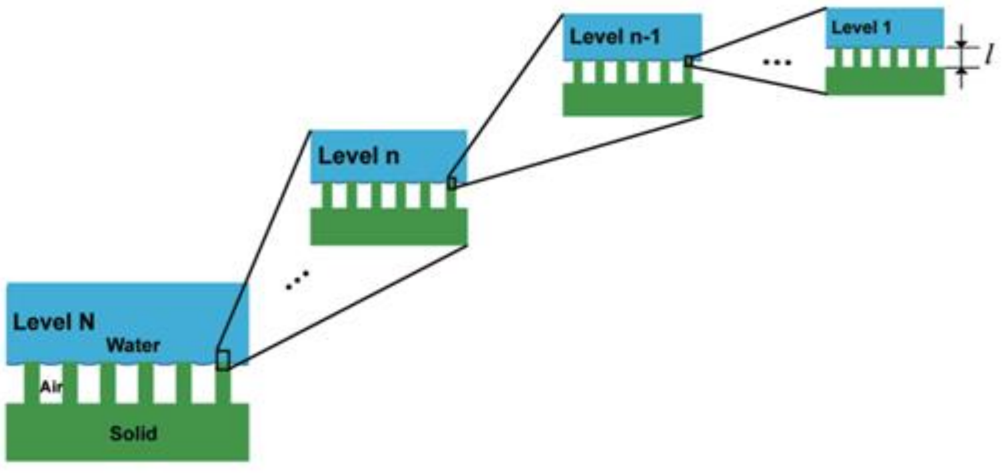

Figure 4. Hierarchical structures (nanopillars). Reproduced from Su et al., 2010 [16].

2.2.3. Self-cleaning and Contact angle hysteresis

Self-cleaning is a desired property when fabricating textiles. The most common type of self-cleaning material is hydrophobicity-induced, which is also called ‘lotus effect’. Rain droplets falling onto the surfaces bead up and roll off. During the process, dirt could be waved out by water. This type of self-cleaning material usually refers to those with a static contact angle above 150° and low angle hysteresis. Hysteresis, which is defined as the difference between advancing and receding angles occurs due to surface roughness and heterogeneity, [17] is a significant parameter when designing self-cleaning materials [18]. Generally, the smaller the hysteresis, the easier for droplets to roll off.

Specifically, in order to analyse the sliding properties of certain materials quantitatively, here we introduce sliding angles to measure hydrophobicity-induced self-cleaning ability. Miwa *et al*. deduced that an equation that describes it:

$$\sin\alpha = \frac{W\gamma_{lv}}{mg}\left(\cos\theta_{rec} - \cos\theta_{adv}\right) \tag{5}$$

α is the sliding angle, m is the weight of the water droplet, γ_{lv} is the free energy of the liquid. W is the width of a droplet [19].

On another note, self-cleaning ability can also be induced by hydrophilicity. Water droplets remain on the surfaces and form a thin layer which then penetrate into hierarchical structures and therefore clean the spaces. [16] Notably, under UV-radiation, TiO_2-based materials would become hydrophilic, so it is widely used for hydrophilic self-cleaning materials.

3. The design of hydrophobic and stain-resistant textiles

3.1. The hydrophobic modification of textiles

3.1.1. Carbon-based hydrophobic coatings

Methacrylic or acrylic polymers with long alkyl chains is one class of popular hydrophobic material that can be applied onto the fiber through traditional pad-dry-cure process or grafting. For these polymers, the hydrophobicity is closely related to the alkyl chain length of acrylate or methacrylate. It is reported that long chain alkyl methacrylate has lower surface energy than the short one and thus lower graft density is required to exhibit superhydrophobicity [21]. For acrylate, the optimum alkyl groups are hexadecyl and octadecyl [22].

Another frequently used material is stearic acid (SA). An early method is to apply emulsions that contain stearate by exhaustion or padding, but their lack of durability limits the use. Using stearic acid-melamine compounds is an improved method to increase durability, with N-methylol groups to link with the fiber [23]. Moreover, SA in combination with other materials can lead to greater hydrophobicity compared to SA alone. Manatunga *et a*l. treated cotton with SA alone, hexadecyltrimethoxysilane (HDTMS)/SA, nano silica/SA and silica HDTMS/SA, and reported contact angles of 131.7 °, 141.25 °, 148 °, 158 °, respectively [24]. This also suggested that using multiple hydrophobic materials together is a way to reach superhydrophobicity. Arfaoui *et al*. treated jute fiber-based nonwovens with SA alone and then TiO_2/SA [25]. The contact angle rose from 127 ° to 135 °. Both works show an improvement on hydrophobicity.

3.1.2. Silicon-based hydrophobic coatings

Silicon-based hydrophobic materials have been widely studied due to their easy accessibility, designability, and environmental friendliness.

Polydimethylsiloxane (PDMS) can form hydrogen bonds with hydroxyl groups present on the fiber surface (Figure 5). If $-Si-CH_3$ groups are partially replaced by $-Si-H$ groups, PDMS can be cross-linked by silanol to increase durability [23]. Other polysiloxane materials with reactive groups introduced, such as hydroxyl, halogen or sulfhydryl groups, can be covalently bonded to the fiber surface. The backbone of polysiloxane chains is soft, and after addition to the fiber surface, methyl groups will orientate away from it to realize hydrophobicity. However, methyl groups need to be replaced by other groups in order to obtain better water repellency and oil repellency [11].

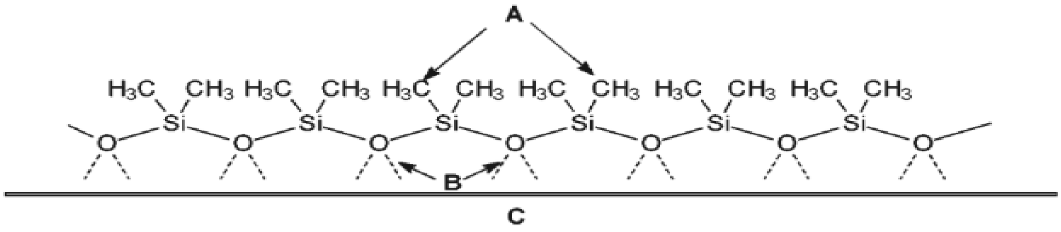

Figure 5. PDMS on a fiber surface. A, hydrophobic surface; B, hydrogen bonds to polar surface; C, fiber surface. Reproduced from Schindler & Hauser, 2004 [23].

The hydrophobicity of silanes ($R_1-Si-(OR_2)_3$) is determined by the length of the alkyl chain (R_1). Chauhan *et al.* simply immersed the cotton fabric into hexadecyltrimethoxysilane (HDTMS) solution and removed the solvent by heating. The modified fabric presented a low sliding angle of less than 10 °, and a water contact angle of 157 ° which still remained stable after 7 days [26]. This research indicates that silanes is a promising material which can be conveniently applied to obtain stable hydrophobicity and self-cleaning property.

To enhance the durability of coatings, silica nanoparticles as one kind of popular crosslinkers are used to create chemical attachment. Typically, silica is combined with silanes. For example, in the research by Gao *et al.* [27], after padded with silica sol, fabrics were immersed in the solution of hydrolyzed HDTMS. Hydroxyl groups of hydrolyzed HDTMS and fabrics then bonded with each other. A common method of preparing silica sol is to add Tetraethoxysilane (TEOS) into NH_4OH-ethanol solution. TEOS will hydrolyze in an alkaline solution and generate silica with hydroxyl groups on the surface. These hydroxyl groups can react with coatings and fibers to form covalent bonds. Besides hydroxyl, there are some other reactive groups. Bae *et al*. hydrolyzed Triethoxyvinylsilane (VTES) to synthesized silica particles possessing vinyl groups, which would crosslink with PLA fabrics through UV induced free radical reaction [28]. Guo *et al.* used γ-mercaptopropyltriethoxysilane (MPTES) to modify silica particles, introducing sulfhydryl groups which would react with fabrics to create crosslinking through an electrochemically assisted deposition process [29]. In addition, silica nanoparticles also presented a second level of roughness other than the fabrics' intrinsic one, so that the textile surface reached a Cassie-Baxter state which is essential to superhydrophobicity and self-cleaning property. Jin *et al.* applied electrospinning method to prepare textile with a mixture of polyurethane (PU) and silica nanoparticles. n-Dodecyl trimethoxysilane (DTMS) was then deposited on the textile through vapor deposition method [30]. Long alkyl chain silanes are like a film covering on the rough surface created by silica particles, which is a combination of low surface energy and roughness. As a result, the contact angle reached 157 ° and the sliding angle was lower than 5 °. Besides silanes, carbon-based materials can also combine with silica. Ramaratnam *et al.* crosslinked poly(glycidyl methacrylate) (PGMA) to polyester fabrics with modified silica nanoparticles as a crosslinker [31]. In this example, by building a rough surface, silica not only helped increase the contact angle to over 150 °, but also significantly reduced the contact area between the fabric and the particulates that contaminated the surface. Therefore, when the droplet rolled off the surface, particulates were collected because of their sufficiently low adhesion towards fabric, and then textile was cleaned.

Polyhedral oligomeric silsesquioxanes (POSS) is a cage-like compound with a silicon-oxygen framework and alkyl groups on the corners. It can improve hydrophobicity by forming a multi-scaled roughness on the fiber surface [32] and tuning the alkyl groups. It also possesses advantages such as being commercially available, easily synthesized, highly compatible in blended polymers and thus easily processed [33]. Sun *et al.* synthesized a series of POSS derivatives by a photochemical thiol-ene click reaction and covalently bonded it to fibers. The hydrophobic properties of different derivatives were compared and the contact angle was ~ 148 ° at best [34]. Recently an interesting research by Jung *et al.* [35] has developed a method to directly and uniformly grow the zirconia-based metal-organic framework (Zr-based MOF) UiO-66-NH_2 on cotton fabrics. Then, a thin layer of aminopropylisooctyl POSS (O-POSS) was added by dipping. The modified fabrics show a static contact angle of over 150 ° for water and 107 ° for sulfur mustard (HD), a toxic chemical warfare agent with a surface tension of 42.5 mN/m. This fabric, being superhydrophobic and partially oleophobic (especially HD) as a result of the hierarchical structure created by both MOF and O-POSS and the low surface energy due to the long alkyl chains of O-POSS, shows potential for military protective clothing. Furthermore, Zr-based particles are proved to be effective photocatalysts for degradation of various toxic chemicals [35]. So far as we know, this research is the only example showing oleophobicity from non-fluorinated fabrics, indicating a possibility of combining MOF (or other tunable, porous and multi-sized materials) with POSS to realize repellent textiles. However, repellency against other low-surface-energy liquids still needs to be tested.

Since nano-scaled roughness is important for hydrophobicity, recently growing silicone nanofilament (SNF) has been widely noticed. Li *et al*. provided a convenient method with low-temperature chemical vapor deposition (CVD) to grow nanofilament on the fabrics [36]. Trichloromethylsilane (TCMS) was absorbed into the fabrics, hydrolyzed and subsequently polymerized to form a nano-scaled coating of filament. Artus and Seeger presented a cheap scaled-up reaction chamber and successfully produced a SNF-coated polyester suit coat [37], which shows the commercial potential of this technique.

3.1.3. Hyperbranched polymer

Hyperbranched polymers are tree-like-structured macromolecules with many unique properties, such as low viscosity at high molecular weight and good solubility [38], showing great compatibility with other agents. Among all those features, the most attractive one is the high number of end groups that can be chemically modified [39]. Therefore, hyperbranched polymers have a wide range of applications, especially in coating design and the potential to be produced on a large scale at reasonable cost [39]. Though there is a lack of research into non-fluorinated hydrophobic coatings using hyperbranched polymer, some of the patents are already in use.

Hu *et al.* invented a multifunctional finishing liquid containing dendrimer molecules with different terminal groups [40]. Thereinto, polyamidoamine (PAMAM) was modified with $–CH_3$ end groups as the hydrophobic composition. The $–CH_3$ of hyperbranched molecules cannot reverse and are orderly arranged on the surface, forming a hydrophobic layer. Besides, BIONIC-FINISH®ECO (ECO) is a non-fluorinated highly water-repellent finishing product from Rudolf Group [41] with long hydrocarbon chains. The reactive end groups grow exponentially in each synthetic step and are finally functionalized with hydrophobic residues, resulting in a high density of water-repellent groups. Due to the network structure, the hyperbranched polymers tend to self-organize and crystallize. “Comb” polymers are also used to optimize orientation and attachment to the fiber surface (Figure 6). Other than comb polymers, Zhao *et al.* used blocked isocyanate crosslinker to ensure strong attachment to the fiber surface, and successfully fabricated waterproof breathable membranes (Figure 7), reaching a contact angle of 132.2 ° [42].

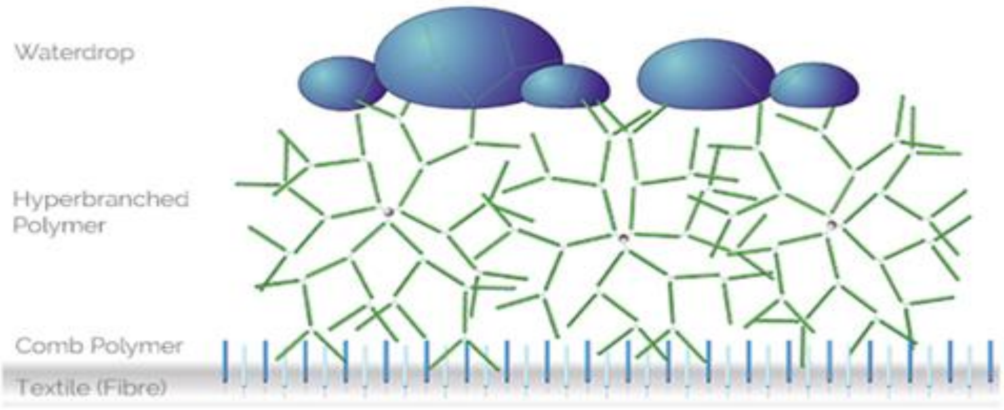

Figure 6. Schematic of ECO product applied on the textile with comb polymer. Reproduced from Rudolf Group website: https://www.rudolf.de/en/technology/bionic-finish-eco/ [41]

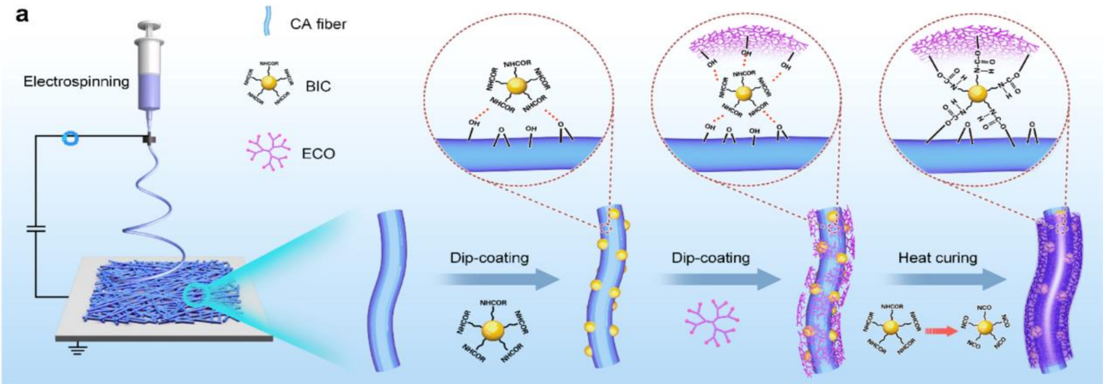

Figure 7. Schematic illustration of the synthetic procedures of environmentally friendly and high-performance WBMs. Reproduced from Zhao et al., 2020 [42].

3.1.4. Nanoparticles

One of the most popular fabric surface modifications is incorporating nanostructures in the fabric with polymeric finishes using nanoparticles or other nanoscale additives [43]. It can effectively reduce the surface energy of textiles and therefore achieve properties such as super-hydro/oleophobicity, self-cleaning, UV shielding/protection, antimicrobial ability, surface roughness, and durability. Many different nanoparticles, such as TiO_2, ZnO, Silver, Zinc and Copper Nanoparticles, are used to impart different properties to fabrics. Although approaches to preparing textiles with superhydrophobic and stain-resistant vary, namely plasma treatment and electrospinning method, one must take into consideration the cost and scalability of the fabrication system. Therefore, preparation techniques like spray-coating, layer-by-layer self-assembly, and in-situ coating are widely adapted to produce superhydrophobic and/or stain-resistant textiles.

Titanium Dioxide Nanoparticles (TiO_2 NP) is a common semiconducting oxide and it is popular among chemists and manufacturers to prepare self-cleaning textiles i.e functional cotton fabrics [44] because of its unique photocatalytic activity and qualities such as cost-efficiency, high chemical stability, and non-toxicity[45]. Attia *et al.* concluded that the TiO_2 NPs performed better in terms of uniformly wrapping the fiber, ultraviolet protection factor, and antibacterial activity compared to other nanoparticles such as ZnO[46].

In order to stabilize the TiO_2 particles on the surface of the cotton fibers, some cellulose crosslinking agents have been used, including dicarboxylic acids [45], polycarboxylic acids [47,48], acrylate-based copolymers [49], citric acid [50].

An example of treating cotton fabric samples with dicarboxylic acids is from the report by Khajavi and Berendjchi. They dipped oxalic, succinic, and adipic acids in TiO_2 NP solution (Figure 8). Using dicarboxylic acids with longer chain length results in decreasing surface energy and reducing TiO_2NPs removal during washing by increasing the amount of TiO_2NPs absorbed onto cotton fibers. They also found that oxalic acid has a better self-cleaning property while the best durability was obtained from adipic acid [45], which is useful for further research on the properties manufacturers desire using different kinds of polymers.

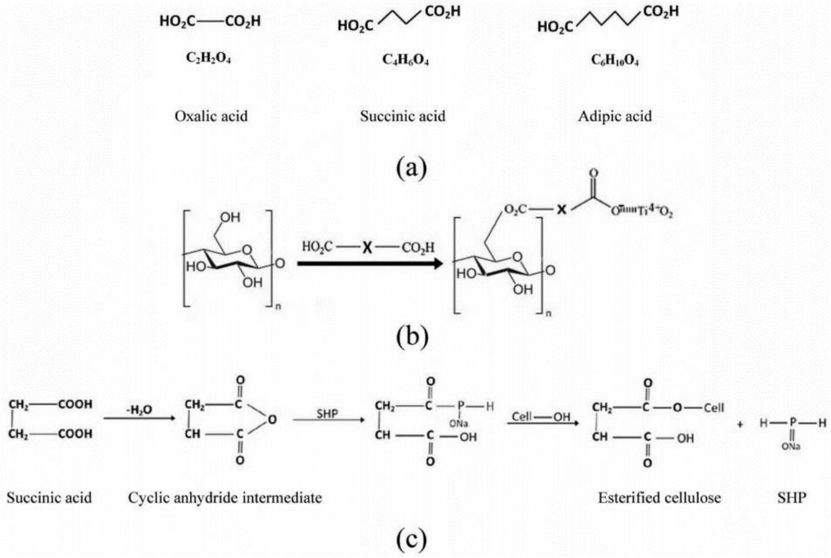

Figure 8. (a) Structure of dicarboxylic acids; (b) ester covalent and electrostatic bonds between dicarboxylic acids, cellulose, and TiO2 NPs; and (c) formation of cyclic anhydride intermediates during esterification of cellulose with succinic acid. Reproduced from Khajavi et al. [45].

Another example to develop superhydrophobic, UV-blocking, and robust cotton fabrics is embedding the nano-TiO_2 particles in the polyvinyl silsesquioxane (PVS) film layer on the cotton fiber surface by covalent Ti-O-Si bonds after curing, as reported by Chen *et al.* This treatment of composite coatings also significantly enhanced the mechanical properties of the finished cotton fabrics [44].

On the other hand, TiO_2 can be used to prepare self-cleaning fabrics. In Addition to the commonly known superhydrophobic approach, based on the lotus effect[15], that creates low surface energy and increases surface roughness, another approach is based on the hydrophilicity of the textile. By using the photocatalysis process, self-cleaning can be achieved by breaking down organic impurities accumulated on textile surfaces into smaller species i.e water and CO_2 after light exposure.Afzal *et al.* reached both superhydrophobicity and visible-light active self-cleaning by first fabricating the cotton through TiO_2-coating and deposition of meso-tetra(4-carboxyphenyl)porphyrin (TCPP), and then hydrophobizing the TCPP/TiO2-coated fabrics with trimethoxy-(octadecyl)silane (OTMS).This measure ensures the water repellency and self-cleaning of fabrics that avoids the accumulation of water-soluble dirts and the remains of organic impurities after visible light radiation.[51]

However, some disadvantages of applying TiO_2 to natural textile fibers are still being discussed. Taking cotton fiber as an example, there is a low durability resulting from a relatively weak electrostatic interaction between the TiO_2 and hydroxyl groups of cellulose.[45]. Measures that can enhance surface adhesion are taken to solve this problem, including in situ coatings of nanoparticles on textile fibers, using adhesives and resins, surface modification techniques (plasma treatment), and cross-linking between TiO_2 particles and cotton fabrics [45]. Due to another detrimental property of the functional cotton fabrics-"the degradation of cotton fabrics from photocatalytic nano-TiO_2 [52, 53, 54]"- other methods to modify nano-TiO_2 and inhibit its photocatalytic activity are still being explored to impart multifunctional properties to the finished fabrics [50].

Other metal nanoparticles such as silver, Zinc and Copper Nanoparticles (Ag, Zn, and Cu NPs) are widely recognized for their antibacterial properties [55]. These NPs are able to impart superhydrophobic properties when they are incorporated into the fabrics. Ag is also reported to exhibit antimicrobial properties in recent studies [56]. Lee *et al* [57] reported that Ag NP coated cotton fabric has bactericidal effects on pathogenic bacteria while no direct skin irritation is caused. This is shown after soaking the cotton fabric in ethanolic solutions of $AgNO_3$ and butylamine. Chao *et al.* fabricated superhydrophobic conductive textiles with antibacterial property. The researchers hydrophobized in situ-Ag NPs-coated fibers with hexadecyltrimethoxysilane. The nanoparticles impose a roughening effect on the textile surface which helps construct a superhydrophobic surface, and silver also contributes to the antibacterial properties of the finished fabrics against the gram-negative bacteria, *Escherichia coli* [56]. Comparing the three NPs, although all of them demonstrate some antimicrobial properties and can be fabricated to produce superhydrophobic textiles, Zinc and Copper have their advantages of rich content and cheap price [55] and these can be taken into consideration as part of scalability and cost-efficiency.

3.1.5. Alkylamines

Alkylamines have been extensively applied as superhydrophobic treatments for textiles in recent years. For instance, with strong adhesion and aggregation behavior in alkaline solution, self-polymerization mussel protein-polydopamine (PDA)-is used on a wide range of substrates to control wettability by forming lotus-leaves-liked structure and trapping air within. PDA nanoparticles usually play a crucial role in designing substrate-independent superhydrophobic materials [58]. Xue *et al*. fabricated a bio-inspired hierarchical-structured superhydrophobic textile by forming a thin layer of PDA which acts as a template initially and then attracts more PDA nanoparticles onto the as-formed layer [59]. However, treatment using polydopamine is expensive and time-consuming and therefore other cheaper and time-saving methods are still required [60].

Polyphenol chemistry has recently been widely used to fabricate hydrophobic surfaces due to its faster adhesion rate and low cost. For example, Gu *et al*. fabricated a hydrophobic Fe(III)/tannic acid (TA)/Octadecylamine(ODA)-treated cotton. Firstly, three galloyl groups provided by TA were as polydentate ligands to react with Fe(III) ions, forming a stable metal-polyphenol complex to achieve bioadhesion. Secondly, ODA was applied on the surface of Fe(III)/TA-coated fabrics through Michael addition or Schiff base reaction in alkaline condition. The combination of the two processes results in excellent stability and hydrophobicity (Figure 9). When TA and Fe are used in a 4:1 ratio, the water contact angle can reach 145 º[60].

Figure 9. The process of fabrication of Fe(III)/TA/ODA-treated cotton fabric. Reproduced from Gu et al., 2017 [60].

Apart from those mentioned above, Liu *et al*. developed a kind of mechanically induced self-healing hydrophobic material by using PDA nanocapsules incorporated with ODA or Fe_3O_4, to modify cotton textiles. Under near-infrared (NIR) light within 40 seconds, Fe_3O_4 nanoparticles accelerated the transfer of heat generated by photoexcitation to ODA (Figure 10). The rise in temperature led to faster fusion of ODA molecules, enabling ODA to migrate to the surface of the PDA capsules, and hence, self-healing of hydrophobicity could be achieved [61].

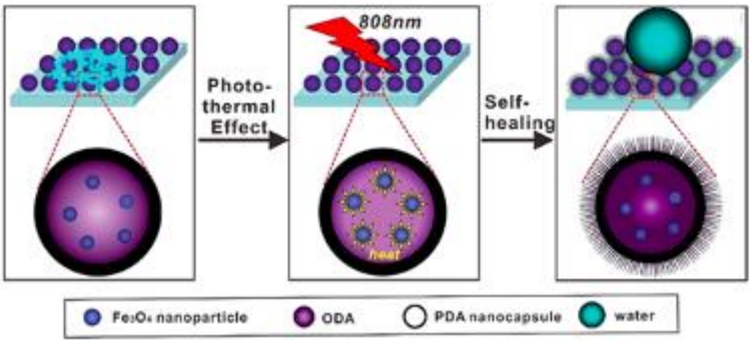

Figure 10. A textile surface with self-healing superhydrophobicity depending on the photothermal effect using NIR irradiation. Reproduced from Liu et al. [61]

In another study, Archroma *et al*. introduced a stable DWR melamine-based resins (Figure 11). The branched-structure melamine with N-methyl groups crosslinked with the fiber surfaces achieved hydrophobicity by the terminal group based on stearic acid [11].

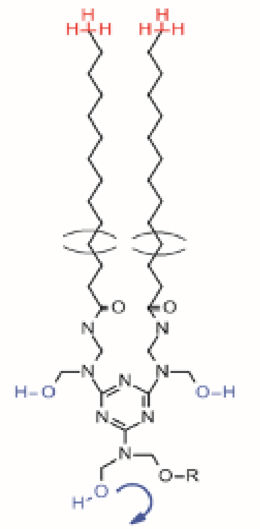

Figure 11. Melamine structure. Reproduced from Archroma et al., 2014 [11].

3.2. Techniques for producing fabrics with desired texture and chemistry

3.2.1. Electrospinning

In section 3.1, we have discussed several materials that can be used to create a hydrophobic surface. For most materials, their surface energy and thus the Young’s contact angle is fixed, which is not always enough to acquire better repellency. We can further improve the repellency by changing the surface morphology of the material.

Electrospinning [62] is a fiber producing technology with an extensive set of parameters [63]. It can have efficient control of surface morphology while fabricating nano- and micron-sized fibers. During the electrospinning process, a high voltage electrostatic field enables the polymer solution or melt in the capillary to overcome surface tension and viscoelastic force, forming a Taylor cone at the nozzle. When the electric field intensity exceeds a critical value, a jet will accelerate in the electric field. With solvent evaporation or melt cooling to solidify, the jet ultimately falls on the collecting plate to form disordered fibers.

By simply electrospinning a mixture of polymers that includes at least one hydrophobic composition, we can obtain a hydrophobic fiber-mat [64]. For the improvement of hydrophobicity, two crucial properties that need to be controlled are fiber diameter and fiber-mat structure. Low fiber diameter causes one degree of roughness, while the fiber-mat structure, such as the bead-on-string structure, creates a hierarchical structure to further induce superhydrophobicity [63]. Scholars have done a great deal of research on the relationship between process parameters and the morphology of the textile. At present, there is still no complete theory to describe the whole process of electrospinning, which makes it difficult to precisely control the electrospun fiber morphology, but some empirical trends have been concluded. Fong *et al*. reported that low viscosity, high surface energy and low net charge density were conducive to the formation of beads. Viscosity was mainly affected by the concentration of polymer solution, while surface energy was determined by both the polymer and the solvent. Net charge density was largely affected by the applied voltage and could also be adjusted by adding an additional electrolyte to the solution. Meanwhile, high net charge density, (in contrast to bead formation conditions), and high surface energy were beneficial to the formation of low-diameter fibers [65]. Wang *et al*. found that flow rate was the dominant factor of fiber diameter [66]. Larger flow rate led to larger diameter. Buruaga *et al*. successfully obtained hydrophobic textiles with four kinds of biodegradable and biocompatible hydrophilic polymers respectively, and stated that lower concentration was more conducive to the formation of beads and higher contact angle. Under a certain limit concentration, however, it became impossible to obtain a hydrophobic surface, possibly because of non-evaporated solvent reaching the collector, destroying the texture [67]. In general, flow rate, concentration and voltage are essential parameters. The influence of other parameters was also reviewed by Sas *et al*. [63]. Electrospinning technology needs more theoretical research to realize the accurate control of fiber morphology. Per our understanding, it might be of help to study the entanglement of polymers with dipole or charge under the electric field, bending instability of jet, as well as the changing rheology due to solvent evaporation during jet flight [68, 69].

Electrospinning, because of its special technical process, should be suitable only for polymers with certain properties, such as having a dipole moment and being able to convert from viscoelastic liquid to solid, etc. [63]. In addition, insufficient strength is often a drawback of electrospun fibers. By adjusting the experimental methods, scientists are solving these problems, enabling electrospun fibers to be adaptable to an expanded application range. For example, PDMS is a hydrophobic material, but cannot solidify. Ma *et al*. synthesized polystyrene (PS)-PDMS di-block copolymer and electrospun it from a mixture with pure PS in the THF: DMF solution, obtaining the highest WCA of 163 ° [70]. Coaxial electrospinning technology uses a nozzle with a needle nested in another and can produce core-sheath-structured fibers. The products have properties from both core and sheath (good mechanical properties from core fiber and hydrophobicity from the sheath, e.g.). Through coaxial electrospinning technology, it is possible to produce fiber or functional coating from unspinnable materials with the guidance of electrospinnable polymers [71]. Furthermore, using double or multi nozzles can also combine different capabilities. Ding *et al*. used the four nozzles to manufacture composite electrospun webs of polystyrene with Nylon 6 [72] and polyacrylonitrile (PAN) [73], in order to enhance the mechanical properties. Zhan *et al*. used two nozzles, and the final textile had both bead-on-string structure for hydrophobicity and microfiber for mechanical strength [74]. These methods can balance the hydrophobic and mechanical properties by applying different mass ratios of polymers in the nozzle, so as to optimize the materials, adapting to different usage scenarios. These works reflect the flexibility and wide application prospect of electrospinning technology.

3.2.2. Flash-spinning

A well-known industrial company DuPont gained its popularity not only for its use of 100% high-density polyethylene fibers, but also for the unique flash-spinning process without using binders. Through flash-spinning, Tyvek® brand materials produced are superhydrophobic, unreactive to most organic and inorganic chemicals, and durable even under the roughest environmental conditions [75].

The mainly used polymers for flash-spinning are polyethylene and its blends, though there are many other applicable polymers, such as polypropylene, polyacrylates, polyethylene acetate, polyesters, polyamides, polyacetals, and polyurethanes. In order to realize a phase separation phenomenon, the flash-spinning process takes advantage of polymers with lower critical solution temperature (LCST) and upper critical solution pressure (UCSP) [76].

The pretreatment is to dissolve the fiber-forming polymer in appropriate solvents. During flash-spinning process, the polymer solution undergoes an extrusion process under high pressure and high temperature. The solution then goes through an orifice into a considerably low-pressure region, where the solvent evaporates rapidly [76]. The extrudate left behind is a 3-D (three-dimensional) interconnected network of very fine fibrillated filaments which are less than 4 μm in average thickness covering 2 m^2 area per gram of material. The fibrous material ensemble, shown in Figure 12, is called “plexifilament” [77]. The continuous and extremely fine fibers lead to small pore size of the fabric, making it an inherent barrier towards some liquids and small particles, without losing its breathability.

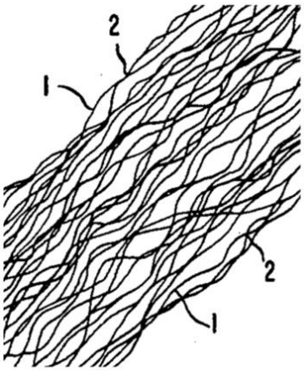

Figure 12. Schematic of plexifilament. Reproduced from Batra & Pourdeyhimi, 2012 [77]

3.2.3. Pre-roughening and post-functionalization

In addition to spinning technologies, desired roughness can also be generated by some pre-roughening treatment. Immersing fabrics in a solution containing nanoparticles, such as SiO_2, ZnO and TiO_2 is the most common method, as mentioned in section 3.1. A rapid and simple solvent swelling method is also reported. By immersing polypropylene (PP) fabrics in cyclohexane/heptane mixture at 80 ℃, the PP macromolecules became swollen and then recrystallized to form protuberances which significantly increase roughness [78].

After the pre-roughening process, the fabric needs to be functionalized with low-surface-energy substances. Usually a repellent coating will be added to cover the fabric, mostly through methods like dip-coating, spray-coating or vapor deposition. As for the dip-coating method, substrates are usually immersed in solutions and then pulled up, before excess liquid drains to form a thin superhydrophobic film layer [79]. For example, Wang *et al*. successfully fabricated a water-repellent material by immersing fabrics in fluoroalkyl surface-modified SiO_2 nanoparticle solution firstly and then dipping the fabrics in FAS and FD-POSS solutions. In terms of spray-coating, a low-cost and also simple approach, it generates nanostructures on the fabrics by spraying composite materials. For instance, polymerized organosilane/attapulgite (POS/APT) nanocomposites are sprayed onto surfaces to achieve hydrophobicity. Notably, materials modified by this method can usually be repaired easily [80]. Chemical vapor deposition (CVD) technology can also be used to form a thin film on surfaces of fabrics. Briefly, two or more gaseous materials interact with each other in a sealed space to form new materials and then deposit on substrates under certain circumstances. For instance, Bao *et al*. treated fabrics with nanoparticles and PDMS via CVD to realize superhydrophobicity. CVD technology has several advantages. Temperature for CVD is relatively low compared with other methods, and therefore it is more suitable for the fragile fibers. Additionally, films formed by CVD are uniform and their thickness can be controlled easily as it increases proportionally to time [81]. Notably, among different CVD methods, plasma enhanced chemical vapor deposition (PECVD) can produce much more reactive groups with low temperature plasma as energy resources.Daniela *et al*. introduced a water-resistant and also durable Diamond-like carbon (DLC) coating, which is obtained through PECVD.

Besides covering fabrics with coating layers, here we also introduce grafting methods. First of all, there needs to be reactive groups on the fiber surface, acting as the grafting sites. For example, cotton fiber is a natural material with abundant hydroxyl groups. However, fibers like PET have no reactive groups and therefore the surface is generally inert. To introduce reactive groups on PET textile surfaces, Xue *et al*. chemically etched the surfaces by putting them into a specific alkaline solution, where PET hydrolyzed to form carboxyl and hydroxyl groups [82]. Plasma treatment is also a typical way to introduce functional groups on surfaces of fabrics. The plasma treatment is performed in a vacuum chamber. Delocalized electrons collide with atoms and molecules to obtain energy, which is then transferred to the molecules. Those steps trigger the formation of various species, which then interact with surfaces of fabric [83]. Plasma treatment leads to the erosion of surfaces and to some extent generates roughness. Also, it introduces some functional groups such as C=O, –O–C=O, –COH, –COOH which could act as terminal groups when attaching alkyl groups [81].

With active groups present on the surface, repellent materials can bond with the fiber. Specially, here we introduce atom transfer radical polymerization (ATRP), a controllable, surface-initiated polymerization method that has been widely studied. Active sites like hydroxyl react and link with an initiator (usually bromoisobutyryl bromide (BiBB)) [14]. Then low-surface-energy monomers polymerize to strengthen hydrophobicity. For instance, fluorinated methacrylate polymer grafted on PET-Br fabrics through ATRP successfully impart hydrophobicity to the fabrics. Poly(2,2,2-trifuoroethylmethacrylate) (PTFEMA) are also feasible materials. However, with the consideration that fluorinated materials are detrimental to the environment, research on this field is expected to pay more attention to non-fluorinated polymers.

Apart from methods mentioned above, it is also noteworthy that acetoacetyl groups can be anchored directly on cotton fibers via heterogeneous transesterification, reported by Rong *et al*. Then the cotton with acetoacetyl groups (cotton-acac) was further modified with gentamicin (Gen) as antimicrobial and the low-surface-energy ODA to achieve hydrophobicity (Figure 13) [84].

4. The design to enhance durability

Hydrophobic coatings are vulnerable to environmental damage that may cause the loss of hydrophobicity, limiting their applicability. In our daily life environment, fabrics are most frequently exposed to the damages of abrasion, stretching, ultraviolet (UV), detergent corrosion, etc. In the last section, we have already mentioned some of the methods to enhance durability, such as crosslinking between fibers and coatings, as well as coatings of crosslinked polymer, and blended fibers. In this section, we will further introduce a series of methods to improve the durability of hydrophobic coatings. Although some fluorinated materials are included, the methods can still be learnt and then applied to the design of non-fluorinated materials.

4.1. Mechanical durability

Abrasion is essentially mechanical damage. Roughness is an indispensable factor for hydrophobicity. However, materials with greater roughness may suffer greater friction force and will be damaged more easily by abrasion. Therefore, a well-designed hierarchical roughness is needed.

As shown in Figure 13, for a surface with only one scale of roughness, the Cassie-Baxter state is prone to be broken by abrasion, which causes surface wetting. Zimmermann *et al.* demonstrated the feasibility of a two-scaled roughness to maintain Cassie-Baxter state on fabrics [85]. The fiber itself is micro-sized. Then a layer of silicone nanofilament was grown on it to form a nano-sized structure. The directly abraded part of the nanostructures was destroyed, but the majority was protected by the 3D microstructures and thus hydrophobicity was retained. Notably, sliding angle is affected most, rising from 2 ° to 25 ° after abrasion [86]. This method is bio-inspired by the two-tier structure of lotus leaves-u. Under friction, only wax crystals on the top of papillae are destroyed while superhydrophobicity is retained [87,88].

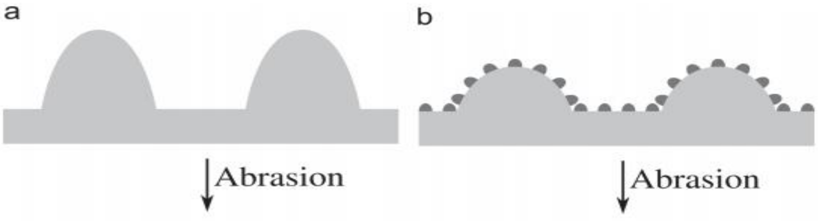

Figure 13. The effect of wear on surfaces with topography in one or two length scales. (a) Only microroughness is present. Abrasion causes the bumps to wear off, making the Cassie state no longer stable. (b) The pattern consists of shallow, mechanically stable microbumps with a nanoroughness on them. Most of the nanoroughness is unaffected by wear and the Cassie state remains stable. Reproduced from Verho et al., 2011 [85].

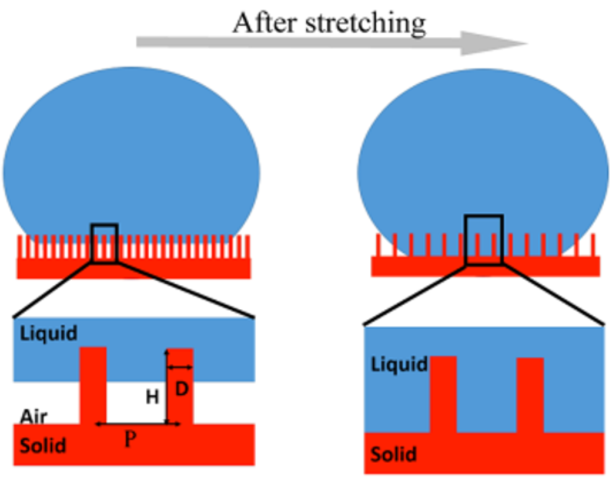

Figure 14. Schematic of stretching a 2D nanopillar array, showing the surface undergoes a transition of the Cassie-Baxter state and Wenzel state. Reproduced from Wang et al., 2014 [91].

Stretching may also reduce hydrophobicity. Spacing factor S_f = D/P (where D is the diameter of features and P is the distance between them). When it is less than a critical value, transition from Cassie-Baxter state to Wenzel state occurs [89,90]. The introduction of S_f can easily predict the resistance of hydrophobicity against stretching. When a material undergoes tensile deformation, P increases, S_f decreases, the Cassie-Baxter state may transform to the Wenzel state, and the material will get wetted (Figure 14). In the long-term use, textiles will inevitably undergo deformation. To solve this problem, in addition to the requirement of durable elasticity of the fiber itself, it is also important to construct self-similar 3D microstructure. For instance, Wang *et al.* developed a method to in-situ generate silica microstructure on a self-assembled hydrogel template. Subsequently, silanes were deposited on the silica layer. This method proved successful to uniformly fabricate a superhydrophobic coating on cotton fabrics. At a certain strain, the stretched coating was chapped to form micron-sized mastoid domains. However, nanofibers on the mastoids remained unaltered as those on the unstretched surface. The research demonstrated that even at 100% strain, the S_f values of both mastoid domains and the nanofibers on them were still larger than the Wenzel/Cassie transition point. Moreover, the 3D self-similar structure also allowed fabrics to maintain a similar structure after the top layer is damaged by friction [91].

In addition, inspired by rubber, whose strength, wear resistance and UV aging resistance can be drastically improved by well-dispersed carbon black nanoparticles, Zhou *et al.* reported a nanocomposite of polydimethylsiloxane (PDMS), fluorinated alkyl silane (FAS) and high-contented silica nanoparticles as durable superhydrophobic coating. Silica nanoparticles not only enhance strength, but also possess lots of cavities. Even if the top layer is abraded away, the voids left still remain rough and bring about hydrophobicity [92,93].

4.2. Self-healing strategy

Self-healing refers to the recovery of certain properties. Healing processes are divided into autonomous healing and non-autonomous healing which are stimulated by external triggers such as heat, UV, chemicals and mechanical forces, etc. [94]

Self-healing ability of a superhydrophobic material enables the fabric to become water-repellent again after abrasion [95]. Generally speaking, the most common way of fabricating chemically self-healing superhydrophobic surfaces is to embed an excess amount of species with low surface energy into microstructure [96]. Once water-resistant fabrics are frayed, the hydrophobic healants (hydrophobic components) migrate from capsules to surfaces to recover its properties. Some healants with significantly low surface energy can migrate autonomously. However, the migration is more often stimulated by external triggers [97].

The most common stimuli is high temperature. When temperature rises above a certain value, coatings become significantly mobile and therefore can recover the substrates. For instance, Lin *et al.* fabricated self-healing materials through the co-deposition of dopamine with an alkyl silane, hexadecyltrimethoxysilane (HDTMS). At above 140 ℃, the mobility of molecules is increased and then low-surface-energy chains are exposed to the surface [97]. In another paper, Wang *et al*. developed a superamphiphobic (both superhydrophobic and oleophobic) fabric coating that was prepared from hydrolyzed fluoroalkyl silane (FAS) containing well-dispersed fluorinated-decyl polyhedral oligomeric silsesquioxane (FD-POSS). This coating showed excellent durability and remarkable self-healing ability against both physical and chemical damages [98]. Similarly, Li *et al*. fabricated a coating by using a suspension of epoxy resin (EP), polydimethylsiloxane (PDMS), and modified SiO_2. The coating could regain superhydrophobicity by heating at 150 ℃ for 10 min after O_2 plasma etching that increased wettability. Heating promoted the migration of the low-surface-energy component PDMS towards the top layer [99]. It is quite interesting to find that the rise in temperature can sometimes be realized on a daily life basis. For example, Wu *et al*. developed a self-healing material fabricated by graft polymerization of lauryl methacrylate (LMA) and n-hexyl methacrylate (HMA), which could recover their properties by steam ironing. In this case, self-healing materials are more likely to be manufactured on a large scale as they can easily recover properties[100].

When it comes to the autonomous self-healing materials, Xue *et al*. fabricated a surface treated with polystyrene/ SiO_2 nanoparticles and PDMS. The self-healing process, which is achieved by the migration of polystyrene and PDMS, would need 12 hours. Adding THF and heating could accelerate the migration process. Combined with silica nanoparticles which have a roughing effect, hydrophobic surfaces were created[101] .

4.3. UV durability

In recent decades, severe ozone depletion caused by the release of fluorinated chemicals like chlorofluorocarbon (CFC) into the atmosphere has led to an increase of ultraviolet radiation (UVR) [102] reaching the surface of the earth. The transmission of UV radiation indirectly onto skin through fabrics could result in an increase in potentially carcinogenesis by DNA damage [103,104]. Thus, UV protective clothing is gaining interest from both textile manufacturers and customers. Nanoparticles have shown good performance of antimicrobial and UV protection. In particular, Zinc oxide (ZnO) and Titanium Oxide (TiO_2) are good candidates of fabricating UV-protective textile, for their UV-blocking, self-cleaning properties, non-toxicity and chemical stability at high temperature[103,105].

In addition to the demand on UV-shielding property, UV-durability is also an important consideration in order to protect the multifunctional coating that has properties such as superhydrophobicity and stain-resistance. In other words, the exposure to UV radiation causes negative change in physical properties of the textile surface such as deterioration of mechanical properties[106] and other chemical changes resulting in the breaking of polymer chains[106], modification of the size or shape of the macromolecular backbone [107], and change in average molar mass[106]. In the investigation of enhancing UV-durability of textile, ZnO is often chosen for its UV-blocking property, especially in the UV-A region, therefore, it has been applied widely in the UV absorbing system by incorporating into different materials[102]. However, the photoactivity of ZnO will cause the production of radicals and catalyze the degradation of fabrics [108]. Therefore, many reports are found modifying ZnO particles to both utilize their UV blocking property and inhibit the photodegradation of the textile surface, protecting its usable lifespan and designed properties. For instance, Chao *et al.* layer-by-layer coated ZnO nanorod decorated PET fibers with silica. The coating of silica shell can suppress the photoactivity of ZnO, inhibiting photodegradation and the hydrophilic transformation of the textile surface, as shown in Figure 15 [109].

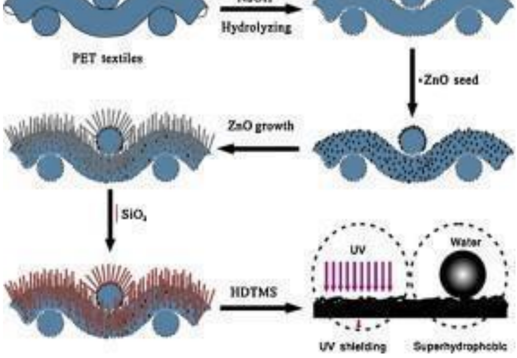

Figure 15. ZnO nanostructures with different morphologies were grown on poly(ethylene terephthalate) fibers by a hydrothermal process at a low temperature of 93 ℃. Then the ZnO nanorod decorated fibers were layer-by-layer coated with silica forming ZnO/SiO2 core/shell structures on the textiles, and hydrophobized with hexadecyltrimethoxysilane. Reproduced from Xue et al., 2013 [109].

Other than SiO_2, PDMS is also commonly fabricated with ZnO for its inherent hydrophobicity, UV resistance and low cost [110, 111]. For example, Ren *et al.* filled polydimethylsiloxane (PDMS) with ZnO nanoparticles, and fabricated superhydrophobic textile by dip-coating and thermal treatment. As shown by Figure 16, ZnO-PDMS coated fabrics are crosslinked, enabling high durability. Apart from exhibiting UV shielding capacity, the fabrics' high UV stability is also shown through its long-lasting superhydrophobic property after long term UV illumination [112].

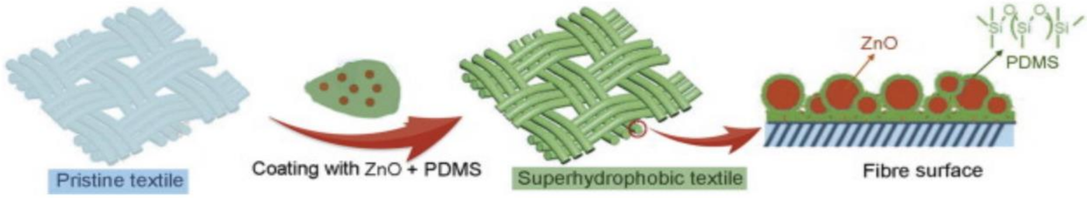

Figure 16. Textile coated with ZnO and PDMS which are being crosslinked and therefore well-dispersed onto the fabrics to produce a UV-durable and superhydrophobic textile. Reproduced from Ren et al., 2018 [112].

Another example demonstrating the good UV resistance and hydrophobicity of PDMS is reported by Pan *et al*., who fabricated PDMS- copper stearate ($CuSA_2$) superhydrophobic coating on cotton fabric, by a simple in-situ growth and dip-coating method. The finished fabrics exhibited a WCA of about 156.7 ° [113] after 24 hours of UV radiation and kept their properties even after undergoing harsh conditions, suggesting its good and long-lasting superhydrophobicity, UV durability and high stability.

4.4. Washing and contamination

During washing, in addition to being damaged by the possible abrasion and stretching mentioned above, hydrophobic coatings may also be affected in the following ways.

First, washing leads to disorientation of side chains (Figure 17) [8], exposing the internal less hydrophobic segments and the interaction spot between the coating and the fiber (such as hydrogen bonds and cross-linked covalent bonds), making it more vulnerable to chemical corrosion. This leads to not only the loss of repellency of the coating, but also the consequent destruction of the coating structure. Side chain crystallization or reorientation requires a flexible polymer backbone or spacer segments (e.g. $R_1–O–CH_2–CH_2–R_2$ or $R_1–O(CH_2)_2N(R–)–SO_2–R_2$). For the reorientation of side chains, usually the method requires heating at more than 100℃ [8], which is hard to be achieved by instruments in everyday life. However, many washing directions still include the advice of tumble drying (60℃) after washing [114]. Therefore, on the one hand, it is necessary to develop feasible methods of reorientation. On the other hand, repellency and the self-cleaning property of textiles still need to be improved to reduce washing frequency.

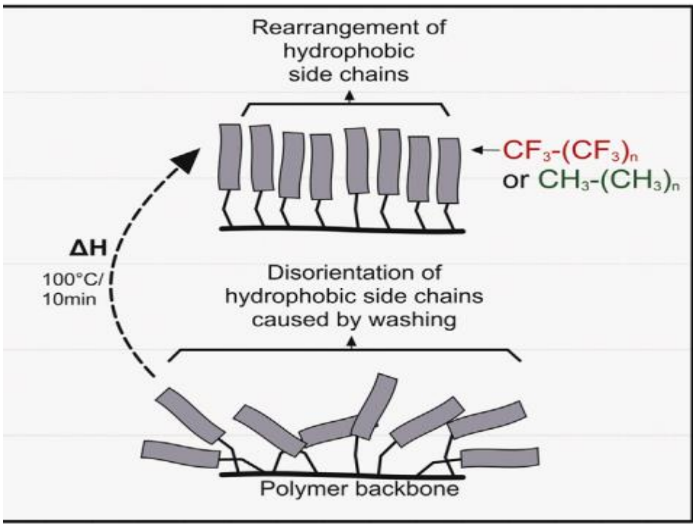

Figure 17. Disorientation of hydrophobic moieties after washing and rearrangement after heat treatment. Reproduced from Schellenberger et al., 2018 [8].

Second, the swelling of fibers can decrease the compatibility of the heterogeneous interface between coatings and fibers, which results in the cracking of the coating. Covalently bonding coatings and fibers can well solve this problem. Huang *et al.* applied nine polycarboxylic acids as cross-linkers and found that the durability is related to the number of carboxyl groups and the distance between them. Among all those acids, 1,2,3,4-butanetetracarboxylic acid (BTCA) led to the best durability, with a recovery percentage of 94.2% after 30 washing times [115]. Four carboxyl groups on every BTCA molecule increased the chance to form ester bonds with the hydroxyls on fibers, so it should be harder to hydrolyze all of them and disconnect the coating with the fiber. There need to be more studies on other crosslinking agents and how they affect durability.

In addition, contamination is a usual condition for outdoor wearings. If a stain on the textile cannot be removed in time, it will also become a surface defect that reduces hydrophobicity [116]. Besides, some contaminants may also cause corrosion or degradation of the coating [117, 118]. Therefore, further development of self-cleaning ability, which is strongly related to maintaining stable Cassie-Baxter state and low hysteresis, is crucial to the improvement of durability.

5. Discussion

All of the non-fluorinated materials we have mentioned above have already achieved hydrophobicity, and some have even achieved superhydrophobicity and self-cleaning. However, it should be mentioned, one of the challenges in the field is that there is limited past and current research regarding oleophobicity or stain-resistance of non-fluorinated textiles. Several research made comparisons between fluorinated and non-fluorinated materials, and demonstrated that only fluorocarbon presented oil repellency [8,119]. In fact, some studies have proved that on some substrate, though not including textile, such as paper, woods, glass, etc., applying non-fluorinated coating is able to present oleophobicity [120-124]. This can be easily explained in theory, fluorine-free groups also have a very low surface energy, which is lower than most of the oil. Together with purposefully designed roughness, oil repellency is attainable. Though fabrics have intrinsic roughness, which is conducive to the construction of hierarchical structure, there are also many limitations. For example, due to their porosity, liquids, especially oils, can easily permeate into their texture [122]. As fabrics are fragile, soft, and the surface morphology cannot be completely controlled, many methods to achieve oleophobicity on other substrates do not have the same effect on fibers. At the same time, most fabrics are used for clothing, so comfort and cost must be taken into consideration. The addition of coating will lead to changes in touch, softness and breathability, and thus affecting comfort. Mechanical properties such as bending stiffness, modulus and maximum elongation at rupture point, are also dependent on the coating quantity [43]. Material design is often a balance of various properties, and the expected result should be consistent with end-use requirements. Hill *et al.*, Holmquist *et al.* and Schellenberger *et al.* proposed some examples of classification based on the usage scenarios (Figure 18) [125,11,5].

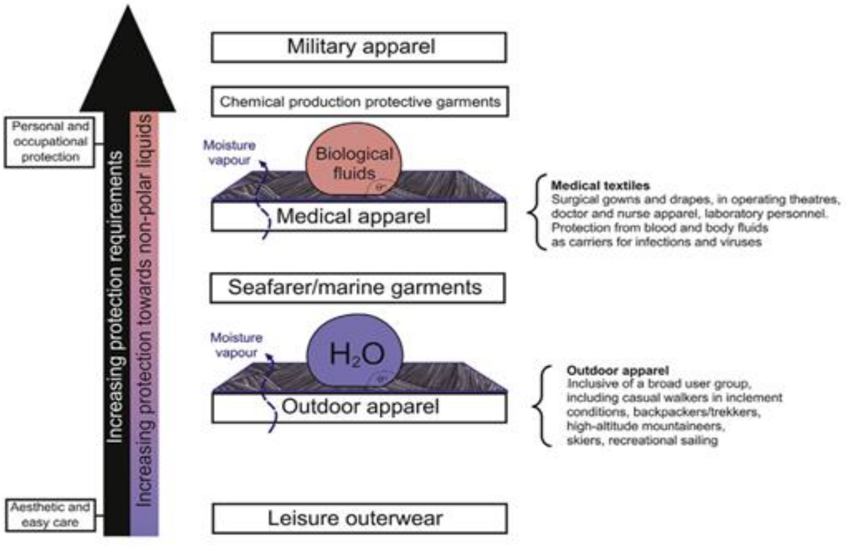

Figure 18. Repellency performance segmented by requirements by end-use. Reproduced from Schellenberger et al., 2019 [5].

For everyday applications, such as outdoor wearing, many respondents did not consider oil repellency but highlighted good water resistance and durability according to a survey [5]. Hydrophobic materials have a certain degree of repellency against water-based stains, such as ink, milk, coffee and juice [26,126]. Oil can be easily washed away by detergent. Actually, the primary demand of waterproof outdoor wearing is not for its stain resistance, but for protection against rain and for thermo-regulation of the body [127]. Insufficient water repellency increases the risk of hypothermia [128]. Therefore, already with satisfying hydrophobic performance, non-fluorinated materials can meet the demand of most outdoor wearing, but are still resisted by some manufacturers and retailers [5]. In addition to the insufficient transformation from academic research to industrial production, it may also be due to a lack of solid research foundation and comprehensive tests of material properties. In addition to the regular surface characterization and measuring contact angle and roll off angle, repellent textiles also need to go through tests on mechanical properties, durability (by exposing to simulate outdoor conditions), time-dependent hydrophobicity, in order words, long-term robustness, and vapor transport rate, etc. For scenarios with higher requirements of repellency, oleophobicity and even antimicrobial properties become necessary. For medical textiles, for example, these properties are currently provided by fluorinated polymers [129] or by special manufacturing process, such as Tyvek from Dupont [130]. In order to reach high repellency, sacrificing comfort and increasing cost are sometimes inevitable. However, inefficient moisture transport will lead to heat stress so that moisture management [128] is an important aspect of improving comfort. At present, great efforts have been made to reconcile repellency and comfort. Asymmetric wettability with a hydrophilic inner side (usually the original fabric) and a hydrophobic outer side is a crucial strategy to produce waterproof, breathable and less skin-irritating textile. This requires selectively hydrophobizing only one side of the fabric. Feasible methods are plasma/ion beam methods [131], applying photo-induced hydrophobic particles such as TiO_2 [132], electrospray [133], multilayer with different wettability [134,135], vapor deposition [136], thickener customized coating [137], etc. Asymmetric wettability allows one-way transportation of water vapor, which is from the skin to the environment, prevents vapor from condensing and blocking the pores of the fabric, and thus increases breathability.

6. Conclusion

This review provides a thorough insight to the newly-developed “non-fluorinated textiles” field concerning the harmful nature of fluorination, while the design of hydrophobic, durable and stain-resistant textiles, and fabrication techniques are the focus.

Different terminal groups with strong adhesion force could enable alkyl chains to attach to fibers, therefore the chemical nature for hydrophobic materials differs. These materials can be categorized into carbon-based coatings, silicon-based coatings, alkylamines and hyperbranched polymers, while some researchers may also use modified nanoparticles as crosslinkers. Specifically, the currently popular repellent materials are carbon-based coatings which are easily synthesizable and PDMS, one of the silicon-based materials, that is recognized for being low-cost, soft, robust, non-toxic and UV-resistant. Other silicon-based coatings, such as silanes, POSS, SNF, are expensive and the investigation into those materials needs to be more in-depth. Apart from the $-NH_2$ group being a terminal group to combine with alkyl chains, some alkylamines i.e. PDA and ODA have special attractive characteristics. PDA can efficiently form a robust hierarchical structure due to its strong adhesion and aggregation ability, while ODA has significant self-healing ability. Last but not least, hyperbranched polymer coatings are welcomed by some manufacturers for its good water solubility and processability.

In order to attach the coatings onto fibers, methods including grafting (i.e. plasma treatment, ATRP, transesterification), CVD, dip-coating and spray-coating are discussed. Among them, the latter two are also used to modify surface roughness and structure with nanoparticles. Besides, with controlled process parameters, we could employ spinning techniques i.e. electrospinning and flash-spinning to obtain desired fiber diameter and surface texture.

Other than the abilities to create roughness and crosslink, nanoparticles with special properties can be used to fabricate multifunctional textiles that fulfill human needs in real life. NPs are well-known for qualities including cost-efficiency, high chemical stability, and non-toxicity. TiO_2’s unique photocatalytic activity can help prepare self-cleaning textiles. Silver, Zinc and Copper NPs are well-recognized for their antibacterial properties. Some coatings consisting of those NPs are also UV-resistant.

Durability is also an important function as it reflects potentially the lifespan of the fabrics. Several considerations are taken when designing durable textiles: creating self-similar hierarchical roughness to resist mechanical damage; using NPs for UV-durability; enhancing stain-resistance to prevent damage from pollution and frequent washing. On the other hand, designing self-healing fabrics could also cover up the damages through triggering spontaneous migration or polymerization of hydrophobic components.

To sum up, our review presents methods of hydrophobization, texture control and enhancing durability respectively. Obtaining better performance with more eco-friendly methods and lower cost is a permanent goal of material development. Therefore, for future research, seeking optimum conditions to combine the advantages of various methods is essential to enabling better repellency. Furthermore, we could focus on the precise control of textile surface morphology. For wovens, the surface texture is fixed, whereas nonwovens, such as electrospun fabrics, flash spun fabrics, meltblown fabrics [78], etc., are disordered fibers, the morphology of which strongly depends on the process parameters. Producing extremely fine fibers with controlled pore sizes and roughness structure is important to liquid repellency. Thus, studies on the producing process and parameter control still need to be more in-depth. Last but not least, it is also necessary to develop techniques to attach coatings that are durable, stable, controllable, well-distributed or self-healing, i.e., the maintenance of orientation of long alkyl chains on the surface, the reorientation or other recovering mechanisms that are simple to be realized in daily life.

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