Chapter

Self-Cleaning Surfaces of Polyurethanes

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Abstract

In this urbanized world, people have limited time and access to labors to clean the items one is associated with. Self-cleaning of the items which humans use every day or occasional is more sustainable for long term and is also one of the most important functionalities for improved esthetics, performance, hygiene, and satisfaction. Various approaches have been widely explored to impart self-cleaning properties to different substrates using different chemistries of surface modifications. The current chapter gives an overview of the various mechanisms for self-cleaning including super-hydrophobicity, super-hydrophilicity and photocatalysis with more emphasis on polyurethane origin. Polyurethanes have been widely explored for self-cleaning properties by introducing super-hydrophobicity via incorporation of nano-roughness or low energy functionalities or by introducing photocatalytic property by incorporating photocatalytic nanoparticles. The chapter also provides a connect to the applications of such polyurethane surfaces. Thus, these self-cleaning polyurethanes may find applications in the fields of anti-fogging, anti-icing, anti-reflection, corrosion resistance, drag reduction, sensors, solar cells, and textiles.

Keywords: Photocatalysis, polyurethanes, super-hydrophilic, super-hydrophobic, applications

1. Introduction

The 20th century saw a revolution in plastic and polymer innovation and production. Scientists in both academic and industrial laboratories were synthesizing new monomers from affordable and abundant raw materials. The terms ‘versatility’ and ‘popularity’ apply to a limited number of polymers available in the world, polyurethanes are one among these limits. Polyurethanes are a versatile class of polymers with great control over their physicochemical properties based on the chemical composition. From insulation to surf boards, from car airbags to window sealants, polyurethanes are everywhere in our daily lives.

Polyurethane (PU) was first introduced by a German professor, Dr. Otto Bayer and his co-workers in the 1940s [1], and has been applied in a very broad range of commercial and industrial fields due to its unique combination of unusual features including excellent mechanical strength, good abrasion resistance, toughness, low temperature flexibility, corrosion resistance, processability, etc. The basic repetitive unit in PUs is the urethane group (—NHCOO—), which is produced from the reaction between isocyanate (—NCO), polyols (—OH), and other additives [2]. Segmented polyurethanes are composed of two blocks: the soft segment is formed by a macrodiol (polyether or polyester diol), and the hard segment is composed by a diisocyanate and a low molecular weight chain extender or crosslinkers [3]. Their growing success and increased use are further boosted by the fact that they are affordable, safe and recyclable, and these qualities make them the product of choice for manufacturers and retailers all over the world.

Self-cleaning surfaces are a class of materials with the inherent ability to remove any debris or bacteria from their surfaces in a variety of ways. The self-cleaning functionality of these surfaces are commonly inspired by natural phenomena observed in lotus leaves, gecko feet, and water striders to name a few. The first instance of a self-cleaning surface was created in 1995 [4]. Paz et al. [4] created a transparent titanium dioxide (TiO_2) film that was used to coat glass and provide the ability for the glass to self-clean. The first commercial application of this self-cleaning surface, Pilkington Activ, was developed by Pilkington glass in 2001. This chapter deals with the fundamentals of bio-inspired self-cleaning phenomenon followed by different approaches adopted to achieve such surfaces. Furthermore, recent advancement in polyurethane self-cleaning surfaces and applications have also been analyzed and discussed.

2. Fundamental theories relevant to self-cleaning

2.1 Typical wetting models

The ability of a surface to self-clean commonly depends on the hydrophobicity or hydrophilicity of the surface. Whether cleaning aqueous or organic matter from a surface, water plays an important role in the self-cleaning process. The mechanism of self-cleaning is majorly explained in terms of contact angle of water droplets on the coating surface. Based on the water contact angle, the substrates are categorized into four types- super-hydrophilic, hydrophilic, hydrophobic, and super-hydrophobic, as shown in **Figure 1**. The surface is hydrophilic when the contact angle of water droplets on the surface is below 90° and super-hydrophilic in case the water contact angle is

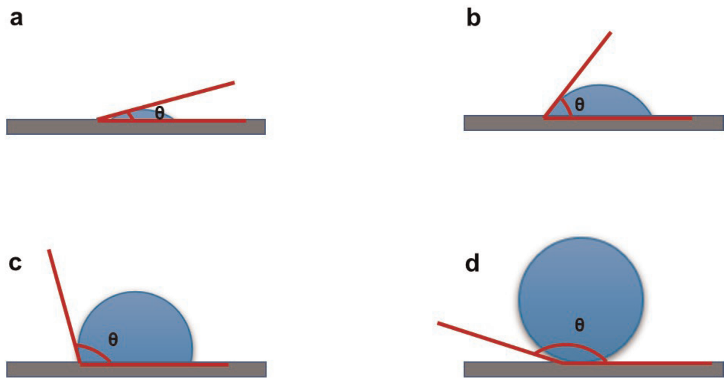

Figure 1.
Schematic representation of water contact angles for (a) super-hydrophilic, (b) hydrophilic, (c) hydrophobic, and (d) super-hydrophobic surfaces.

below 30°. However, the surface is considered as hydrophobic if the water contact angle is above 90°, and super-hydrophobic if the contact angle is higher than 150°.

The contact angle (θ) is a measure of the wettability of the surface and is defined as the angle formed between the solid-liquid interface and the tangent drawn at the liquid droplet at liquid-vapor interface. Contact angle hysteresis is the resistance against the movement of the water droplet along a solid surface. Super-hydrophobic surfaces exhibit water contact angles above 150° and contact angle hysteresis preferably lower than 10°. There are three models used to determine the water contact angle on any surface- Young's model, Wenzel's model and Cassie-Baxter's model [5].

2.1.1 Young's model of wetting

The Young's model is a very basic model for the measurement of the water contact angle and considers the substrate to be a flat and smooth surface, as shown in **Figure 2(a)**. At thermodynamic equilibrium conditions between the three phases i.e. solid, liquid and vapor phases, the water contact angle is determined using Young's equation (Eq. (1)).

$$Cos\ \theta = (\gamma_{SV} - \gamma_{SL})/\gamma_{LV} \tag{1}$$

where θ represents the contact angle of water droplet on the surface, γ_{SV} represents the surface energy at solid-vapor interface, γ_{SL} represents the surface energy at solid-liquid interface, and γ_{LV} represents the surface energy at liquid-vapor interface.

The Young's equation plays a crucial role in determining the wettability of the surface. The lower the contact angle formed, the higher is the surface's wettability. However, the wettability of the surface is also dependent on the surface roughness. Two models (i.e., Wenzel's and Cassie–Baxter's models) are mainly used to evaluate the water contact angle for the rough and chemically heterogeneous surfaces.

2.1.2 Wenzel's model of wetting

In the Wenzel's model, the substrate is a rough and heterogeneous surface, and the water droplet penetrates the surface cavities, as shown in **Figure 2(b)**. Due to the intimate contact of the water droplet with the microstructured surface, there is a change in the wetting behavior. The effect of roughness on the contact angle is represented by the Eq. (2).

$$Cos\ \theta_W = r\ Cos\ \theta \tag{2}$$

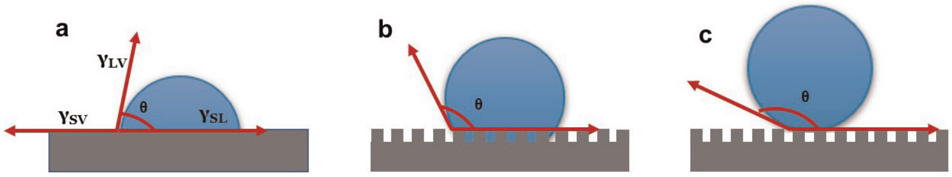

Figure 2.
Schematic representation of water contact angles for (a) Young's model, (b) Wenzel's model, and (c) Cassie–Baxter's model.

where θ_w is the Wenzel contact angle and r is the surface roughness factor, defined as the ratio of surface area of rough surface to the surface area of a flat projection of the same surface.

Since the surface roughness factor is greater than unity, the Wenzel contact angle increases for hydrophobic surfaces turning them into more hydrophobic and decreases for hydrophilic surfaces turning them into more hydrophilic surfaces. The Wenzel state demonstrates higher contact angle hysteresis (more than 10°) due to the penetration of the water droplet in the surface cavities.

2.1.3 Cassie-Baxter's model of wetting

Both the Wenzel and the Cassie–Baxter models explain the effect of surface roughness on the contact angle. In the Cassie–Baxter model, a heterogeneous wetting state is assumed in which air is entrapped in the surface cavities between water and the solid surface, as shown in **Figure 2**(c). Due to this air entrapment, water and solid interface area is reduced, and water and air interface area is increased. In such complex systems, the water contact angle is calculated as per the Cassie–Baxter equation, shown in Eq. (3).

$$Cos\ \theta_C = f_1\ Cos\ \theta_1 + f_2\ Cos\ \theta_2 \qquad (3)$$

where θ_c is the Cassie–Baxter contact angle, f_1 and f_2 are the surface fractions of liquid-solid interface and liquid- vapor interface, respectively, and θ_1 and θ_2 are the contact angles of liquid-solid interface and liquid- vapor interface, respectively.

In the Cassie-Baxter state, as there is no penetration of the liquid in the surface cavities due to the presence of air pockets, lesser resistance is offered against the mobility of water droplets and thus, exhibit lower contact angle hysteresis (less than 10°). With the increase in the surface roughness of a hydrophobic substrate, the water contact behavior transits from the Wenzel model to the Cassie-Baxter model, leading to an increase in the contact angle and thus, changing the surface from hydrophobic to super-hydrophobic.

2.2 Super-hydrophobicity induced self-cleaning

Due to the higher water contact angles (above 150°) and lower contact angle hysteresis (less than 10°), super-hydrophobic coatings, instead of wetting the surface, clean themselves by rolling off water droplets that carry away any dirt. The mechanism of self-cleaning on a super-hydrophobic surface is shown in **Figure 3.**

The wetting behavior of a liquid on any solid surface is dependent on both the surface topography (physical roughness) and surface chemistry (surface energy).

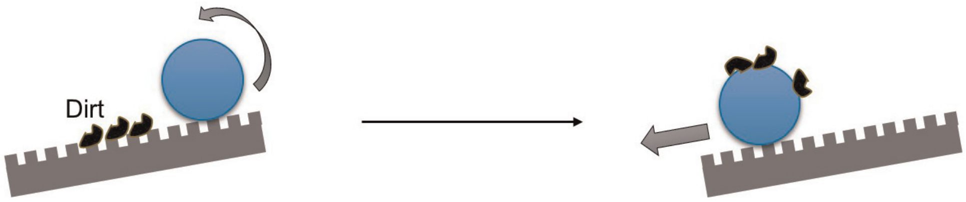

Figure 3.
Schematic representation for the mechanism of self-cleaning from a super-hydrophobic surface.

Based on these factors, the super-hydrophobicity on a surface can be achieved by majorly three different mechanisms [6]. The most common approach is the modification of surface topography by the incorporation of special nanostructures on the surface. The presence of nanostructures/nano-roughness on the surface leads to the formation of a lot of air gaps in between the water droplet and the surface, resulting in the surface morphology similar to Wenzel or Cassie-Baxter model, thus making the surface more hydrophobic. It also reduces the contact area between the surface and water droplet and thus, reducing the contact angle hysteresis. Due to these structures, the contact area between the solid surface and immobilized dirt particle is also reduced which reduces the adhesion force between the dirt particle and the surface, thus, enabling the easier removal of dirt by a drop of water rolling off the surface. The nanostructures-based roughness can be incorporated via different methods such as template-assisted method, photolithography, plasma treatment, electrospinning, chemical deposition method etc., as shown in **Figure 4** [7–9].

The second approach is based on the modification of surface chemistry to lower the surface free energy. When the surface energy of a solid surface is higher than that of a liquid, the liquid will tend to wet the surface of the solid to reduce the surface energy. However, when the surface energy of a solid surface is lower than that of a liquid, the liquid will not wet the surface and will try to achieve spherical shape to minimize the surface energy. Such a surface with lower surface energy is thus more hydrophobic than a surface with higher surface energy, as shown in **Figure 5**. This approach is achieved by the incorporation of low surface energy groups, such as fluoride and silicide, on a surface by grafting, spraying, or mixing.

The third approach utilizes the synergistic effect of both the above approaches. This could be achieved by incorporating low surface energy nanostructures on a solid surface, as shown in **Figure 6**.

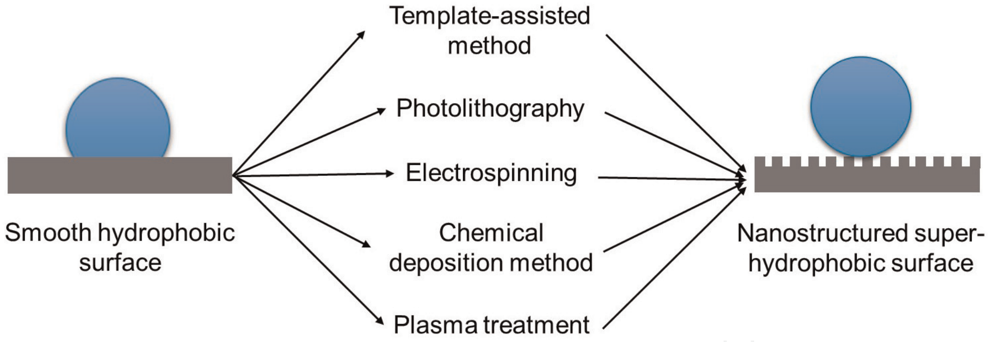

Figure 4.
Generation of nanostructured roughness on a surface for achieving super-hydrophobicity.

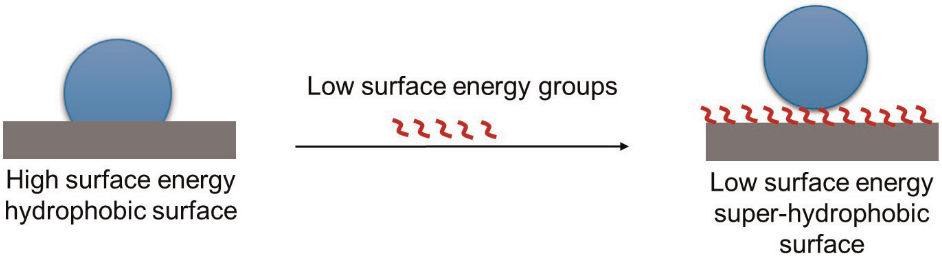

Figure 5.
Incorporation of low surface energy groups on a high surface energy surface for achieving super-hydrophobicity.

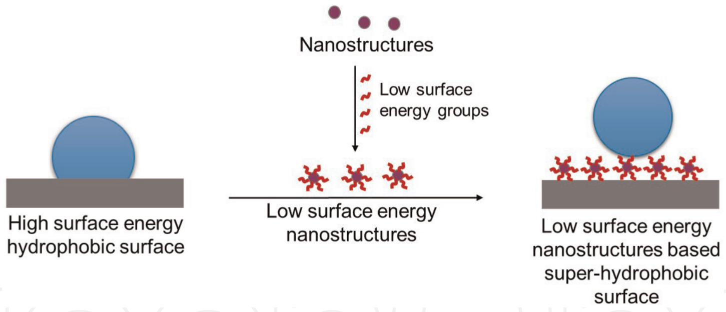

Figure 6.
Incorporation of low surface energy nanostructures on a surface for achieving super-hydrophobicity.

2.3 Super-hydrophilicity induced self-cleaning

Super-hydrophilic coatings exhibit higher surface energy on the solid surface and lower surface energy on liquid droplet. To lower the surface energy, water tends to wet the surface and spreads as a thin film rather than in the form of droplets. Such surfaces retain a thin film of water on the surface and thus, prevent the dirt from adhering to the surface. The dirt on the surface also gets readily washed away with the sheeting water layer, as shown in **Figure 7** [10]. The super-hydrophilic coatings are generally developed by various methods such as sol-gel, layer by layer, chemical vapor deposition, physical vapor deposition, and spraying etc.

2.4 Photocatalysis induced self-cleaning

Photocatalysis is the most widely explored approach for self-cleaning coatings. During photocatalysis, an organic dirt or pollutant is degraded by a photocatalyst in the presence of sunlight. Various semiconductor nanoparticles such as TiO_2, ZnO, CuO, WO_3, and SnO_2 etc. have been explored as efficient photocatalysts for self-cleaning applications.

The semiconductor nanoparticles absorb radiations from the sunlight with energy equal to or greater than their band gap energy, leading to generation of charge carriers i.e. positively charged holes and negatively charged electrons. The electrons in the conduction band reduce the O_2 molecules into superoxide radical anion O_2^{-*} and the holes in the valence band oxidize H_2O into OH^*. The OH^* have an extremely high oxidation potential and can eventually degrade the dirt particles immobilized on the surface into carbon dioxide and water [11]. The mechanism of the photocatalytic degradation of dirt particles is shown in **Figure 8**. The photocatalytic process is majorly governed by the density of active species which is further controlled by the two competing processes of electron–hole pair generation and recombination.

TiO_2, being non-toxic, chemically inert and inexpensive semi-conducting material, has been significantly used for photocatalysis applications [12]. It exists in the form of

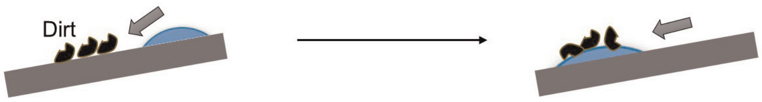

Figure 7.
Schematic representation for the mechanism of self-cleaning from a super-hydrophilic surface.

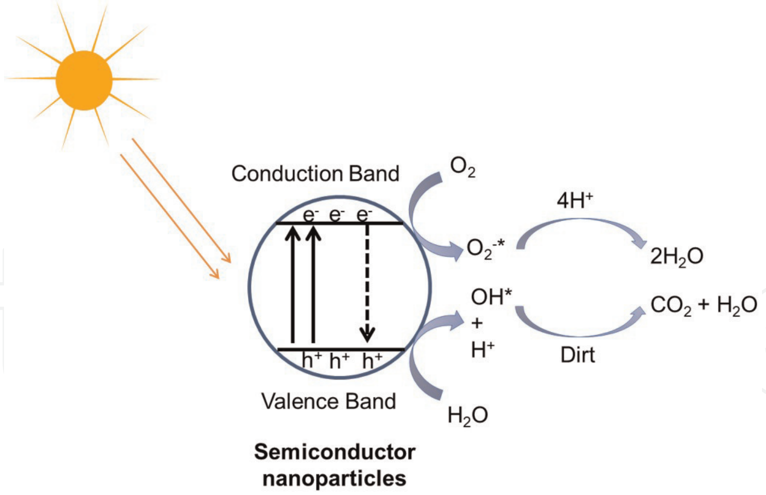

Figure 8.
Schematic representation of mechanism of photocatalysis.

three different crystalline structures, that is, anatase, rutile and brookite. Rutile is the most widely used form as it has a slightly higher refractive index. Both rutile and anatase are photoactive, with anatase form being more active due to a slower recombination rate of charge carriers. Brookite, being rarely found, is not used for any industrial applications. Since TiO_2 has a wide band-gap, the photocatalysis generally occurs in the presence of UV radiations and low energy visible light cannot be utilized to create the charge carriers. However, techniques such as ion-doping and heterostructure fabrication have been explored to achieve photocatalysis in the presence of visible light. Self-cleaning properties could further be improved by including strategies to increase the number and the lifetime of the generated electron-hole pairs.

3. Polyurethanes and their surfaces for self-cleaning

Polyurethane is a versatile polymer used in the coating industry. Polyurethane itself is a type of polymer that is connected to a chemical compound group known as carbamates. This polymer material is also thermosetting in nature; in other words, it burns rather than melts when heated. Another characteristic of polyurethane coatings is its customizability. A polyurethane coating is a polyurethane layer applied to the surface of a substrate for the purpose of protecting it or adding another value to it. These coatings help protect substrates from various types of defects such as corrosion, weathering, abrasion, and other deteriorating processes in addition to providing esthetics.

Based on the type of polyol used, there are three types of polyurethanes- polyester, polyether, and hybrid. The hardness and flexible performances of these coating layers can be controlled by formulation intelligence. These coatings can be formulated to be glossy, muted, opaque or transparent. While polyurethane coatings may appear to be visually similar to other coatings (e.g., epoxy), they possess several distinct properties that make them ideal for specific situations.

- While polyurethane coatings are relatively durable, they are softer and more elastic than their epoxy counterparts. This attribute makes polyurethane-coated floors ideal for moderate to heavy pedestrian traffic. The reduced stiffness gives polyurethane floors a slight elasticity, allowing them to absorb sharp impact loading.

- This durability also makes them more resistant to abrasion and less prone to dents and scratches.

- Improved elasticity also means that polyurethane floors can maintain their shape and mechanical properties in temperatures lower than 30°F (−1°C).

Due to its versatility, self-cleaning is an important value when it comes to polyurethane coatings. Achieving self-cleaning properties for polyurethane requires different formulation strategies as detailed in the Section 4.

4. Approaches to make polyurethane based self-cleaning surfaces

Self-cleaning coatings are primarily categorized into hydrophobic and hydrophilic types based on their behavior towards water. Hydrophobic coatings work on the principle of “lotus effect,” inspired by the water-repellent properties of lotus leaves. Hydrophilic coatings typically contain metal oxides, such as titanium dioxide (TiO_2) or zinc oxide (ZnO), which have the ability to create a thin, continuous layer of water on the surface. In addition to the sheeting effect, metal oxides have an additional property of chemically breaking down complex dirt deposits by a sunlight assisted cleaning mechanism, that is, photocatalytic effect.

These processes are being leveraged by several researchers to successfully create artificial self-cleaning surfaces. For polyurethanes, hydrophilic/super-hydrophilicity, photocatalytic and lotus effect inspired super-hydrophobicity have been widely explored and are well documented [5].

4.1 Super-hydrophobic self-cleaning surfaces

Researchers have been inspired by the lotus leaf’s ability to repel water and keep its surface clean, leading to extensive studies on the mechanistic aspects of this phenomenon [13, 14]. The surface of a lotus leaf is covered with tiny microscale and nanoscale structures, which give it a rough and textured surface. These structures, often referred to as papillae and epicuticular wax crystals, create a hierarchical roughness that minimizes the contact area between the leaf and water droplets. As a result, the droplets rest on the surface with minimal contact, allowing them to roll off easily (**Figure 9**) [15]. With the mechanistic understanding, the concept is well explored by several researchers to create artificial super-hydrophobic surfaces whose water contact angle (WCA) is greater than 150° [16]. The latest strategies to prepare super-hydrophobic polyurethanes (SHPU) are discussed in below section:

4.1.1 Incorporation of low surface energy substance

Surface energy plays a crucial role in determining the wettability of solid surfaces. Silicide and fluoride materials are commonly used for their low surface energy properties in order to create hydrophobic surfaces. These materials can be incorporated into solid surfaces through various processes such as grafting, spraying, or mixing.

Figure 9.
Lotus leaves with super-hydrophobicity.

4.1.1.1 Incorporation of silicide

Silicide possesses low surface energy and its incorporation into the solid can lead to the enrichment of silicon on the surface of PU, thereby decreasing the surface energy and increasing the hydrophobicity. Nano-SiO_2 is the commonly used silicide to improve the hydrophobicity of PU. It can be incorporated onto the surface of the PU substrate by spraying a nano-SiO_2 dispersion to form a coating layer with low surface energy [17]. A study created a SHPU film by spraying a PU/SiO_2/chloroform dispersion onto a PU sponge. The resultant SHPU sponge was able to separate oil from water in an oil in-water emulsion via absorption [18]. SHPU can also be prepared by spraying nano-SiO_2/PU dispersion thus incorporating both on the surface and into the bulk of PU, which is beneficial in retaining the super-hydrophobicity even when the surface of PU is damaged.

Surface functionalization of nano-SiO_2 has also been found to enhance their interaction with PU surface. Furthermore, the functionalization of nano-SiO_2 with long-chain silane has shown to be able to further increase the water contact angle (WCA) value of PU.

4.1.1.2 Incorporation of fluoride

Fluoride substances contribute to low free energy and are widely explored in the preparation of SHPU [19]. The surface energies of various substances containing C–F bonds and/or -CF_3 groups is well summarized in literature [6]. When incorporating fluoride into PU, nano-SiO_2 can be used as a "connector" or coupling agent to facilitate the interaction between the PU surface and the fluoride compounds (**Figure 10**). The incorporation of nano-SiO_2 into PU resulted in a maximum WCA of

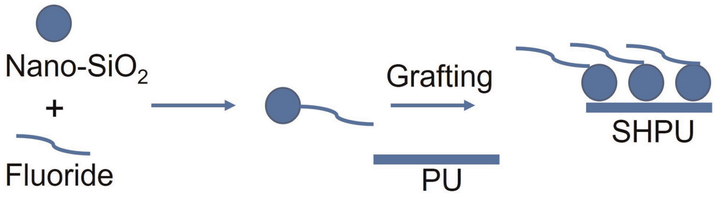

Figure 10.
Grafting of fluoride incorporated nano-SiO_2 onto PU.

160°, however, the fluoride-modified nano-SiO_2 was able to give a maximum WCA of about 170°. A durable and superhydrophobic waterborne PU (SHWPU) coating was prepared by spraying waterborne PU (WPU) on a panel and then fluoride modified nano-SiO_2 was subsequently sprayed on it [20, 21]. In addition, a perfluoroalkyl methacrylic copolymer was used to prepare superhydrophobic polyurethane.

However, currently, usage of fluorine is not considered to be environment friendly, hence, the fabrication of superhydrophobic surfaces without fluorine could become one of the main strategies in the future. In this regard, PDMS has recently been employed by few groups to introduce self-cleaning properties.

4.1.2 Construction of rough surfaces on PU

4.1.2.1 Electrospinning process

Electrospinning is a technique used to prepare nanofibers and is widely explored to construct rough surfaces on PU and several other natural and synthetic polymers. During the process, the polymer solution is stretched into nanofibers under the influence of an electric field. After that, these nanofibers are collected to form a rough film with a nanofiber network, thereby enhancing the hydrophobicity of the film [22].

4.1.2.2 Incorporation of nanoparticles

Incorporating nanoparticles can modify the surface roughness. Currently, nanoparticles such as carbon nanoparticles, that is, carbon nanotubes (CNT) and carbon nanofibers (CNF), and metal oxides, that is, molybdenum disulfide (MoS_2), titanium dioxide (TiO_2), aluminum oxide (Al_2O_3), and zinc oxide (ZnO) have been used to furnish rough surfaces.

4.1.3 Combined strategy of surface energy reduction and surface roughness generation

The combined strategy of surface energy reduction and surface roughness generation has revealed the best results for attaining super-hydrophobicity in comparison to using either of two approaches alone. Using this strategy, some of the common technical methods to achieve super-hydrophobicity are by grafting silane modified nanoparticles onto PU substrate, grafting fluoride onto rough substrate, or by grafting graphene onto PU surface [23].

Organic fluorine and silicone are commonly used as modifiers to enhance hydrophobicity, but they can have limitations such as poor low-temperature resistance and toxicity. To address these limitations and simplify the modification process, a biomimetically hierarchical structure has been reported for achieving superhydrophobic and self-cleaning properties in thermoplastic polyurethane (TPU) surfaces. This approach involves electrospinning TPU fibers and electrospraying TPU microspheres [24]. During the preparation of microspheres, environmentally friendly, fluorine-free hexadecyl trimethoxysilane (HDTMS) is added into the electrospray solution, to reduce surface energy. This approach offers advantages such as using environmentally friendly materials, avoiding toxicity concerns associated with fluorine-modified compounds, and simplifying the modification process.

Another environmentally benign self-cleaning amorphous-SiO_2/nano-TiO_2 based

HDTMS coating with super-hydrophobicity and photocatalytic activity was also studied and reported recently [25].

4.2 Super-hydrophilic (photocatalytic) self-cleaning surfaces

The combination of photocatalysis and water sheeting on hydrophilic surfaces offers another efficient self-cleaning mechanism. The photocatalytic activity of the surface breaks down dirt, while the super-hydrophilic nature (contact angle $<30°$), ensures that water spreads evenly and efficiently to wash away the debris. TiO_2 is one of most widely explored materials for self-cleaning. Due to its special photo-induced properties—photocatalysis and photo-induced super-hydrophilicity - a wide variety of TiO_2-based super-hydrophilic self-cleaning surfaces have been fabricated using different synthetic approaches on different substrates. The photocatalytic performance of TiO_2 is researched to be improved by doping with metals with higher oxidation states. Most of the studies explored using phase separated dopants with the incorporation of nanoparticles. Such phenomenon is also well depicted and published for polyurethanes.

Recent studies showed an introduction of hollow nano-TiO_2 spheres (HNTSs) with high photocatalytic and permeability performances as well as introducing large surface area into the PU film to endue its superior water vapor permeability property, water resistance along with desirable self-cleaning performance [26].

Hydrophilic surfaces prepared by silicon dioxide have also attracted much attention. Studies are also available wherein superhydrophilicity attained by silica nanoparticle film exhibits self-cleaning property without using any photocatalytic materials.

Studies also showed the improved self-cleaning property by using silicon dioxide sol modifying the wettability of acrylate polyurethane from hydrophobicity to hydrophilicity. Transparent hydrophilic photocatalytic TiO_2/SiO_2 thin films were also explored in polycarbonate substrate which was precoated by an intermediate SiO_2 layer. The coated surfaces displayed considerable photocatalytic activity and superhydrophilicity. The self- cleaning coatings usually suffer from photodegradation caused by the nanofiller's photoactivity. From the previous study, it was found that coating of SiO_2 on the surface of TiO_2 nanoparticles influenced the photocatalytic activity of the formed PU composite films, resulting in reduced photodegradation. Recent studies report the integration of SiO_2-coated TiO_2 nanostructures into a PU matrix for the synthesis of self-cleaning coatings [27].

Photochemical additives based on C60 fullerene were incorporated into polyurethane coatings to investigate their coating compatibility and ability to impart chemical decontaminating capability to the coating surface. C60 fullerene molecules have also been observed to exhibit intriguing photochemical properties, including oxidative capabilities, which hold exciting potential for development of a self-decontaminating coating [28].

A combination of easy cleaning with self-cleaning of oleophobic and hydrophilic stains has been recently demonstrated in PU system by using a combination approach of hydrophilic thermo-responsive hydrogel coating and the self-cleaning from the embedded non-metallic photocatalyst g-C_3N_4 [29]. Due to the existence of strong hydrogen bonds between the hydroxyl groups in the hybrid hydrogel coating and the hydroxyl/carboxyl groups in the plasma-treated PU, the hybrid hydrogel coating is very stable on PU. Simultaneously, the acrylamide network in the hybrid hydrogel coating enhances its mechanical strength. Because the transition temperature of oligo(ethylene glycol) methyl ether methacrylate ($OEGMA_{300}$) is well above the room temperature, the cross-linked coating remains hydrophilic in ambient conditions. Thus, oleophilic stains, such as oil and grease, can be easily removed from the coating surface. In addition, the embedded photocatalyst g-C_3N_4 in the hybrid hydrogel coating introduces the extra capability of decomposing organic compounds under sunshine, which favors the removal of hydrophilic stains such as dyes and wines.

4.3 Oleophobic surfaces for self-cleaning

Oleophobic surfaces play a crucial role in self-cleaning and anti-fouling applications, particularly in industries such as oil, steel, and marine environments where oil spills can cause significant damage [30]. Super-oleophobic surfaces, which exhibit strong repellency towards oil and organic liquids with lower surface tension, have garnered interest for their potential in preventing oil adhesion and facilitating easy cleaning. To create super-oleophobic surfaces, one approach is to design solid surfaces with a lower surface energy than that of oil. By reducing the surface energy of the material below the surface tension of the oil, the oil droplets tend to minimize contact with the surface, leading to oil repellency. Hydrophobic and oleophobic coatings can be formulated using ceramic particles such as SiO_2 (silicon dioxide), SiO (silicon monoxide), and Al_2O_3 (aluminum oxide). These ceramic particles offer thermal and chemical durability, making them suitable for various applications. Such coatings serve as alternatives to materials like Teflon, which is known for its oil-repellent properties but may have limitations in certain environments. Super-oleophobic coatings are also developed by employing techniques like spray casting of nanoparticle-polymer suspensions. This process allows for the deposition of a thin film containing ceramic nanoparticles onto a substrate, creating a surface with excellent oil-repellent properties [31].

4.4 Amphiphobic surfaces for self-cleaning

Amphiphobic coatings repel both water and oil, hence surface combines both hydrophobicity and oleophobicity. Inspired by nature, researchers have fabricated superhydrophobic-superoleophobic surfaces. A stable superamphiphobic coating using electrospinning technique was fabricated on glass substrate with nano/mesostructured TiO_2 [32]. Also, a novel hydrophobic and oleophobic surfaces using polyurethane with hydrogenated polyisoprene soft segment have been fabricated and reported recently [33].

5. Applications of polyurethane self-cleaning coatings

Polyurethane based self-cleaning coatings are popular in different applications such as antifogging, anti-icing, anti-reflection, corrosion resistance, drag reduction, sensors, solar cells, and textiles etc. Potential application sectors include but not limited to textile industry (self-cleaning clothing), automobile industry (self-cleaning windshield glass, car bodies and mirrors), optical industry (cameras, sensors, lenses and telescopes), marine industry (anticorrosion protection) and aerospace industry (non-sticky surfaces) and so on. Moreover, self-cleaning coatings can also be used in windows (window coatings), solar modules (self-cleaning coatings for solar modules) and in paints (exterior paints with self-cleaning properties) etc. Commonly desired properties for such applications include durability, water and dirt repellency, easy cleaning, scratch resistance, chemical resistance, UV resistance, etc.

5.1 Anti-fogging

Polyurethane-based self-cleaning coatings can be designed to provide an anti-fogging effect, which can be particularly useful in applications where visibility is important. This is achieved through the hydrophobic properties of the coating, which prevent moisture from condensing on the surface. When a surface is cooled below the dew point, moisture in the air can condense on the surface, leading to the formation of fog. Interestingly, a hydrophobic polyurethane coating can prevent this from happening by repelling water droplets and preventing them from coalescing into larger droplets that can cause fogging. By preventing fogging, these coatings can help to improve safety and performance, as well as reduce the need for frequent cleaning.

Along with hydrophobicity, the polyurethane formulations for self-cleaning coatings may also contain anti-fogging agents that help to further reduce the formation of fog. These agents work by lowering the surface tension of the water droplets, causing them to spread out and evaporate more quickly. This type of polyurethane-based self-cleaning anti-fog coatings can be particularly beneficial in applications such as automotive windshields, eyewear, and medical equipment where visibility is crucial.

A steel surface coated using polyurethane, SiO_2 nanoparticles and hexadecyltrimethoxysilane by a spin-coating technique has been reported to show excellent superhydrophobic and anti-fogging effect [34]. Highly transparent antifogging polyurethane coatings have been fabricated via a UV-assisted cross-linking method by Li et al. [35].

5.2 Anti-icing

In cold regions, especially during winter season, layers of ice get deposited on solid materials exposed to open environments. Polyurethane-based self-cleaning coatings when applied to surfaces, the coatings create a water-repellent layer due to the hydrophobic nature that prevents water from adhering to the surface. This can help to reduce the formation of ice significantly well [36]. Self-cleaning polyurethane superhydrophobic coating having excellent anti-icing property at $-10°C$ could be a viable strategy for transmission line and wind turbines icing mitigation [37].

5.3 Anti-reflective

The anti-reflective effect of polyurethane-based self-cleaning coatings can be particularly beneficial in applications such as eyewear, camera lenses, and electronic displays, where clarity and visibility are important. By reducing glare and reflection, these coatings can improve the performance and usability of these devices. Polyurethane-based self-cleaning coatings can also provide an anti-reflective effect, which can improve visibility and reduce glare. This is achieved through the use of special coatings that are designed to reduce the reflection of light on the surface. When light hits a surface, some of it is absorbed while the rest is reflected back. This reflection can cause glare and reduce visibility, particularly in bright sunlight or under certain lighting conditions. However, an anti-reflective coating can reduce the amount of light that is reflected back, allowing more light to pass through the surface and improving visibility. In addition, some formulations of self-cleaning polyurethane coatings may also contain anti-reflective agents that further reduce the reflection of light. These agents work by altering the refractive index of the coating, causing light to be refracted in a way that reduces the amount of reflection. A polyurethane coating with photocatalytic properties can help to reduce the accumulation of ice and snow on the coated surface. Ko et al. [38] have reported a replication route to non-planar, three dimensional microlens arrays with an antireflective poly(urethane) surface with “moth-eye” nanopattern.

5.4 Enhanced corrosion resistance coatings

Polyurethane can directly adhere to metals without the use of adhesion promotors. Hence, polyurethanes are used in direct-to-metal coatings. Polyurethane-based self-cleaning coatings can provide an effective barrier against corrosion and protect metal surfaces from environmental damage. The hydrophobic and/or photocatalytic properties of these coatings prevent the accumulation of moisture and contaminants on the surface, which can potentially cause corrosion. The formulations of self-cleaning polyurethane coatings can be designed to contain corrosion inhibitors that provide additional protection against corrosion. These inhibitors work by forming a protective layer on the surface of the metal, preventing corrosive agents from penetrating the surface. The corrosion resistance effect of polyurethane-based self-cleaning coatings can be particularly useful in applications such as automotive, marine, and aerospace industries where metal components are exposed to very harsh environments. By protecting these components from corrosion, these coatings can help to extend the lifespan of the equipment and reduce maintenance costs. Nosrati et al. [39] have prepared anti-corrosive polyurethane coating modified with titanium dioxide/polyaniline/halloysite nanotube/carbon nanotube nanocomposite having excellent effect to improve environmental protection. Ye et al. [40] reported that ZnO/polyurethane nanocomposite coatings can enhance the corrosion resistance of stainless-steel. Zhang et al. [41] fabricated slippery coating by spraying silicone-oil soaked SiO_2 with irregular coral cluster structure on the acrylic polyurethane having corrosion resistance with self-cleaning and good coating stability. Fluorine-modified hyperbranched waterborne polyurethane resin applied to a water-based nano anti-corrosion self-cleaning finish paint has been reported to show excellent anti-corrosion property [42].

5.5 Drag reduction

Frictional drag is a major source of resistance that affects the speed and efficiency of vehicles and equipment. By reducing friction, a polyurethane-based self-cleaning coating can improve the flow of fluids around the surface, reducing drag and increasing speed and efficiency. Polyurethane-based self-cleaning coatings can also provide a drag reduction effect, which can improve the performance of vehicles and equipment that move through fluids, such as air or water. The hydrophobic properties of these coatings reduce the surface tension of the fluid, allowing it to slide more easily over the surface and reducing friction. In addition, some formulations of self-cleaning polyurethane coatings may also contain additives that further reduce drag, such as nanoparticles that modify the flow of the fluid around the surface.

The drag reduction effect of polyurethane-based self-cleaning coatings can be particularly beneficial in applications such as aerospace, marine, and automotive industries, where reducing drag can improve fuel efficiency and reduce operating cost. By improving the performance of these systems, these coatings can help to reduce environmental impact and improve sustainability. Superhydrophobic PDMS assisted immobilized fluorine functionalized SiO_2 nanoparticles have been reported to improve coating adhesion to substrate materials [43].

5.6 Sensors

Polyurethane-based self-cleaning coatings can be applied in various sensor applications to improve their performance and longevity. In optical sensors, the anti-reflective properties of the coating can reduce the reflection of light and improve the accuracy of the sensor. Similarly, in gas sensors, the hydrophobic and/or photocatalytic properties of the coating can prevent the accumulation of moisture and contaminants on the surface of the sensor, reducing interference with the sensor's performance [44]. The anti-fouling properties of polyurethane-based self-cleaning coatings can help to prevent the buildup of biofilms and other materials on the surface of sensors used in medical and biological applications. A group of researchers fabricated a pressure sensor consisting of PU mesoscaled dome arrays embedded with gradient-distributed silver nanowire (AgNW) for flexible electronic applications [45].

5.7 Solar

Polyurethane-based self-cleaning coatings can be applied to solar cells to improve their efficiency & reduce maintenance requirements. The coatings can provide several benefits, including self-cleaning, anti-reflective, anti-scratch, hydrophobic and UV-stability. Interpenetrated polymer networks prepared using polyurethane- acrylic colloidal suspension when applied on glass covers of solar cell panels is reported to give excellent super-hydrophobicity, transparency, and durability [46].

5.8 Textile

Textiles coated with these types of coatings can resist dirt, dust, and other contaminants, making them easier to clean and maintain.

The hydrophobic properties of polyurethane-based coatings can prevent the absorption of moisture and liquids, making textiles more resistant to water damage.

Aliphatic Polyurethane-based coatings can provide protection against UV radiation, which can cause damage to textiles and fade their colors over time.

The textiles coated with these types of coatings can be more durable, with improved resistance to wear and tear, stretching, and abrasion. Chen et al. [47] fabricated coating with self-cleaning and pH-controllable oil/water separating ability on account of the pH-responsive UV-cured PU having good super-hydrophobicity and can maintain their self-cleaning ability even after mechanically damaged, seawater immersing and UV irradiation.

5.9 Others: electrowetting and other functions

Electrowetting is a phenomenon that occurs when an electric field is applied to a liquid droplet on a surface, causing the droplet to spread or contract. Incidentally, polyurethane based self-cleaning coatings can exhibit electrowetting behavior, which can be beneficial in certain applications. By applying an electric field to the surface of a polyurethane based self-cleaning coating, the contact angle between the droplet and the surface can be modified. This can change the wetting behavior of the droplet and allow for precise control of its movement and positioning on the surface. This behavior can be useful in microfluidic systems and lab-on-a-chip devices, where precise control of droplet movement is important.

6. Current challenges and possible solutions

Along with versatility of polyurethane self-cleaning coatings, there are still several challenges that must be addressed to develop multi-functional robust and effective self-cleaning coatings to take the next level. The current challenges and possible solutions are highlighted below:

6.1 Durability

One of the main challenges with aromatic polyurethane based self-cleaning coatings is maintaining their durability over time, particularly in the UV light-based environments. Possible solutions to this challenge include incorporating additives that enhance the coating's UV resistance, abrasion and scratch resistance or modifying the coating's structure to improve its UV resistance and adhesion and cohesion properties.

6.2 Compatibility with different substrates

Although polyurethane is versatile, another challenge is developing coatings that can be applied to a wide range of substrates, including metals, plastics, and ceramics. Possible solutions to this challenge include optimizing the coating's composition and application process to improve its adhesion to different substrates, or developing surface pre-treatments that improve the substrate's surface energy and adhesion properties.

6.3 Environmental impact

Many current self-cleaning coatings contain toxic chemicals or are not biodegradable, which can have negative environmental impacts. Possible solutions to this challenge include using eco-friendly raw materials and production processes, or developing coatings that are biodegradable or recyclable.

6.4 Cost

Polyurethane based self-cleaning coatings can be more expensive than traditional coatings, which can limit their adoption in some applications. Possible solutions to this challenge include developing more cost-effective production processes, or identifying applications where the benefits of self-cleaning coatings outweigh the higher cost.

6.5 Performance under extreme conditions

Self-cleaning coatings may not perform as well under extreme conditions, such as high temperatures (>200°C), humidity, or exposure to chemicals. Possible solutions to this challenge include developing coatings with improved thermal stability, resistance to chemical exposure, or moisture resistance.

Overall, developing a robust, high performance and cost-effective polyurethane based self-cleaning coatings requires a combination of material chemistry, and engineering. In order to provide a solution-based approach to these challenges, researchers can continue to improve the performance and applicability of self-cleaning coatings in a wide range of industries and applications.

7. Characterization of polyurethane self-cleaning surfaces

The self-cleaning property of a polyurethane surface is mainly governed by its *phobic* and *philic* nature towards oil and water. The exact characterization is made by quantitatively measuring (1) surface energy, (2) surface roughness and (3) liquid droplet contact angle by using various characterization techniques and correlate this with the self-cleaning effect. Typically, higher surface energy polymers offer to be potential adhesives since, higher their surface free energy higher will be their ability to interact with the substrate. The surface energy aspects can be simulated with different mathematical models to design new surfaces.

8. Conclusions

In conclusion, all the research efforts, as we have seen here, are explored to mimic the supreme strategies perfected by nature over billions of years. The self-cleaning surface on naturally occurring leaves and wings of certain insects is multipurpose in achieving self-cleaning, anti-reflective, camouflage and various other functionalities which has got researchers across the globe take stock and attempt to mimic. Though the self-cleaning surfaces designed by them are yet to match their naturally occurring counterparts, the fabrication techniques have indeed evolved into more environmentally compatible and cost-effective and polyurethane is one amongst them.

Polyurethane is a well-accepted polymer-based coating material in the market. Polyurethane polymers can be tailored very easily to meet the *phobic* and *philic* nature to oils and water. Therefore, polyurethane-based self-cleaning coatings have potential for reducing maintenance and cleaning costs in various industries. Polyurethane coatings can be tuned to utilize hydrophobic and/or photocatalytic properties to repel dirt, dust, and other contaminants, which can then be easily washed away as exemplified in this chapter. Polyurethane based applications for self-cleaning coatings are currently in automotive, aerospace, and marine industries.

As the market expands more effort on building a strong structure performance analysis is critical to develop a robust self-cleaning surface for different applications. The future outlook for self-cleaning polyurethane coatings is promising, with potential for further improvements in the smartness, durability, efficiency, sustainability/eco-friendliness and circularity of the coatings along with the development of easily scalable manufacturing processes. As and when more industries adopt these coatings, there may be an increased demand for customized formulations to meet specific application requirements in this domain.

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Conflict of interest

The authors declare no conflict of interest.

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