

Best Method to Make a Material Self Cleaning

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Abstract

Super hydrophobicity could be engaged to play a major role in modern world of science due to its self-cleaning, anti-fouling, anti-sticking, anti-corrosive, anti-icing and water repelling properties. This critical review compares the methods available to form self-cleaning super hydrophobic surfaces in different materials and attempts on giving a concluded comprehensive answer about which one of those is the best method to prepare such surfaces. According to the author's perspective when considering cost, simplicity, industrial scale or mass scale production most convenient method to form such surfaces in a wide range of materials such as rubber, plastics, glass, and apparels is addition of non-metallic chemically treated super hydrophobic filler such as treated Diatomaceous Earth in to the material.

Keywords: Super-hydrophobicity; Self-cleaning materials; Rubber; Plastics.

1. Introduction

Super hydrophobic surfaces with self-cleaning and anti-sticking properties are very important in industries such as medical, engineering, rubber, plastic, glass and many more[1]. Hydrophobicity can be measured using static contact angle and sliding angle. Stickiness of the surface can be measured using dynamic contact angle [2,4,1]. A surface is called super hydrophobic if contact angle of water droplet on it is greater than 150° . Possessing of a water sliding angle lesser than 10° is also a property of anti-sticking good super hydrophobic surface. Stickiness depends on the contact angle hysteresis which is measured by the difference of advancing and receding contact angle difference. Higher the difference of contact angles in an instance higher the contact angle hysteresis and higher the stickiness. As any other innovation, tailoring of super hydrophobic surfaces is also learnt from nature. Lotus leaf and wings of some insects are examples for naturally super hydrophobic surfaces[5].

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This literature review focuses on different methods use to form super hydrophobic surfaces. Water contact angle depends on the attraction forces between each phase (Interfacial tension forces between solid, liquid and gaseous phases). The forces can be demonstrated by modified young's equation in **figure 1** [4,6].

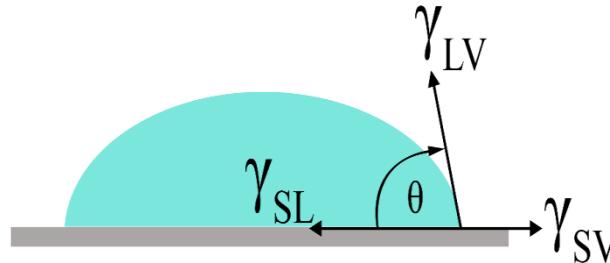


Figure 1: Water contact angle with respect to the interfacial tension forces

$$\gamma_{sv} - \gamma_{sl} = \gamma_{lv} \cos\theta + \frac{\gamma_{slv}}{r}$$

Modified Young's equation

γ_{sv} - Interfacial tension between solid and vapor phase

γ_{sl} - Interfacial tension between solid and liquid phase

γ_{lv} - Interfacial tension between liquid and vapor phase

θ - Contact angle

γ_{slv} - Line tension which is attributed to the excess energy associated with the three-phase contact line

r - Radius of the bottom of drop

There are various methods to prepare super hydrophobic or enhanced hydrophobic surfaces such as lithography, sol-gel methods, plasma etching methods, layer by layer deposition, chemical etching, chemical deposition, laser treatments, polymer reconfirmations, electro spinning, electro deposition and etc.[7, 9]. A chemically treated filler can also be added into the material to make its' surface super hydrophobic by migration of the particles onto the surface. When the diffused particles have both low surface energy and surface roughness which are the needs to obtain super hydrophobicity, the aim to prepare such surface gets success [2,7]. There are two models to describe the state of a water drop on a surface. In **Wenzel model** water drop has penetrated asperities and in **Cassie-Baxter model** it is suspended on the asperities. There is no clear cut answer what model demonstrates the best hydrophobicity but according to the literature when water acts according to Cassie-Baxter model it shows higher hydrophobicity[1,10,11].

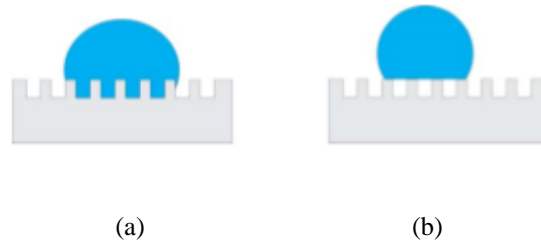


Figure 2: Pictorial demonstration of (a) Wenzel model and (b) Cassie-Baxter model

2. Methods to make surfaces self-cleaning

2.1 Templatation

Here in this method a master is used to generate nano roughness on the preferred polymer surface. It forms both less surface energy due to formation of lot of air gaps and the roughness which gives the surface morphology as in Wenzel or Cassie-Baxter model. The master used can be a natural one such as lotus leaf or manmade polymeric one (PDMS - polydimethylsiloxane) with lithographically formed roughness. In [12] a taro leaf has used as the template to form super hydrophobic polystyrene surface. PDMS is used there as the master to get negative replication of the taro leaf which can then use for multiple times to form positive replication of taro leaf on the polystyrene surfaces. It reaches $158^\circ \pm 1.6^\circ$ maximum average water contact angle and 3° sliding angle as its best. In [13] the same method is used taking lotus leaf as template and PDMS sheet as the master. The positive replication on polymer surfaces made by nano casting, which show totally equal morphology to lotus leaf surface in micro and nano level shows maximum 160° contact angle where negative replica only shows 110° contact angle. Similarly in [14] master was developed using micro-machining to form preferred hydrophobic surface on polymers. It shows higher the height of asperities on surface and bigger the air gaps between those pillars it shows more hydrophobic nature and most probably water drop acts according to the Cassie-Baxter model other than Wenzel model. At the same research it was concluded but the way water drop acts also depends on how water drop is suspended on the surface. If it drops from a certain height it might follow Wenzel model and surface might get wet. In [15] nano imprint lithography has used where pattern replication method is a heat and pressure driven process. There a hard master is used on thermoplastic polymers over their glass transition temperature. They used textured aluminium sheets and anodic aluminium oxide (AAO) membranes as the master. After the printing it's cooled down to room temperature and applied pressure is released. After that Al master is dissolved away by saturated HgCl_2 solution. They showed best water contact angle between 155.8° and 147.6° . Although these methods give a good contact angle and less stickiness, they are highly dependent on the material type. So if the polymer is hydrophilic originally, achievable hydrophobic level is less. Chemical composition of the polymer surface also affects hydrophobicity because there can be functional groups with more affinity to water. Polar groups such as OH, COOH decrease the hydrophobicity. If the surface get scratched surface morphology can get destroyed and again hydrophobicity can be decreased due to the alteration of micro and nano structure of surface. This method is better to form small super hydrophobic surfaces at laboratory level but not good for industrial level mass productions because only a small area of surface can be made with template and it is not scattered all over the product. So there are many disadvantages of this method

to use in mass scale industrial level, although it's a promising way to form small surfaces with super hydrophobic nature.

2.2 Capillary force lithography

In capillary force lithography elastomeric soft master is used, which is applied on the polymer for negative replication above the glass transition temperature of polymer. Pattern is formed on the polymer either before solvent is evaporated or after it is evaporated. Reference [16] describes how capillary force lithography is used govern by UV radiation. According to [17] the best water contact angle it reaches with the best height nano pillars on surface is 95° . PEG (polyethylene glycol) is a hydrophilic polymer so hydrophobicity it reaches is limited. Although in [18] 162° water contact angle (Cassie-Baxter regime) was achieved on polystyrene aligned nanotubes using capillary lithography methods, water drops were not roll off the surface even at 180° tilt due to high stickiness. It describes this sticky nature is due to the strong van der Waals bonds generated between water molecules and high-density nanotubes. Other than the stickiness all the previous mentioned disadvantages are applied to this method also. Another limitation of templation method is surface morphology totally depends on the master used and all the materials are not suitable for this method.

2.3 Photolithography

In photolithography X ray or electrons are used to irradiate a surface through mask to form roughness on it. A photoresist is used for this process which is followed by chemical etching or surface treatment steps to make the surface super hydrophobic. According to [19] electron beam lithography is used to form preferred rough surface on thermoplastic polymers followed by silanization as a surface treatment to enhance hydrophobicity. In [20] with the best measurement of nano asperities 163° water contact angle was achieved. In [21] X ray lithography has used to form super hydrophobic surface which is gold sputtered and dipped in hexadecanethiol solution to hydrophobize the surface after energy irradiation. Water contact angles were measured with variation of micro spikes height, diameter and spacing. With higher height and space between spikes high contact angle has achieved around 161° . Photolithography method use high energy waves or electron beams which are expensive. Using of gold sputtering in order to increase the hydrophobicity is yet again a plus point for high cost of the method. Again because this is a lithography method dependency of the material type to hydrophobicity, interactions between water molecules and surface, surface morphology dependency on used mask, Limitation of types/surface nature of the mask, replication area is limited on the material, only limited number of materials can be make super hydrophobic using this method are the main disadvantages of this method.

2.4 Plasma treatment

Plasma treatment is a dry etching method where highly reactive gaseous molecules or ions are used to alter a surface to acquire micro roughness and enhance hydrophobicity. Sometimes the type of gas used for etching alters chemical composition of the surface with possessing its ions on the surface. According to [22] surface of a poly(ethylene terephthalate) was nano textured with pits and asperities with oxygen plasma etching. But to keep enhanced hydrophobicity organosilane precursors are applied as a coating on the surface. Surface shows a water

contact angle greater than 150° after the surface modification. In [23] a super hydrophobic PTFE surface was tailored with oxygen plasma etching with show a water contact angle around 160° and no contact angle hysteresis. But it is again plasma etched with ammonia gas to supply amino groups on to the polymer surface for further surface treatments. Here the modified surface show switchable wettability as it becomes hydrophilic when gets contacted with acidic water. This method also carries all the disadvantages expressed in previous methods and most predominant one out of them is high cost.

2.5 Colloidal assemblies

In this method inorganic or polymeric beads were assembled in monolayers on a preferred substrate to assure super hydrophobicity with the promised surface roughness. CaCO_3 , silica, polystyrene beads are some examples that can be used for this purpose. After the assembly of particles plasma etching is used to enhance hydrophobicity and most of the times surface treatment such as gold sputtering was also done to keep less surface energy. In [24] silicon substrates were loaded by CaCO_3 beads followed by gold deposition on surface. It reached 160° water contact angle for silica-based surface and 156° with PS (polystyrene) assembly. Although this method is relieved from the costly lithographic methods still all the other previously mentioned disadvantages lie on it. Mostly it cannot be used as a mass industrial production method of super hydrophobic surfaces. Still the cost is high with usage of plasma etching and gold sputtering surface treatment methods.

2.6 Layer by layer deposition

Here electrostatic attractions are generated between layers of polycations and polyanions. It's easy to control the thickness of surface with controlling the deposition of layers on surface. Hydrophobization or addition of nano particles are needed for these multilayer systems in order to increase roughness and hydrophobicity since polyelectrolytes are hydrophilic. In [25] super hydrophobic surface was tailored with layer by layer deposition of poly(diallyldimethylammonium chloride) and sodium silicate multilayers on silica sphere coated substrate. The aforementioned layers give micro and nano structured hierarchical surface and it was then surface treated with fluoroalkylsilane to enhance hydrophobicity. Surface showed water contact angle of 157.1° and sliding angle of 3.1° . Although this method is not consuming so much energy to achieve enhanced hydrophobicity several steps should be followed such as incorporation of nano particles, hydrophobization using a super hydrophobic solution and surface treatment to increase the surface stability [26].

2.7 Chemical deposition

This is a self-assembly or self-organization method of small particles, chemicals to form a super hydrophobic surface. Chemical deposition methods used to form super hydrophobic surfaces can be separated into three types according to how it is making. Chemical bath deposition (CBD) [27, 28, 29, 30], chemical vapor deposition (CVD) [31, 32,33] and electrochemical deposition [34, 35, 36] are the methods under chemical deposition. In [37] CBD method was used to tailor water repelling surface. There $\text{Zn}(\text{NO}_3)_2$, NH_4Cl , urea, and ammonia were used to form ZnO nano rods on glass slides. Nano rod diameters were kept around 400 nm to 600 nm and then surface modification was done using SAMs of alkanolic acids with different chain lengths. Chain length depends

on the hydrophobicity level because higher the chain length lesser the surface energy. The surface reaches a water contact angle greater than 150° . CVD method was used in [32] to form a super hydrophobic surface from one step using chemicals TEOS, vinyltrimethoxysilane (VTMS) and ammonia. All gas phase reactions were done in comparatively lesser temperature around 40°C to the other CVD experiments. So, energy consumption is less in this method as well as the time consumption. It achieves a water contact angle around 160° . Generally, deposition methods take lot of time and very few types of materials can make super hydrophobic with this method. Cost for chemicals is pretty much high while it takes longer time to end the process. Surface nature changes with the energy or chemicals contact with it most the times as in [38]. So, the surface is not much stable and nature depends on the chemicals used for modifications. After deposition modification step should be followed.

2.8 Sol-gel methods

Hydrolysis of a preferred oxide in a solvent forms sol. When a large number of solvent traps in system it becomes a gel. They can be made using filler like nano silica or without them. Method used to make the sol, functional groups in surface of formed gel affects the properties of sol-gel system. According to [39] sol-gel method was used to prepare a durable super hydrophobic surface on cotton fabric. Silica sol prepared with water glass and citric acid as the aid catalyst was coated on cotton. Then in order to obtain low surface energy silica coated cotton was padded with hydrolyzed hexadecyltrimethoxysilane. Although good hydrophobicity can be achieved from these deposition methods and they are better in controlling molecular deposition rate and nature process is complex as well as not suitable for mass productions other than laboratory level small scale production.

2.9 Membrane casting

This is a method to prepare porous polymer surfaces. A template is used to do casting of polymer solution. Here phase separation method is used. Polymer solution at cloud point is submerged in a non-solvent or heated to occur phase separation to show micro porosity. Then interactions were generated between both solvent and non-solvent with the macro molecules. So, in the polymer rich area when nucleates polymer complex is formed, but in polymer free area pores are generated after the solvent has vaporized. In [40] super hydrophobic surfaces were formed using temperature and different solvents. There xylene was used as the solvent for polymer and non-solvent was compared to search for the best one. The research work resulted in several conclusions as methyl ethyl ketone is the best non solvent, Low drying temperature form loose polymer formations and the best achieved water contact angle was 160° . There are various examples for using of membrane casting for the development of super hydrophobic surfaces with combination of other methods such as thermally induced phase separation [41], block polymer system [42] and patterning with photolithography [43]. Although phase separation micro molding seems to be a promising method in formation of super hydrophobic surfaces a lot of parameters should be controlled in this membrane casting method such as solvent, non-solvent, temperature and other conditions for membrane casting. It is a much complex laboratory level method to form self-cleaning surfaces and not suitable for industrial level simple methodology mass productions.

2.10 Micelles

When molecules and ions are in equilibrium with their aggregates in a solution with surfactants, is called micelles. They are formed due to microscopic phase separations. Normally block copolymers constituted with different solubility blocks in solvent form micelles due to the difference in depend. In [44] copolymer system of PtBA and PDMS was used to form a super hydrophobic surface. It was achieved water contact angle of 162° as the best and with silica nano particles even 170° CA was achieved with only 2° sliding angle. But as membrane casting here also CA depends on the used solvents, polymers as well as the humidity level at atmosphere.

2.11 Chemically treated DE as a filler

For many years scientists studied about various methods for developing super hydrophobic surface using diatomaceous earth

Ana B. López, José C. de la Cal and José M. Asua (2016) in [45] conduct a research on highly hydrophobic coating from waterborne latexes. The film formation was carried out at ambient temperature when copolymers of 2-ethylhexyl acrylate and perfluorodecyl acrylate was used the maximum contact angle obtained was 114° . When increase the surface roughness 137° WCA was achieved with increasing perfluorodecyl acrylate (PFDA). PFDA was coated on to latex by spin or spray coating. They reported spray coating was more successful because sprayed particles dried on top of the air film interface covering it completely.

Helanka J. Perera, Bal K. Khatiwada and his colleagues (2016) in [46] prepared super hydrophobic coating using fluoro-silane treated DE. Polyurethane or epoxy was used as the binder. The percentage of fluoro-silane used to treat DE was varied. They obtained a surface with 150° WCA using 20 % loading of particle to coating which as 0.02 ratio of fluoro-silane: DE. Also, they discovered the super hydrophobicity was independent from the binder type. The treatment reduced the specific surface area by restricting the pores. Bhishma R. Sedai, Bal K. Khatiwada and his colleagues (2016) in [47] studied the impact on amount of silane used to treat DE. 3-(heptafluoroisopropoxy)-propyltrimethoxysilane was used as coupling agent. Polystyrene or poly(vinyl acetate) was used as the binder. 1.8 % silane incorporated DE showed 164° WCA. They found that if the particle loading is above 40 %, the WCA is independent from polymer. Also, when the particle loading is increased the more amount of treated DE move to air interface.

Helanka J. Perera, Frank D. Blum and his colleagues (2017) studied the variation of WCA with chain length of alkyl silane which used to treat DE. Polyurethane was used as the binder. Constant adsorption amount was maintained while chain length of silane was varied. When silane chain length was increased, WCA also increased and reached a plateau with chain contains 12 carbon atoms or high. They showed that high chain length allows more ordered packing and ordered packing is critical for super hydrophobic surface, it showed the maximum WCA is around 30 % particle loading in polyurethane binder. Loading higher than 50 % reduced the WCA.

Bhishma R. Sedai, S. Habib Alavi and his colleagues (2017) in [8] conducted a research to study how the morphology of DE particle effects on super hydrophobic properties. The DE was treated with 3-

(heptafluoroisopropoxy)propyltrimethoxysilane and polystyrene was used as binder. Untreated DE consists of disk shape, rod shape and irregular shape. The trend of hydrophobicity with silane amount was different but after 2.4 % adsorption all showed same WCA. The loading to the binder was highly dependant on the morphology. The less dense disk shaped required 30 %, rod shaped 40 % and irregular shape 60 %. Disk shaped DE are more porous so the final conclusion was pores present in the particles were exposed to the air surface interface. Air trapped in their pores made disk DE particles more super hydrophobic.

Nuno M. Oliveira, Rui L. Reis and João F. Mano (2013) in [2] conducted a research to manufacture super hydrophobic surface using DE and modifying surface with plasma treatment. They used 1H,1H,2H,2H-perfluorodecyltriethoxysilane to treat DE and use glass and polystyrene as the substrate. Depending of the substrate material the temperature used for treatment is varied. When super hydrophobic surface is exposed to plasma, the WCA is decreased with time of exposure. This can be used to control the WCA and by exposing controlled area to plasma the certain patterns can be turned into hydrophilic.

Georgios Polizos, Kyle Winter and his colleagues (2014) in [48] focused their study on abrasion resistance of super hydrophobic surface with the size and the shape of DE particle. DE was treated with tridecafluoro-1,1,2,2-tetrahydrooctyl trichlorosilane. Approximately 170° of WCA was obtained. The substrate was subjected to abrasion and its ability to retain super hydrophobic property was observed. A porous surface was resulted from circular DE with poor abrasion resistance. The cylindrical DE particles arrange in a way that retains their pattern and super hydrophobic property. It can withstand around 100 abrasion cycles according to the literature.

3. Conclusion

When considering methods used to manufacture super hydrophobic self-cleaning surfaces within the past couple of decades with all pros and cons it is crystal clear most of them are either costly processes or not suitable for mass industrial process. So it makes adding DE as filler is a simple, cost-effective, industrial method to follow with all the literature and research projects conduct at present all around the world. All advantages were mentioned previously; however, it proves that no matter the material is DE treatment could make it super hydrophobic. So, this suggests using **Chemically treated DE as a filler** is the best method to make a material self-cleaning.

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