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SUPER-HYDROPHOBICITY ON TEXTILES – A REVIEW

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Abstract: *Engineering interfaces with unique chemical, physical and mechanical properties has become a major branch of material science. Surfaces that combine a low surface energy with a high surface roughness, so called superhydrophobic surfaces, are ascribed the greatest potential in terms of their exceptional water repellent properties. Superhydrophobic surfaces have developed great deal of interest among researchers because of their unique ability to shed water off the surface. The two key elements that determine superhydrophobicity are surface energy and surface roughness. Superhydrophobicity is somewhat ambiguously applied to surfaces exhibiting a water contact angle of more than 150°. Surfaces with water and oil repellency have attracted increasing interest for their applications in diverse fields such as self-cleaning paint, sports and outdoor clothing, biomedical layers, integrated sensors, micro-fluidic channels. Such surfaces are usually achieved by the combination of surface geometrical structure and low surface energy chemical compositions.*

Key words: *superhydrophobicity, self-cleaning, nanoparticles, surface energy etc.*

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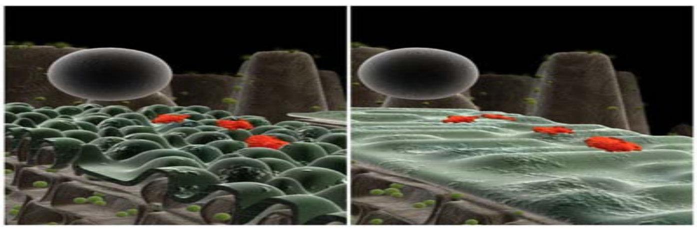
1. INTRODUCTION

Wettability is one of the most important properties of a solid surface and the contact angle has been commonly used to characterize the surface wettability. Superhydrophobic surfaces have attracted much interest because of their potential practical applications such as anti-sticking, anti-contamination, and self-cleaning coating. Attracted by their potential industrial applications, numerous attempts to preparing artificial superhydrophobic surfaces have been done by mimicking the lotus leaf structure. Porous structures, nano-fibers and carbon nanotubes have also been used to develop superhydrophobic surfaces.

1.1. Superhydrophobicity

For many years, people have been attracted by the self-cleaning property of the lotus leaf, and dream to develop man-made superhydrophobic surfaces. Superhydrophobic and self-cleaning surfaces exist widely in nature. Butterfly wings, legs of a water strider and leaves of some plants are good examples. Thanks to the innovation of scanning electron microscopy, today, scientists know the plant's ability to repel water and dirt results from the superhydrophobicity, due to the combination of micrometer-scale hills and valleys and nanometer-scale waxy bumps, in combination with the reduced adhesion between surfaces and particles. A surface with water contact angle large than 150° and a low sliding angle (the critical angle where a water droplet with a certain weight begins to slide down the inclined plate) is usually called a superhydrophobic surface. A combination of low surface energy and adequate surface roughness is necessary to obtain superhydrophobic and superoleophobic surface. High contact angles are achieved by reducing the surface energy of the solid surface and increasing its roughness in an appropriate manner, thus reducing wetting. Techniques involved in developing such surfaces include plasma treatment, chemical etching, chemical vapor deposition, lithography, and so forth.



1.2. Nanomaterials and Nanotechnology

Nano's (Greek) means dwarf and nano-materials are measured in units of nanometer which is 1 billionth of a meter i.e.1×10^{-9} m and involves developing materials or devices within that size. Nanotechnology is defined as the precise manipulation of individual atoms and molecules to create layered structures. Nano size particles can exhibit unexpected properties different from those of the bulk material. Small size of nanoparticles leads to particle – particle aggregation here by making physical handling of nanoparticles difficult in liquid and dry powder forms. The basic premise is that properties can dramatically change when a substance's size is reduced to the nanometer range.

The nano-technological approach starts from producing nanofibers or nanocomposite fibers to nanostructure formation and nano-electronics embedded garments to produce a wide range of smart and intelligent textiles.

Therefore, real applications of such super-hydrophobic surfaces have been very limited so far. Currently, many researches are focusing on super-hydrophobic surfaces. However, oil repellency is also a very important property for the super-hydrophobic surface to maintain its self-cleaning property. If a self-cleaning surface is not oil repellent, when it is in a dirty environment, oily materials can accumulate on the surface, eventually fill the textures, leading to the loss of the super-hydrophobic and self-cleaning properties

2. PRINCIPLE OF SUPERHYDROPHOBICITY

Wetting of a solid surface is dominated by three interfacial tensions and can simply be evaluated by the spreading parameters(S).

$$S = \gamma sv - (\gamma sl + \gamma lv) \quad \text{..................(1)}$$

If the spreading parameter S>0, the liquid tends to spread completely on the solid. While for S<0, the liquid partially wets the solid and forms a spherical cap with a contact angle Θ_C, which is usually used for quantitative characterization of the wetting phenomena (Fig.a).

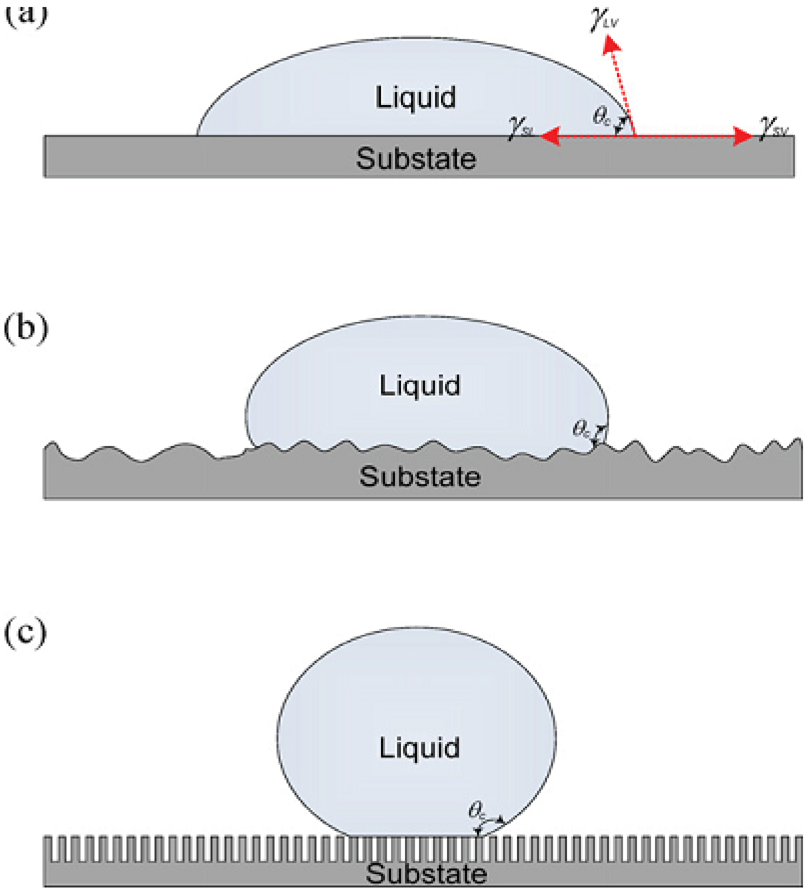


Fig. 2. Wetting behavior of a liquid droplet on solid surface and their mathematical models. (a) A liquid droplet on an ideally flat surface, Young's equation, (b) Liquid droplet on a rough surface, Wenzel model, (c) Vapor pockets are trapped between the grooves and the liquid droplet, Cassie-Baxter model.

The value of the angle is determined by three surface tensions where the chemical potential in the three phases should be at equilibrium. Therefore, the contact angle relationship Θ_C derived by balancing the three tension forces onto the solid surface

$$\text{Cos}\ \Theta c = \frac{\gamma sv - \gamma sl}{\gamma lv} \qquad (2)$$

This is Young's equation for the determination of contact angles.

The case we are specifically interested in is how liquid droplets act on solid surfaces. Hydrophobicity or wettability of a surface **is** often characterized by the static and apparent contact angle measurement of water. If the value of the static contact angle is $0^0 \le \Theta_C \le 90^0$, the liquid tends to spread on the surface. It is usually referred to as hydrophilic or oleophilic surface in terms of aqueous or oily liquid, respectively. If the value of the contact angle is $90^0 < \Theta_C \le 180^0$, the wetting area tends to shrink. It is then referred to as a hydrophobic or oleophobic surface in terms of aqueous or oily liquid, respectively. Surfaces with the water contact angle between 150^0 and 180^0 are usually referred to as super-hydrophobic.

2.1. Classical models for contact angles on rough surfaces

Homogeneous solid–liquid interface: Wenzel model Young's equation is an oversimplified expression, and is only valid for ideally flat surfaces that are atomically smooth and chemically homogeneous. Conversely, very few solids are atomically flat. Wetting on rough surfaces was first considered by Wenzel In the Wenzel state, where the roughness grooves are completely filled with liquid (Fig. 2b), the contact angle (Θ_W) can be described by.

$$\text{Cos}\ (\theta_w) = R_f\,[\gamma_{SV} - \gamma_{SL} / \gamma_{LV}] \ldots\ldots\ldots \textbf{(3)}$$

where R is the surface roughness factor, which is defined as

$$R_f = \text{actual area/projected area} \ldots\ldots\ldots\ldots \textbf{(4)}$$

Combining Eq. (4) with Young's equation yields

$$\cos\ (\theta_w) = R_f.\ \cos\ (\theta_c) \ldots\ldots\ldots\ldots\ldots\ldots \textbf{(5)}$$

Since the roughness factor is always larger than unity in practical situations, it is obvious that the apparent angle on a roughened surface will become smaller if its intrinsic contact angle on a smooth surface is less than 90^0. Similarly, the apparent contact angle will be larger, if its intrinsic contact angle is larger than 90^0.

2.2. Heterogeneous solid–liquid interface: Cassie–Baxter model:

The Wenzel regime is usually recognized as homogeneous wetting, since the liquid completely penetrates into the grooves. Under some circumstances, especially with high surface rough-ness, vapor pockets may become trapped underneath the liquid yielding a composite interface (Fig.2c). This heterogeneous wetting phenomenon is usually described by Cassie–Baxter (CB) theory, from which the apparent contact angle (Θ_{CB}) is given by Eq. (6):

$$\cos\ (\theta_{CB}) = f_s.\ \cos\ (\theta_c) + f_v.\ \cos\ (\theta_v) \ldots\ldots\ldots\ldots \textbf{(6)}$$

where Θ_C is the intrinsic contact angle on the original smooth surface, and f_S and f_v are the area fractions of the solid and vapor on the surface, respectively. Since $fs + fv = 1$, and $\Theta_V = 180^0$ (implying that a suspended liquid droplet in air is a perfect sphere.), Eq. (7) can be rewritten as follows:

$$\cos\ (\theta_{CB}) = f_{s.}\ (\cos\ (\theta_C) + 1) - 1 \ldots\ldots\ldots\ldots\ldots \textbf{(7)}$$

From Eq. (7), it can be found that droplets will have a higher apparent contact angle if less area is in contact with the solid substrate. The CB equation simply indicates the contact angle can be increased even when the intrinsic contact angle of a liquid on the original smooth surface is less than 90^0.

3. APPLICATION TECHNIQUES

Numerous techniques were employed to obtain super-hydrophobic and super-oleophobic surfaces:

- Covalent layer by layer assembly.
- Polymer film roughening.
- Chemical vapour deposition.
- Sol-gel process

3.1. Covalent Layer by layer assembly

Ming, Wu, van Bentham and De With (2005) developed a procedure for preparing Super-hydrophobic films with a dual-size hierarchical structure composed of raspberry-like particles. These particles were silica based with amine-functionalized surface and were chemically deposited on the epoxy films. Another layer of poly (dimethylsiloxane) was grafted on the raspberry-like particles, thus hydrophobic characteristics were achieved. Manca et al (2009) adopted a sol - gel process to produce a double-layer coating consisting of silica nanoparticles with a trimethoxysiloxane-functionalized surface which were partially embedded into an organosilica binder matrix. A glass substrate was used and the treated surface showed super-hydrophobic contact angles.

3.2 Polymer film roughening

This process uses phase separation of a multicomponent mixture as a means to super-hydrophobic polymer films. Franco, Kentish, Perera and Stevens (2008) designed a super-hydrophobic polypropylene membrane by a solvent casting of polypropylene and utilizing the surface roughness and porosity developed with a nonsolvent. Levkin, Svec and Frechet (2009) used the phase dispersion technique where, in situ polymerization of common monomers such as butylmethacrylate, ethylene dimethacrylate in the presence of a pathogenic solvent such as 1-decanol, cyclohexanol and/or tetrahydrofuran resulted in superhydrophobic surfaces with micro- and nanoscale roughness. Yuan, Chen, Tan and Zhao (2009) prepared a stable super-hydrophobic high-density polyethylene (HDPE) surface using ethanol in a humid atmosphere at 5 °C. Zhang et al (2008) created an emulsion copolymerization of acrylates with silicone oligomers. Wool fabric was treated with this emulsion and it exhibited excellent water repellency. Cao et al (2009) fabricated superhydrophobic surfaces with anti-icing properties using a combination of organosilane-modified silica nanoparticles and an acrylic polymer binder. Steele, Bayer and Loth (2008) described a technique of spraying a super-oleophobic coating of ZnO nanoparticles blended with water borne per fluoro acrylic polymer emulsion on practically any surface.

3.3. Chemical vapor deposition

In this method gaseous reactants can be deposited onto a substrate to form a nonvolatile solid film. Zimmerman et al (2008) used one-step gas phase coating a layer of poly-methyl-silses-quioxane nano-filaments onto individual textile fibres. Li, Xie, Zhang and Wang (2007) used a sealed chamber with a saturated atmosphere of trichloro-methyl-silane to deposit on a hydrophilic cotton fabric. Polymerization of Si–OH groups resulted in nanoscale silicone coating rendering superhydrophobicity.

3.4. Sol-gel process

This method synthesizes gels and nanoparticles. Sol-gel method can be easily tuned by varying the method and composition of the reaction mixture. Gan Zhu, Guo and Yang (2009) created hydrophobic cotton and polyester fabrics using sol-gel coating and treatment with hydrolyzed hexadecyltrimethoxysilane. Daoud, Xin and Tao (2004) prepared transparent durable knit/woven cotton substrates using a modified silica sol formed by co-hydrolysed and polycondensed mixture of hexa-decyl-trimethoxysilane, tetra-ethoxy-orthosilicate and 3 glycid-oxypropyl-trimethoxysilane.

They showed this treatment was persistent even after 10 cycles of washing. Yu, Gu, Meng and Qing (2007) used a combination of silica-sol and perfluorooctylated quaternary ammonium silane coupling agent and were applied to cotton fabrics using a conventional pad-dry-cure process. The fabrics were super-hydrophobic after treatment.

4. MATERIALS

Super-hydrophobic coatings can be made from many different materials. The following are known possible bases for the coating:

- Manganese Oxide Polystyrene (MnO_2/PS) nano-composite
- Zinc Oxide Polystyrene (ZnO/PS) nano-composite

- Precipitated Calcium Carbonate
- Carbon nano-tube structures
- Silica nano-coating

5. TECHNICAL APPLICATIONS

Since the Lotus-effect is solely based physico-chemically and is not bound to a living system, a self-cleaning surface can be technically manufactured. The materials for such new coatings are available. Until today, however, the contradictory demand for rough surfaces as a basis for clean surfaces was ignored. Still scientific investigation and industry have made intensive efforts to develop dirt-repellent or self-cleaning surfaces. Some materials allow the production of coatings with hydrophobic and oleo phobic properties. They are thus neither wettable nor can they get oil-slicked, and can be called ultra phobic. Possible fields for application are facade paints, roof tiles, textiles and the rich field of coatings. If application is successfully managed, the Lotus-effect surely is one of the most impressing examples of biomimicy of the last years.

6. CONCLUSION

Nanotechnology holds an enormously promising future for textiles. The development in functional finishes based on nanotechnology has endless possibilities and at present the application of nanotechnology merely reached the straight line. The new concepts exploited for the development of nano-finishes have opened up exciting opportunities for the further research and development. Nanotechnology does not affect other properties of the fabric which gets affected in other types of finishes. Nanotechnology involves a three-dimensional surface structure on the textile surfaces which is very beneficial and does not affect the properties of the substrate like the handle and breathability and does not add more extra weight to the treated textile. When nanosols technology is used for water repellency then finish involves a three-dimensional surface structure with gel-forming additives which repel water and prevent dirt particles from attaching themselves. The mechanism is similar to the lotus effect occurring in nature. With this technology we can achieve super hydrophobic surfaces which are rough and textured.

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