STUDY ON HYDROPHOBIC SURFACES OF TEXTILE FABRIC USING HYDROPHOBIN

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Abstract

Hydrophobin is an organic protein-rich compound and amphipathic membrane that can be produced by filamentous fungi. Textile materials play an important role in everyday life in various forms and they require functional properties to effectively fulfil the purpose of the application to meet the need of the user. Surface wettability properties are one of the key properties that can provide comfort, protection and safety in many textile applications. The surface wettability properties of the textiles, the availability and production of hydrophobin and the application of hydrophobins as a surface coating on textile materials are discussed in this study. Due to the amphipathic nature of hydrophobin, suitable textile materials are considered and testing methods for surface wettability of textiles are briefly discussed.

Key words: hydrophobin hydrophobic hydrophilic textile materials wet ability surface modification

1. Introduction

Textiles applications are categorized based on the end-user requirements to facilitate easiness of the purpose. Ultimately all the users are searching for a high-performance product to enhance the living quality. Hydrophobicity is one of the requirement to achieve water-repellent property in several textile applications such as sportswear, protective clothing, medical, automotive, home, technical and industrial textile applications(Mahltig & Ttcher, n.d.; Park et al., 2015a; Scholtmeijer et al., 2001) to satisfy user expectations. This can be achieved by treatments on the textile surface in means of plasma treatments, hybrid finishing, nano-coating, etc.(Park et al., 2015a; Scholtmeijer et al., 2001) This functional textile should satisfy other required parameters to fulfil the purpose. For example, protective clothing should be capable of protecting the human body, as well as providing other comfort and aesthetic parameters for the human body to wear when they are strong, breathable, lightweight, and more.

There is a significant difficulty in achieving other properties by adding an additional surface finish on the textile that loses other properties. Textile material that can lose tensile strength, air-permeability, abrasion resistance, shear properties and appearance during operation(K. Chowdhury, 2018; Dastjerdi & Montazer, 2010; El Messiry et al., 2015). Failure to meet basic attributes can lead to wastage of the end-use function. Therefore, it is necessary to change the surface of the fabric without interfering with other required properties. Existing studies have been carried out to avoid loss of property while providing another property on textile surface to keep the balance of all required properties. Microporous membranes and coatings, hydrophilic membranes and coating, the combination of microporous and hydrophilic membranes and coating, use of retro-reflective micro beads, ultraviolet irradiation, smart breathable fabrics using shape memory polymers and fabric based on biomimetics are some of the recent research studies to avoid mentioned problems (Mukhopadhyay & Vinay Kumar Midha, 2008; Wei, 2009).

Although the advanced solutions are available, some of the coated materials have non-biodegradable polymers or finishing agents. Complex techniques are widely used to achieve water repellent property by using some of the hazardous chemicals(Williams, 2018). The purpose of this study is to recommend a simple solution without using hazardous chemicals to analyze hydrophobicity of the textile surface without losingnecessary properties. Hydrophobin is selected as a coating material, a lightweight molecular protein that isextracted from a filamentous fungus. It has a bi-functional molecular structure with a hydrophilic and hydrophobic side which contains 100 amino acid molecules having mass around 20 KDa(Hungund et al., 2016; Opwis & Gutmann, 2011). Through research on surface modification of hydrophobin, it is possible to realize the potential solution to avoiding synthetic chemicals that are harmful to the environment and man. It has been found that hydrophobin can provide two-way properties to obtain hydrophilicity and hydrophobicity (Opwis & Gutmann, 2011). This would be a solution to some of the inevitable health problems associated with nano-coated materials with harmful chemicals to achieve these specification characteristics.

2. Surface wet ability in textiles

At current, technical textiles are preferred over traditional textiles due to their characteristics other than the appearance. Each type of end uses such as automotive applications, medical textiles (implants and surgical textiles), geo textiles (textiles used in geotechnical applications), agro textiles (textiles for crop protection), protective clothing (fire, bullet, moths, bacteria, electricity and chemicals) have unique properties to called them as technical textiles. The above applications are prioritising the performance properties than the aesthetic properties. Among the functional performance properties, wettability is taking more applications due to comfort requirement from end user.

Textile surface wettability is the tendency for a water droplet to spread on the fabric surface, which mainly depends on the contact angle of the water droplet and the fabric surface(K. P. Chowdhury, 2018a).Hydrophilicity and hydrophobicity are the two phenomena of the wettability based on the tendency to absorb or repel the water accordingly. Many textiles need the hydrophobicity or hydrophilicity based on the end use application.

The hydrophilicity of a surface is measured by analysing the surface contact angle of the liquid applied on the surface of the material, ass depicted in figure 1. The surface contact angle (θ) is less than 90°as the liquid droplet shown in figure1. (a) then the material is called as hydrophilic while the surface contact angle is higher than 90° as shown in figure 1. (b), the material is called as hydrophobic. But in some cases, the contact angle is much higher than 140°, the surface is called as super-hydrophobic (Liu et al., 2015).

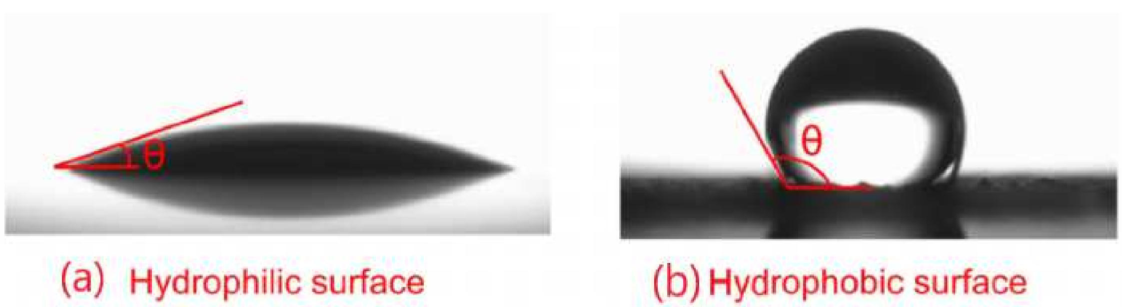

Figure 1:Water contact angle for hydrophilic (a) and hydrophobic (b) surfaces

The young's model and Wenzel's and Cassie-Baxter's models are commonly used to explain the surface wettability principles. Young's model shows the kinetic equilibrium relations of the interface energy of the surface and the water droplets on the flat surface. It assumes that the surface is smooth and explains the relationship of the constant contact angle, the interface tension between the solid and vapour phases, and the interface tension between the liquid and vapour phases(*III. An Essay on the Cohesion of Fluids | Philosophical Transactions of the Royal Society of London*, n.d.). But actual material surface is not smooth and flat.Therefore, Wenzel's and Cassie-Baxter's model can be used for practical scenarios where the surface nature is considered as rough and not flat. Therefore, this model consists of surface roughness and surface free energy as critical parameters in the model(Wenzel, 1936). And this model further says the surface wettability can be determined by chemical structure of the solid material when the liquid is in the contact with solid material. According to this point, the higher interfacial tension is obtained with low surface energy of the material due to high static surface contact angle. This concept is commonly used in the material which needs surface modification for wettability. To reduce the surface energy of the textile material, water repellent agent is coated on textiles to achieve the hydrophobicity property (Park et al., 2015b).

However, another study suggested that the surface contact angle is higher than 65° is considered as hydrophobic surface. In particular, this study mentioned about two forces which are attractive and repulsive forces. Attractive forces appeared when two planes exposed water to contact angle higher than 65°. On the other hand, repulsive forces appear to contact angle less than 65°. Support to this, another research stated that the distinguishing between hydrophilicity and hydrophobicity happens at the contact angle of 62.7° (Guo et al., 2008).

2.1 Necessity of surface modification in textiles

Cotton is a cellulosic fibre which is used in almost all apparel sectors due to its higher moisture regain. This helps the fibre to absorb more moisture and keeps the wearer comfortable. This is the main reason to use cotton as a global fibre material in clothing manufacture. Since cellulosic structure has more hydroxyl links, the cotton absorb more water which is not a desirable property in some cases(Bae et al., 2009). Recently, most of the technical textile's applications need the comfort property as well as the hydrophobicity expected from cotton fibre. Some of the examples are medical bandages, self-cleaning garments, winter clothing, soft packaging materials, etc(K. P. Chowdhury, 2018b; Shi et al., 2013).

Polyester plays another important role in the sports textile due to high packing factor and low tendency to absorb moisture. Not only the active wear but also polyester became an essential part in casual wear since its cheap and light weight(McCann, 2015). Quick drying is one of the key properties of textiles shows high wicking ability over a large surface area which exhibit low water absorbency and low swelling(Bechtold & Pham, 2019). Even though the polyester is avoiding the cold sensation due to heat loss by evaporating sweat during workouts, the human body microclimate will disturb due to this reason (Fujii et al., 2017; Hes et al., 2008). The moisture management should be optimised to keep the microclimate of the body to be constant. Therefore, some of the developments were taken place to overcome this issue. Combination of hydrophilic

fibres with polyester by blending and adding layers of fabrics in the garment were taken place. It gave a huge sustainability issue when recycling the garment. Fibre separation was impossible due to the combination (Dai et al., 2008).
It was reported that 10% and 15% cotton blends are more comfortable than 5% and 20% cotton blends. PC blends reduce texture roughness compared to 100% polyethylene terephthalate. Combinations of PET with thermo regulated outlast viscose gives better wicking ability, but poor drying capability. PC composite yarn spun with profiled PET filament in the core is reported to have higher absorption capacity due to the hydrophilicity of cotton and diffusion rate as compared to PC spun yarn because of the greater siphoning capacity of PET filaments. Fabrics made from cotton–acrylic blended bulked yarns are reported to have better thermal resistance, air permeability and moisture vapour transmission as compared to 100% cotton fabric (Manshahia & Das, 2013)

The above two scenarios were clearly indicating that the necessity of both fibres in different applications but the expected properties in surface wettability is the question to be solved. As an alternative approach, the coating and finishing of textile material surfaces were developed, and this concept allows the blended textile fibre material to be a hybrid structure to allow water transport and water absorption. It is proposed here that the best fabric will have a hydrophobic surface but will allow wicking to promote evaporation and effective cooling. At the same time it is hygroscopic to block the moisture vapour near the skin(He et al., 2019; Senthilkumar et al., 2012; Tausif et al., 2015; Vargas et al., 2018).

2.2 Significance of moisture management properties in textiles

Moisture transmission properties have a higher attention among moisture absorption and the content in textile industry. In case of two layers fabrics, liquid water transmission directly depends on the water absorption of the fibres in inner and outer layers and the difference of water absorbency of them where two types of fibres used to knit two layers separately. Structural features of knitted fabric also affected to the moisture transmission as well as the water absorbability of fibres(Long, 1999). As the heat and moisture transmission shows a significant effect on comfort properties, many research works are focused on that. Comfort property of the fabric can be categorized under the mechanical properties of the fabric. Mr. Morihiro Yonedahas stated "Water absorption perpendicular to fabric plane by capillary action is an important property in clothing comfort and hygiene" in his research on measurement of Water Absorption Perpendicular to fabric Plane in Two- and Multi-layered Fabric Systems(Yoneda et al., 1994). Then he has mentioned that layering fabric was an effective way of controlling water absorption properties in order to design comfortable clothing.

Water vapour permeability rate is an indicator of the wearing comfort property. Knitted fabrics have obvious resistance to water vapour transmission from human skin to environment as water vapour transmission rate apparently influenced by the porosity within the fabric(Long, 1999). Wetting and wicking are two sequential processes for liquid transfer through a porous structure (Manshahia & Das, 2013).

There are two ways of water loss from a human body as water vapour and liquid water. When fabric subjected to hot and humid environment conditions and sweats liquid water deal with the fabric. When wearer engaged in strenuous exercise conditions, generate higher sweat amount and relative humidity can be found high near the skin than away from the body. Then liquid sweat need to transfer through the fabric in order to retain the comfortability hence human rely on the evaporation to feel comfortable and prevent overheating. In case of two layer fabrics, hydrophobic filaments are used in the inner layer with reduced stitch density to obtain higher degree in water transmission (Long, 1999). Hydroscopic fibres which are employed near skin absorb moisture vapour and then desorbs at when it is allowed to evaporate at dry air conditions (Manshahia & Das, 2013). Hydrophobic fibres tend to move the moisture without leaving moisture on skin while hydrophilic fibres absorb moisture vapour. In some situations, evaporation rate may slower than the sweat secretion therefore discomfort generates with the remaining sweat on the skin (Barnes & Holcombe, 1996).

Moisture content and moisture regain are the standard measures which used to indicate the amount of moisture level in materials. Moisture content and moisture regain are the standard measures which used to indicate the amount of moisture level in materials. Moisture content is amount of moisture of the material as a percentage of the total mass of the material. Moisture regain is expressing the amount of moisture as a percentage of oven dry weight of the material.

2.3 Existing surface modification of wettability of textile materials

Globally, there are several textile applications of hydrophobic and hydrophilic textile materials commercialised and sometimes these textiles serve as protective and functional clothing. Recent studies revealed that so many developments, evaluation methods, surface modification techniques are developed with time (Nishimoto & Bhushan, 2013; Vassiliadis, 2011). Naturally varieties of hydrophobic surfaces can be found such as lotus leaf, cicadas wings, water strider legs, etc(Shi et al., 2013). All the above natural material surfaces have low surface energy so that the surface contact angle would be higher and make the surface hydrophobic as mentioned in the Young's model(Huang, 2016).

When developments take place to mimic the nature, people adopt two methods to modify the material surface to achieve wettability. The first method is to apply chemical finish on the surface and the other one is to make the small hierarchical structure to increase the roughness of the surface. When the chemical finish on a textile surface, it will directly affect the air and vapour permeability and the comfortness of the clothing. It will increase the weight of the clothing so that required properties of the clothing will be lost. Some of the chemical finishes which can lower the surface energy are, paraffin waxes, paraffin emulsion, silicone, fluorocarbon, betulin and etc.(Bae et al., 2009; Hagenmaier & Shaw, 1991; Shi et al., 2013). The surface structure texture modification by increasing the roughness is a complex process which will not affect the comfort properties compared to the first method. In order tocreate micro and nano scales texture on textile fabric surface, chemicals such as TiO_2, SiO_2, ZnO, fluorinate silanes etc. are added to the surface. These substances are harmful to the human skin and the waste water after process(Shi et al., 2013). Therefore, a necessity to come up with the sustainable solution is needed to achieve the wettability property in textiles.

3. Recent Developments on surface modification of wet ability of textile materials

Clothing materials are very closely related to the safety and health of the people. Therefore, recent studies are needed on the safety of the materials used the environmental responsibility of the processing methods and the functional compatibility or durability of the developed materials as well as the effects of superhydrophobic textiles. In particular, by reviewing studies on theoretical development and fabrication techniques for creating superhydrophobic surfaces, adequate design techniques for superhydrophobic textile surfaces may be recommended.

In such research, nanoparticles were artificially designed to convert surface free energy or surface hardness by methods such as nano implants or lithography(Bhushan & Chae Jung, 2007; Patankar, 2004). Patankar created a double-sided coarse paraffin wax structure and confirmed that binary structures greatly contributed to the improvement of hydrophobicity. In the study, the size ratio of micro- and nano-scale protrusions and the distance between protrusions were studied as having an impact on hydrophobicity and self-cleaning effects(Patankar, 2004). Similarly, Bhushan & Jung developed a superhydrophobic surface that adjusts the diameter, height and distance of the bumps and declared that column distance, by influencing the closed air pocket, can have a major impact on the binding or unobstructed movement of droplets. On the surface, indicating that super hydrophobicity can be increased by adjusting the distance of the rough structures (Bhushan & Chae Jung, 2007).

The initial development of superhydrophobic textiles was often done by coating the textile surface with a low surface non-energy material to reduce surface energy. Recently, efforts have been made to provide nano-scale hardness on micro-rough fibre surfaces, emphasizing the importance of micro/nano binary structures. To achieve this, textile surfaces are coated or processed with nanoparticles so that nanostructures can be created by self-assembly or surface engraving, while low surface free post-processing adds energy. There are several studies that provide empirical data on the development of superhydrophobic surfaces. In summary, it is clear that the size ratio of micro and nanoscale coarse structures, the vertical and horizontal ratios of surface protrusions, and their geometric shapes affect super hydrophobicity (Huang, 2016).

4. Modification of surface free energy in textiles

Textile structures are not flat, and it has unique surface roughness which can be altered by using different types of yarns, fibres, fabric structure, packing density, etc. These factors can control the wettability of the fabric easily during the manufacturing stage. A study was done using polyethylene terephthalate micrometer filaments to weave a woven fabric and dip coated with siloxane. This combination with surface roughness and with water repellent coating shows the surface contact angle as 170° (Gao & McCarthy, 2008). This is caused by high packed filaments in the fabric structure and air pockets created on surface so that the water and dirt particles are rolled off from the fabric surface.

The chemical application to achieve the hydrophobicity is using the repelling agents which are categorized as pyridine, silicone, and fluorocarbon compound types. Among the repellent agents, silicone and fluorocarbon types are commonly used(Huang, 2016). Surface roughness can be formed by spherical particles using layer by layer assembly method on cotton fabrics by adding polyelectrolyte and silica nanoparticle multilayers and post-treating with fluoroalkyl silane(Wu et al., 2013). A durable fabric suggestion was developed by using toluene with silica nanoparticles containing long hydrophobic alkyl side-chains(Ramaratnam et al., 2008). A hierarchical fabric surface created using TiO_2 nano aggregates using sol-gel method using perfluorodecyltrichloro silane to lower the surface energy of polyester fabric (Xue et al., 2008).

Another method is to achieve the hydrophobicity by forming pillar type particles. Instead of using spherical shapes of nanoparticles, the use of high rates of nanoparticles such as carbon nanotubes (CNT) and nanofilament type graphene was introduced. Multiwall carbon nanotubes were introduced in the coating solution and applied by dip coating method(Huang, 2016). These CNT shows high substantively with fabrics and application also was simple and efficient. Oxidized grapheme also dispersed in the dip solution and applied to an electronic textiles to create hydrophobicity(Shateri-Khalilabad & Yazdanshenas, 2013). Chemical vapour deposition method used on cotton, wool and polyester to produce nano-scale roughness using silicone to make the lotus leaf effect. This produces superhydrophobic textile surfaces which can have high durability during the usage phase(Zimmermann et al., 2008).Similarly, a binary roughness is built on cotton surface using ZnO nanorod by using sol-gel method. On the other hand ZnO nanorod and spherical SiO_2 particles were added to give the higher water repellence and further it explains that the air gap between the nanorod structures is maintained rather than the spherical shapes, making it more difficult to absorb water droplets on solid surfaces so that water droplets can roll easily (Xu et al., 2010).

Surface itching on textile fibres is another successful method to achieve hydrophobicity on textile surface. When the cotton is treated with UV-laser or plasma, the chemical bonds of the treated surfaces are broken and radical groups are formed, resulting in friction and adhesion or physical / chemical deposition. In particular, plasma treatment can be adjusted to hydrophilic hydrophobic wettability according to the types and treatments of the injected gases, such as oxygen, argon, helium, and fluorine(Bhat et al., 2011; Hegemann, 2005; Xu et al., 2010). Another method of obtaining the surface modification is using nano fibres through electrospinning method. This creates a nanolayer on textile surface with nanopores which easily creates the nano scale roughness. This method is successfully used to produce two layers of textile fabric with hydrophobic and hydrophilic surfaces in the face and back sides. Polyacrylonitrile fabric is produced with the same principle to have both properties(Baji et al., 2020). This application was applied on micro-sized lyocell filaments, acetate, fluorinated polyurethane and polystyrene fibres recently (Miyauchi et al., 2006; Szewczyk et al., 2019; Wang et al., 2012).

The conventional modification of the surface of polyester to achieve hydrophilicity by adding strong alkaline treatment at high processing temperatures. Alkaline finishing of polyester fabric with sodium hydroxide changes fabric weight, strength, moisture and aesthetics(Cho & Lee, 2010; Pitchai et al., 2014). Changes in the PET surface have been reported using various techniques such as the chemical introduction of sugar on PET fabric using cyanuric chloride8, protein immobilization on PET film , the application of silk sericin to polyester fabric and cyclodextrin-based finishes for polyester fabric (Natarajan & Moses, 2012).

5. Introduction to hydrophobin

It is an amphipathic protein membrane created by a specific type of filamentous fungi. This substance is composed of 100 hydrophobic amino acids. The selection of this particular chemical substance for this study is that the hydrophobin is having the capability to modify the surface energy of the material surface based on the base characteristics(Opwis & Gutmann, 2011). Countable numbers of research studies were done on hydrophobin application on textiles lately and still the characterization of surface modification in textiles is at the beginner stage. One biggest advantage of the hydrophobin is the bifunctional molecular structure with hydrophilic and hydrophobic sides (Opwis & Gutmann, 2011) as shown in figure 2. This advances the option to use on cotton and polyester surfaces in this study.

Both nature in the chemical substance strongly affect the surface energy of the material surface so that the wettability can be automatically assembled by their properties for self-integration into hydrophilic-hydrophobic interfaces such as water and air, oil or water in water, and solid molecules [56]. Some of the non-textile materials such as glass, polytetrafluoroethylene and polyolefin films were treated by using hydrophobin to modify the wettability of the surface [56], [57]. It is clearly visible that the hydrophobins are controlling the surface forces by reducing or increasing the surface tension.

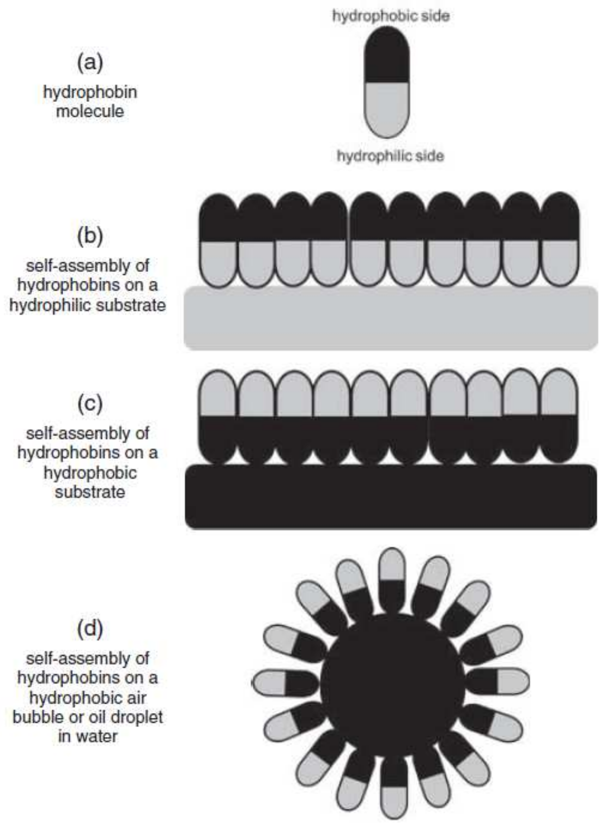

Figure 2:Adhesion and self-assembling of hydrophobins on various hydrophilic and hydrophobic substrates (schematic description).(Opwis & Gutmann, 2011)

5.1 Surface activity of hydrophobin

As said earlier, hydrophobins are amphipathic protein which has distinct hydrophilic and hydrophobic parts. The self-assembly of encapsulating hydrophobic particles or hydrophilic particles as soap in the liquid media is the main chemical characteristic of the hydrophobin. This happens only with low molecular weight chemical substances.

Hydrogen bonds between water molecules give the physical properties of water. External molecules in a drop of water experience a different environment when exposed to air or solids. Water molecules at the interface / surface cannot make positive interactions, and to reduce energy, the system will reduce the number of water molecules that need to interact with the surroundings. One worse effect is that water droplets take on a spherical shape when placed on a hydrophobic support because the ratio of total molecules to surface molecules in a sphere is very low. Any molecule that forms hydrogen bonds has water on one side and no hydrogen on the other bond-forming tendencies on the other hand are solid and move in favour of water or air and water-to-interfaces, thus allowing the drop to propagate. This type of molecule is called an amphibian, and it is a surface because it migrates to the surface and keeps the surface active. It seems that all hydrophobins tend to lower the surface tensionof water by roughly the same degree(Linder et al., 2005).

Other than the surface wet ability properties, hydrophobin is a sustainable chemical substance which is eco-friendly and non-toxic. Therefore, it is commercially available to help farmers to avoid fungus on plants. Other than this, hydrophobins are produced at bulk scale in food and medicine industries. These are produced by using in the fungus Aspergillus nidulans and inserting it into the bacterium Escherichia coli(Scholtmeijer et al., 2004).

According to the solubility of the hydrophobins, they are classified into two categories which are class I and class II. Class I will dissolve in strong acids and class II hydrophobins can dissolve in diluted aqueous solutions or in organic compounds. Trichoderma reesei is a class II hydrophobin and it is the only type of hydrophobin has been produced at good scale. Producing hydrophobins at large scale needs lot of purification stage(Linder et al., 2005). According to past studies, class I hydrophobins are form rod-like structures and class II hydrophobins are forming hexagonally ordered self-assembly structure.

5.2 Assessing the surface wettability of treated fabrics

There are various standardized testing methods for evaluating repellent fabrics, including water and oil repellent and soil, which are offered by several companies: British Standard Institution (BSI); International Organization for Standardization (ISO); American Association of Textile Chemists and Colourists (AATCC). In most cases the pass / fail criteria are not specified within the standard, but rather it is established by individual retailers depending on the product end use and consumer needs. Surface wettability of a textile material is generally, assessed by methods such as moisture regain, water imbibition, drop absorbency, water absorption, vertical-wicking test, water-vapour transmission, and water-repellence index(Madan et al., 1978).

The simplest method of evaluating a superhydrophobic surface is visualization. When water flow is applied to the substrate surface, an intuitive moisturizing behaviour and a self-cleaning phenomenon are observed.However, it is necessary to measure the super hydrophobic property with an accurate resolution of the constant water contact angle. (WCA) and contact angle hysteresis (CAH)(Li et al., 2017).A controlled amount of water droplet is introduced onto the fabric surface and images of the droplet are recorded using a Goniometer system video microscope. These images are used to calculate the contact angle between the water droplet and the fabric surface. To show the water repellence of the fabric, the average value is calculated from several images. Theoretically higher contact angle indicates higher efficiency, the equations are based on better, smoother surfaces and wetting a textile surface is often more complicated than indicated by this method(Williams, 2018).

Rather than going with static tests, textile surface wettability can be easily analysed by using dynamic tests such as spray test (AATCC 22-2001), impact penetration test (BS/EN/ISO 18695:2007 Textiles), rain shower test (BS/EN/ISO 29865:1993), hydrostatic head test (BS/EN 20811:1992 ISO 811:1981 Textiles) and moisture management test (ASTM D1558-10).

6. Conclusion

Hydrophobin is an excellent organic compound and possessesamphipathic property that can be used in the surface modification process for both hydrophobic and hydrophilic materials. The study proves that the fungi are available and can be used to cultivate the hydrophobin substances for bulk production. Since those fungiare used in the food industry, the safety and health concern of textile requirement is also fulfilled. Further this development can be improved, and super hydrophilicity and super hydrophobicity can be obtained after analysing the durability properties of coated fabrics. This will open a new eco-friendly and economical solution for commercial products. However, the release of hydrophobin of filamentous fungusis unclear and the chemical compound is to be further analysed for strong applications in technical textiles.

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