CHAPTER 1

Introduction

Hydrophobic is “water-repelling”. A molecule of something that doesn’t mix well with water, it repels water. Hydrophobic materials are used for oil removal from water, the management of oil spills, and chemical separation processes to remove non-polar substances from polar compounds. The hydrophobic property of solid surfaces is mainly dependent on chemical composition and surface morphology on their surfaces. Many papers have since presented fabrication methods for producing superhydrophobic surfaces including particle deposition, sol-gel techniques, plasma treatments, vapor deposition, and casting techniques. Many efforts have been devoted to the chemical modification of the processes involved in cotton in order to develop industrial products with hydrophobic characteristics. This thesis focused on the superhydrophobicity enhancement on cotton cloth by pretreating with nanoscale inorganic surface layers of $SiCl_4$ followed by 1H, 1H, 2H, 2H-perfluorooctyltriethoxysilane (POTS), dimethyl-dichlorosilane (DMDCS), and stearic acid (SA). In addition, the total contents of the constituents were also determined.

1.1 Hydrophobic

Hydrophobic molecules tend to be non-polar and thus prefer other neutral molecules and non-polar solvents. Hydrophobic molecules in water often cluster together to form micelles. Water on hydrophobic surfaces will exhibit a high contact angle. Chemical groups that tend to make substances hydrophobic include -CH_2- chains and rings (hydrocarbons). These substances lack the ability to form hydrogen bond and their surface free energy is relatively low. Water does not tend to wet hydrophobic surfaces; rather, the droplets stay beaded up with high values of contact angle [1].

Hydrophobic surfaces are often seen in nature as evolutionary survival responses in frogs and spiders. These surfaces do not get wet, but the water curves around them. The breakthrough here is indeed making this possible through mechanical properties, which may make it applicable to packaging. Examples of hydrophobic molecules include the alkanes, oils, fats, and greasy substances in general [2]. Hydrophobicity of any material is its resistance to flow of water on its surface. A material is highly hydrophobic if it resists to flowing water dropped on it and is least hydrophobic if dropped water flows in form of tracks on its surface. The hydrophobic surface is water repellent, in contrast with a hydrophilic surface that is easily wetted [3]. Hydrophobic coatings used mainly in sealed environments that are not exposed to wear or cleaning, such as electronic components and air conditioning heat transfer fins to protect from moisture and prevent corrosion.

After some time virtually all surfaces in a natural environment get contaminated. Cleaning them requires high efforts; additionally, often surfactants are applied with negative effects on the environment. Some years ago many researchers showed that the leaves of several plants are cleaned completely from dust pollutions by a simple rain. Such leaves are called “superhydrophobic”; that is, water droplets form spheres with very little adhesion to the surface and roll off very quickly even at small inclinations. A main characteristic of superhydrophobic surfaces is a roughness on the micro and nanometer scales. Water droplets as well as dirt particles only lie on the tips of these structures. Therefore, contaminating particles develop low adhesion forces to such rough surfaces and can be removed very effectively by rain [4]. Hydrophobicity is usually determined by measuring the contact angle of a water droplet contacting a surface. The angle between the surface and the water meniscus near the line of contact, measured through the droplet, gives an indication of the wettability of the surface.

In 2004, it was found that the wettability of mats made from smaller diameter electrospun fibers was decreased. As might be expected for rough and hydrophobic surfaces, electrospun surfaces showed excellent water repellency. The self-cleaning properties of these surfaces were discovered by Menceloglu *et al.* with a water contact angle of 172º and very low hysteresis being reported. Dust- and stain-resistant surfaces were suggested using poly(bis(trifluoroethoxy)phosphazene) spun fibers. Trifluoroethoxy polyphosphazene was reported to be one of the most hydrophobic polymers;

resistant to oils and having high radiation stability they had obvious applications in biomedical and advanced materials. Ma *et al.* reported the superhydrophobicity of an electrospun block copolymer (poly(styrene-block-dimethylsiloxane)), showing that the water repellency was due not only to the chemistry of the surface and the structure of the fibrous mat, but also to the distinct phase segregated nature of the fibers, Figure 1.1(A). Agarwal *et al.* reported the electrospinning of a range of fluorinated homo- and co-polymers to produce a variety of textured surfaces, Figure 1.1(B). By changing the process conditions fibers ranging from uniform cylinders to globules were formed, with some nano-fibers being connected by micro-particles. Similar morphologies were observed for polystyrene spun fibers, Figure 1.1(E), although it was observed that some of the connecting particles were often removed from the surfaces by water. This problem was solved by spinning a secondary layer of fibers over the initial fiber-particle surface. Block copolymer electrospinning has also been shown to result in fibers having concentric ring or aligned core-shell microphases. These types of fibers, having internal self-assembled structures, may be useful in tuning material properties whilst controlling the external surface chemistry.

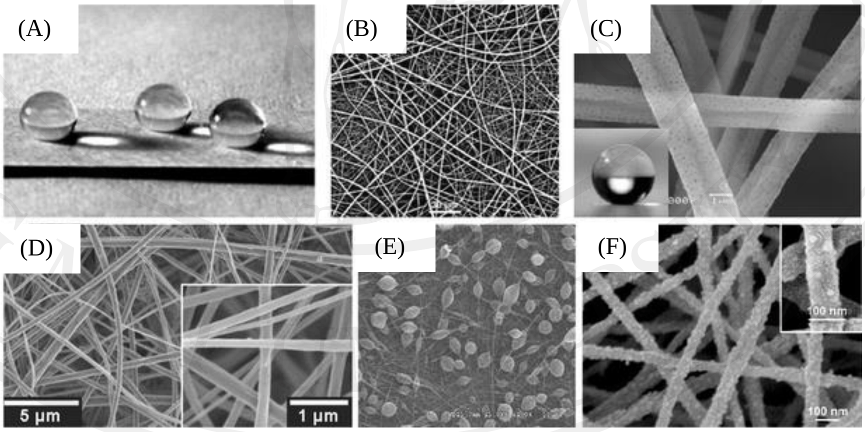

Figure 1.1 Superhydrophobic fiber surfaces: (A) water droplets on a block copolymer electrospun fiber mat, (B) electrospun fluoropolymer mat, (C) porous electrospun fluorinated fibers, (D) cellulose acetate fibrous membrane, and (E) micro-bead connected fibers by elecrospinning [5].

Micro-/nano-porous fibers biologically inspired to imitate the self-cleaning properties of the silver ragwort leaf were formed by carefully controlling the solvent during electrospinning polystyrene. Nanostructured pores were created in the fibers, with fibrous mats having water contact angles of nearly 160º. Ma *et al.* have also shown higher contact angles and lower hysteresis using fibers ‘decorated’ with nanometre-sized pores or particles, Figure 1.1(C). Ogawa *et al.* reported the use of an additional particle layer on cellulose acetate fibers. After electrospinning, the fibers were treated with a layer-by-layer deposition of poly(acrylic acid) and TiO_2 particles and the resulting rough fiber structure was fluorinated to give a superhydrophobic surface, Figure 1.1(D). Secondary coatings to hydrophobise materials are often required, although some have shown that hydrophilic polymers can directly form a superhydrophobic surface. Such surfaces have high contact angles but are not usually “slippy” as the fibers penetrate into the water more than halfway and prevent it from spreading purely by being discontinuous. Other work has led to the inclusion of additives in the fiber-spinning process to vary morphology or to add other properties to the fibers. Zhang *et al.* described the preparation of conductive, magnetic and superhydrophobic carbon nano-fibers, by electrospinning PVA and ferrous acetate. The as-spun fibers were smooth with an average diameter of 180 nm, but after calcination, 20-30 nm diameter Fe_3O_4-filled carbon nano-fibers were formed with ball-like nano-textured surfaces, Figure 1.1(F). The water contact angle on the fiber mats changed dramatically from ~27º on the PVA based as-spun fibers to ~157º when calcined, due to a change in chemistry and topography of the surface [5].

Other objects, aims, and advantages are realized by the present fabrication, which utilizes multilayer deposition technology and chemical immersion method to chemically modify cellulose to yield a wide variety of useful end products. One of the many advantages of the multilayer deposition is that it can deposit any element or compound. Moreover, the delignification process is rapid, environmentally friendly, and energy efficiency.

1.2 Chemical Modification

Chemical modification is the technique of chemically reacting a protein or nucleic acid with chemical reagents. Chemical modification can have several goals, such as identify which parts of the molecule are exposed to solvent, determine which residues are important for a particular phenotype, introduce new groups into a macromolecule, and crosslink macromolecules intra- and intermolecularly.

Hydrophilic and hydrophobic behaviors are due to two key factors: surface energy, a property inherent in the materials, and surface morphology, the micro and nano-scale structure of the surface. A high-energy surface will be driven to reduce the overall energy when coated with a low-energy liquid, driving the liquid to flow out, or have a low contact angle, relative to the surface. A low-energy surface has less need to minimize energy and, in fact, has less energy than most of the liquids wetting it. This surface tries to drive the liquid away, resulting in minimal contact with the surface, or “beading up”, as this behavior is generally described. Hydrophobic coating technologies are more commonly used for self-cleaning applications. The concept is modeled after nature’s hydrophobic materials such as the lotus leaf and other leafy materials. Hydrophobic coatings have a very high contact angle with water. That is, the water tends to bead up on the surface. The beads then tend to roll off the surface, picking up debris as they roll, thus cleaning the surface.

Chemically modified inorganic nanoparticles hold great promise for biomedical applications. In 2014 this review, they examine the recent advances in nanotechnology for targeted drug delivery and controlled drug release. The development of an effective drug delivery system requires good understanding of the chemical and physical properties that affect the interaction of nanoparticles with the biological environment. [6]. Also, chemical modification as a viable alternative to the synthesis of new polymers is a very challenging area of polymer science and technology. It requires the combination of diverse areas of expertise, ranging from the basics of polymer chemistry, reaction kinetics, thermodynamics, and rheology, to knowledge of compounding techniques and polymer processing operations [7]. In 2002 among those efforts, the surface modification of cellulosic fabrics has attracted much attention. The process is primarily to attach the cationic compounds on cotton fabrics by chemical binding or physical adsorption for enhancing the substantively between anionic dye and cotton. Such treated cotton would be dyeable with reactive dyes under neutral or mildly acidic conditions in the absence of electrolyte in the dyebath [8].

Nanosilica is one of the most common nanofillers used in the preparation of nanocomposites. The grafting of organosilane coupling agents on nanosilica surface had been the subject of many investigations in the past. The silane coupling agent can form chemical bond and strong interactions between nanoparticle and matrix. Effectiveness of reinforcement for the polymer depends on the nature of the coupling agent covering the particles surface and the dispersion state of inorganic particles in the polymer matrix. Effective bonding between the filler and matrix component typically by modifying fillers with silane coupling agent improves the mechanical properties of nanosilica polymer composites [9].

But the abundant water-absorbing hydroxyl groups on cotton surface make the fiber absorbent and easily stained by the liquids. Additional finishes are required on the cotton fabrics to make water-repellent and easy-to-clean textiles. Many scientists have demonstrated fabrications of superhydrophobic textiles via anumber of different approaches. For instance, Lihui Xu *et al.* prepared superhydrophobic cotton fabrics by the incorporation of silica nanoparticles and subsequently drophobization with hexadecyltrimethoxysilane (HDTMS), shown in Figure 1.2. The silica nanoparticles were synthesized via sol-gel reaction with methyltrimethoxysilane as the precursor in the presence of the base catalyst and surfactant in aqueous solution. As for the resulting products, characterization by particle size analyzer, scanning electron microscopy (SEM), scanning probe microscopy (SPM), X-ray photoelectron spectroscopy (XPS), and thermal gravimetric analysis (TGA) were performed respectively. The size of SiO_2 nanoparticles can be controlled by adjusting the catalyst and surfactant concentrations. The wettability of cotton textiles was evaluated by the water contact angle and water shedding angle measurements. The results showed that the treated cotton sample displayed remarkable water repellency with a water contact angle of 151.9º for a 5 L water droplet and a water shedding angle of 13º for a 15 L water droplet.

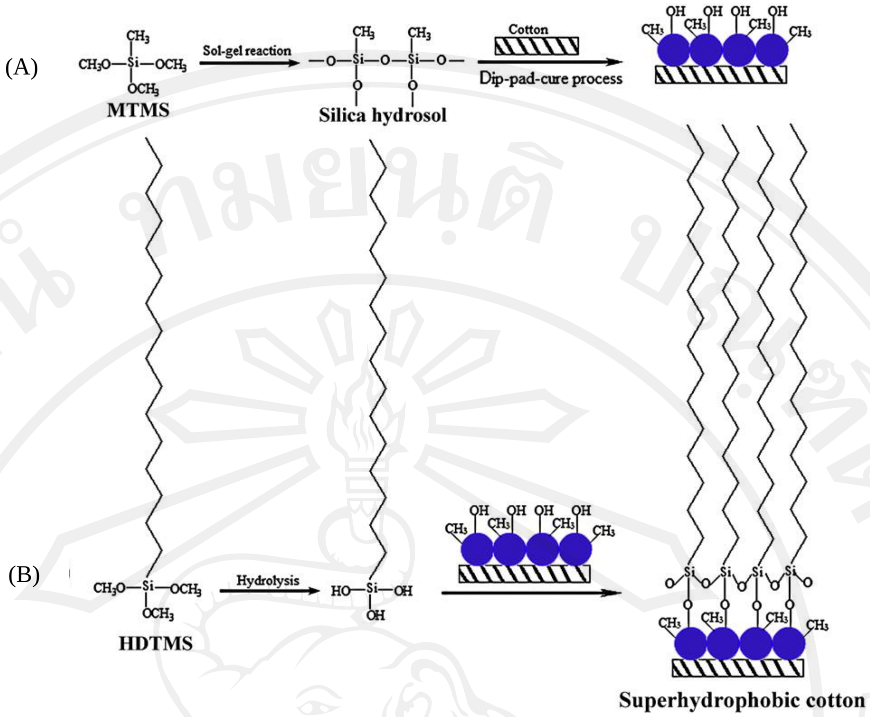

Figure 1.2 Scheme showing (A) the cotton fabric coated by the silica hydrosol and (B) the cotton fabric coated by the silica hydrosol followed by HDTMS modification [10].

Chao-Hua Xue *et al*. fabricated superhydrophobic surfaces by the complex coating of silica nanoparticles with functional groups onto cotton textiles to generate a dual-size surface roughness, followed by hydrophobization with stearic acid, 1H, 1H, 2H, 2H-perfluorodecyltrichlorosilane or their combination (Figure 1.3). The wettability and morphology of the as-fabricated surfaces were investigated by contact angle measurement and scanning electron microscopy. Characterizations by transmission electron microscopy, Fourier transformation infrared spectroscopy, and thermal gravimetric analysis were also conducted.

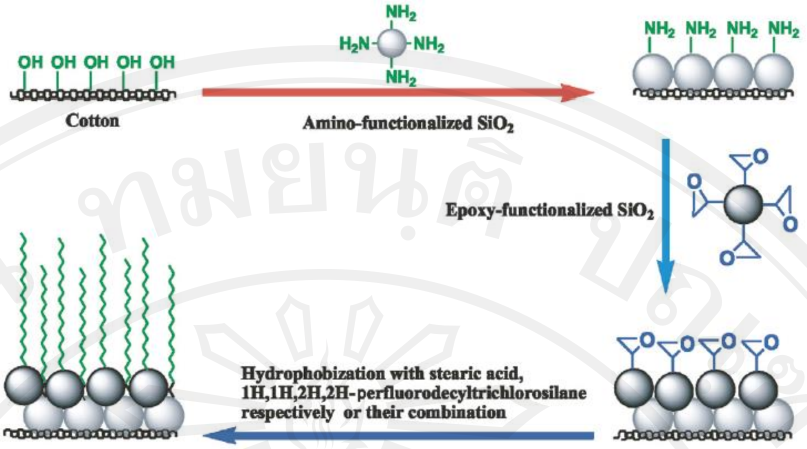

Figure 1.3 Schematic illustration of preparation of superhydrophobicity surfaces on cotton textiles [11].

Meanwhile, chemical vapor deposition and other techniques have been introduced to fabricate super hydrophobic surface on different textile fabrics. Since the discovery of the self-cleaning effect of such things as lotus leaves and insect wings found in nature, superhydrophobic surfaces have received great attention because of their wide range of applications such as frictionless flow water pipes, hydrophobic treatment on vehicle windshields, and superhydrophobic fabrics, etc. It is well-known that superhydrophobic surfaces with self-cleaning properties are caused by the water-repellent double structures of the surfaces. These hierarchical double structures are achieved by the two physical characteristics: surface roughness due to the micro- or nano-structures and hydrophobicity because of waxy materials on top of the rough structures. Thus, to attain superhydrophobic surfaces, modification of surface chemistry is always needed in conjunction with the surface roughness. Recently, roughened surfaces have been commonly obtained by introducing nano-size particles onto the surface. The nano-size particles can be synthesized easily via the sol-gel method. There are several kinds of inorganic nano-size particles such as SiO_2, TiO_2, and ZnO. Surface-modifying chemicals of fluorinated silanes or alkylated silanes have been used to transform the hydrophilic surface of the articles into hydrophobic ones. For practical applications of superhydrophobic surfaces, economic and environmental aspects in treatments of nano-size materials and hydrophobic chemicals have become important parameters. For instance, fluorinated silane used to create a hydrophobic surface of the nano-size particles is too expensive to be applied in general purpose. Furthermore, most fluorinated materials may often cause serious risks for the human health in case of skin contact and for the environment in case of emissions of fluorine during and after the treatment process. Therefore, it is necessary to minimize the usage of fluorinated materials. Recently, as markets in leisure and outdoor sporting textiles have been expanded, the needs for superhydrophobic fabrics have increased. There have been some reports on the improvement of hydrophobic properties of several kinds of fabrics using nanostructures achieved by nanotechnology. Cotton has always been the principal clothing fabric due to its attractive characteristics such as softness, comfort, warmness, biodegradation, and low cost. However the abundant water-absorbing hydroxyl groups on cotton surfaces make the fabrics absorbent and easily stained by liquids. Therefore, additional finishes are required to impart superhydrophobicity and self-cleaning properties on cotton fabrics [12]. In this study, cotton cloths were made hydrophobic by POTS representation of fluorination, DMDCS represent silanization, and SA is the fatty acids.

In this work, hydrophobicity of cotton cloth is going to be improved by multilayer assembly of inorganic and organic layers techniques. In the experiment, firstly, an inorganic layer of silicon tetrachloride ($SiCl_4$) layer will be formed on the cotton cloth surface with various layers using POTS, DMDCS, and chemical immersion using SA. These chemicals deposited on the $SiCl_4$-treated cotton cloth for enhancing its hydrophobic property.

1.3 Cotton

Cotton is a natural fiber and a soft, fluffy staple fiber that grows in a boll, or protective capsule, around the seeds of cotton plants of the genus Gossypium. The fiber is almost pure cellulose. Under natural condition, the cotton balls will tend to increase the dispersion of the seeds. The microsopic appearance of cotton shows in Figure 1.4.

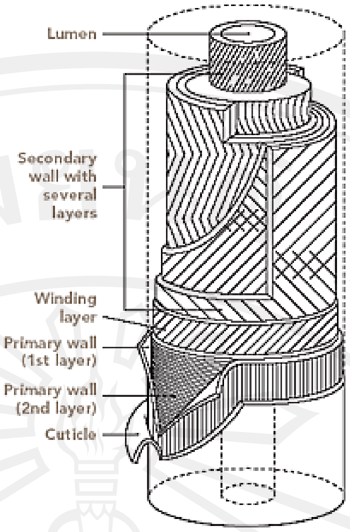

Figure 1.4 Schematic diagram the component layers of the fiber cell wall [13].

Under a microscope a cotton fiber appears as a very fine, regular fiber, looking like a twisted ribbon or a collapsed and twisted tube. These twists are called convolutions there are about sixty convolutions per centimeter. The convolutions give cotton an uneven fiber surface, which increases inter-fiber friction and enables fine cotton. The appearance of the cotton fiber’s cross sections is referred as being kidney-shaped. The chemical composition of typical cotton is 94.0 percent cellulose, 1.3 percent protein, 0.9 percent pectin substances, 1.2 percent ash, 0.6 percent wax (in the primary wall), and 1.9 percent other things, including sugars. The cellulose content of raw cotton varies from 88-96 percent, depending on the variety of cotton, soil, and growing conditions. Cotton that has been scoured and bleached to remove as much of the other materials as possible is about 99 percent cellulose.

Cellulose, the primary component of cotton, is a polymer chain formed of cellobiose (a linkage of two glucose molecules) base units. The cellobiose units form a long, flat polymer chain that exposes a number of hydroxyl groups, bonding sites that allow the polymer chain to form a large amount of hydrogen bonds, as shown in Figure 1.5. Cellulose molecules $(C_6H_{10}O_5)_n$ are essentially polymer chains of β-d-glucose residues covalently coupled via glucosidal linkages.

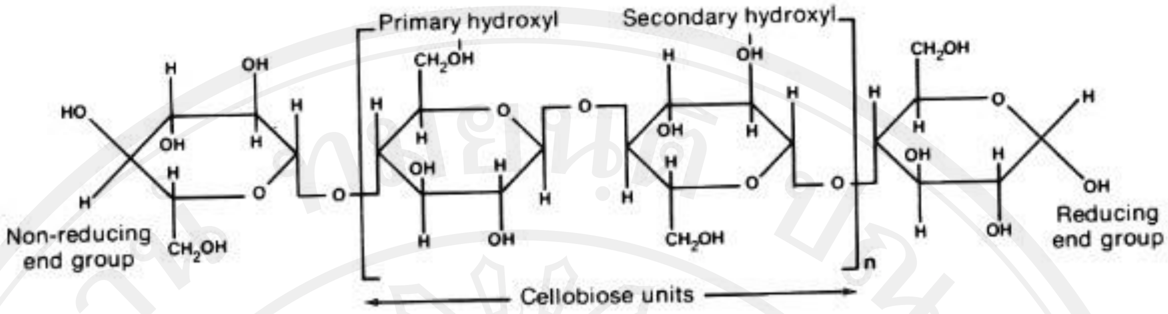

Figure 1.5 Cellulose polymer diagrams [14].

In nature, the cellulose chains are oriented in a parallel structure, creating “microfibrils” within the cell wall. From these basic structures, an entire fiber is assembled, as shown in Figure 1.6.

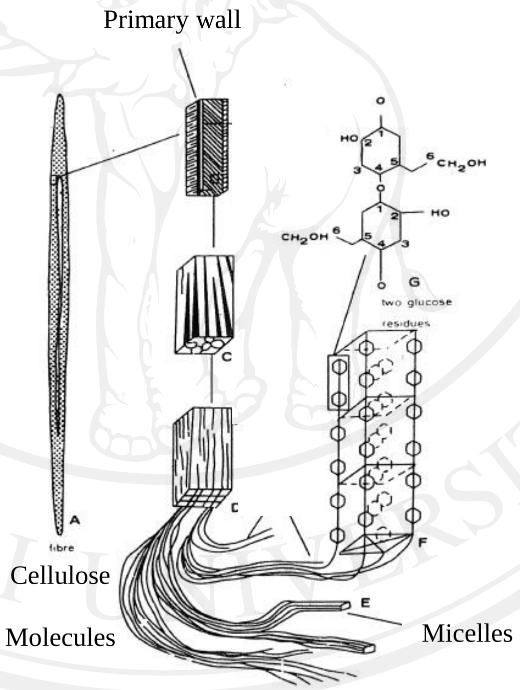

Figure 1.6 Assembly of a cellulose fiber [14].

As seen in this illustration, the cellulose polymer chains that make up the fiber can be quite long, and perfect orientation of these polymers into an entirely ordered, crystalline structure is not possible. The attachments of these species make the cellulose surface more hydrophobic and consequently more compatible with the polymer matrix. However, to link cellulose with these hydrophobic groups the cellulose surface hydroxyl groups are used as reactive sites. For applications primarily based on the cellulose fiber properties, such as paper and cotton cloth, the fiber is rather modified by adsorption interactions or by coating or spraying of the paper or cotton.

The surface chemistry and morphology of the cellulose fibers also restrict its use in a number of important industrial applications. Two important properties essential to all applications and that therefore drive research on the surface modification of paper are wettability and adhesion. Wettability is determined by the contact angle (θ) displayed by a liquid drop on a surface. If the liquid is water, a surface can be classified as hydrophilic ($\theta < 90^{o}$), hydrophobic ($\theta > 90^{o}$), or superhydrophobic ($\theta > 150^{o}$) based on the contact angle values. The wettability of paper surfaces is critical for applications such as printing and packaging. On the other hand, adhesion between fibers or to additives in the paper is critical in determining the internal bonding strength of paper and in making fiber reinforced composites with various polymer matrices [14]. Cellulose fibers can also be modified via mechanical treatments (roughening and polishing), wet chemical treatments, and vapor phase treatments to obtain a variety of surface properties.

The main idea of the increase hydrophobic of cotton cloth in this approach is to obtain new and efficient hydrophobicity. Hydrophobic cotton cloth can be applied to remove oil (organic substance) in water treatments and used to prepare water-resistant food packaging.

1.4 Chemical Modification of Cotton Cloth

1.4.1 Silicon Tetrachloride, $SiCl_4$

Silicon tetrachloride is the inorganic compound with the formula $SiCl_4$. It is a colorless liquid, but if accidentally released to the atmosphere, it may form a visible, fog-like cloud. Silicon Tetrachloride reacts with water, including moisture in the air, to form Hydrogen Chloride or hydrochloric acid and a white residue of SiO_2, or silica (a component of common sand). This residue may become deposited on vegetation, houses, vehicles and other objects downwind of the release point. Pure Silicon Tetrachloride is non-flammable. It is used to produce high purity silicon and silica for commercial applications.

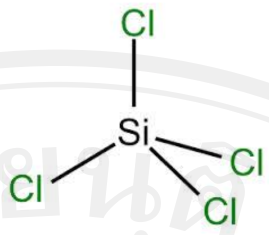

Figure 1.7 The structure of silicon tetrachloride.

Silicon tetrachloride is the starting material for the manufacture of fused silica fiber and sometimes used as an intermediate in the fabrication or purification of silicon. In advanced material fabrication, tetrachlorosilane can be used for the chemical vapor deposition of silicon oxide, nitride or carbide layers.

Table 1.1 Properties of the silicon tetrachloride.

General and Physical Properties	
Molar mass	169.90 g.mol^{-1}
Appearance	Colourless liquid
Density	1.483 g/cm^3
Melting point /Boiling point	-68.74 ºC /57.65 ºC
Solubility in water	decomposes
Solubility	soluble in benzene, toluene, chloroform, ether
Vapor pressure	25.9 kPa at 20 ºC

$SiCl_4$ is hydrolysed via the following reaction. Like other chlorosilanes, silicon tetrachloride reacts readily with water:

$$SiCl_4 + 2\,H_2O \rightarrow SiO_2 + 4\,HCl$$

In contrast, carbon tetrachloride does not hydrolyze readily. The differing rates of hydrolysis are attributed to the greater atomic radius of the silicon atom, which allows attack at silicon. The reaction can be noticed on exposure of the liquid to air, the vapour produces fumes as it reacts with moisture to give a cloud-like aerosol of hydrochloric acid. With methanol and ethanol it reacts to give tetramethyl orthosilicateand tetraethyl orthosilicate:

$$SiCl_4 + 4\ ROH \rightarrow Si(OR)_4 + 4\ HCl$$

1.4.2 1H, 1H, 2H, 2H-Perfluorooctyltriethoxysilane, POTS

1H, 1H, 2H, 2H-Perfluorooctyltriethoxysilane is the hydrophobic reagent with the formula $C_{14}H_{19}F_{13}O_3Si$. It is a colourless volatile liquid. Molecular weight is 510.36 $g \cdot mol^{-1}$.

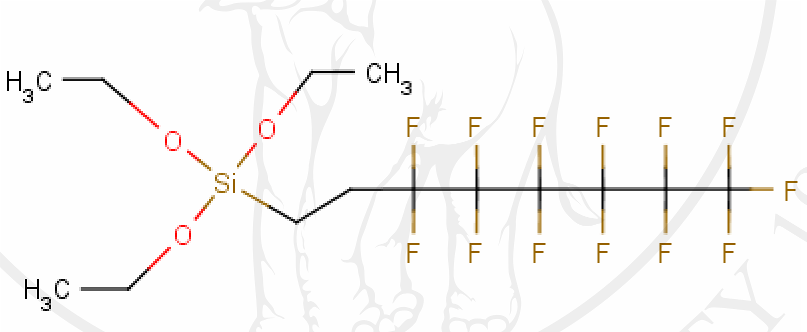

Figure 1.8 The structure of 1H, 1H, 2H, 2H-Perfluorooctyltriethoxysilane.

1.4.3 Dimethyldichlorosilane , DMDCS

Dimethyldichlorosilane is a tetrahedral, organosilicon compound with the formula $Si(CH_3)_2Cl_2$. At room temperature it is a colorless liquid that readily reacts with water to form both linear and cyclic Si-O chains. Dimethyldichlorosilane is made on an industrial scale as the principal precursor to dimethylsilicone and polysilane compounds.

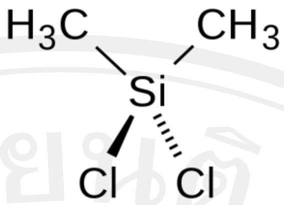

Figure 1.9 The structure of dimethyldichlorosilane.

Table 1.2 Properties of the dimethyldichlorosilane.

General and Physical Properties	
Molar mass	129.06 g mol^{-1}
Appearance	clear liquid
Density	1.064 $g.cm^{-3}$
Melting point	-76 ºC, 197 K, -105 ºF
Boiling point	70 ºC, 343 K, 158 ºF
Solubility in water	Decomposes in water

The main purpose of the applications dimethyldichlorosilane for the synthesis of silicones industry in 2005 was valued at more than 10 billion U.S. dollars per year. It is also employed in the production of polysilanes, which in turn are precursors to silicon carbide. In practical uses, dimethyldichlorosilane can be used as a coating on glass to avoid the adsorption of micro-particles.

1.4.4 Stearic acid, SA

Stearic acid is the saturated fatty acid with an 18 carbon chain and has the IUPAC name octadecanoic acid. It is a waxy solid, and its chemical formula is $CH_3(CH_2)_{16}CO_2H$. The salts and esters of stearic acid are called stearates. Stearic acid is one of the most common saturated fatty acids found in nature following palmitic acid.

Figure 1.10 The structure of stearic acid.

Stearic acid is prepared by treating animal fat with water at a high pressure and temperature. It can also be obtained from the hydrogenation of vegetable oils. Stearic acid is useful as an ingredient in making candles, soaps, and cosmetics and for softening rubber.

Table 1.3 Properties of the stearic acid.

General and Physical Properties	
Molar mass	284.48 g mol^{-1}
Appearance	white solid
Density	0.847 g/cm^3 at 70 ºC
Melting point	69.6 ºC, 343 K, 157 ºF
Boiling point	383 ºC, 656 K, 721 ºF
Solubility in water	3 mg/L (20 ºC)
Refractive index (n_D)	1.4299

Generally applications of stearic acid exploit its bifunctional character, with a polar head group that can be attached to metal cations and a nonpolar chain that confers solubility in organic solvents. The combination leads to uses as a surfactant and softening agent. Stearic acid undergoes the typical reactions of saturated carboxylic acids, notably reduction to stearyl alcohol, and esterification with a range of alcohols.

1.5 Literature Review

Recently, most of the literature concerns the preparation of bulk organic/inorganic composites. Inorganics are much more easily surface modified for a range of applications, such as catalysis, adhesion, wettability, biocompatibility, sensing and protective coating. Quarmyne and Chen [15] fabricated nanoscale inorganic surface layer on three difference polymeric materials consisting of poly(ethyleneterephthalate), PET; poly(4-methyl-1-pentene), PMP; poly(tetrafluoroethylene-co-hexafluoro-propylene), FEP. Firstly, poly (vinyl alcohol), PVOH; was formed on polymeric surface to introduce hydroxyl groups and used glutaraldehyde for cross-linking with PVOH in order to avoid PVOH desorption in organic solvent. Silica and titanium were then reacted with hydroxyl group of PVOH resulting in formation of inorganic layer on polymeric substrate. The processes were summarized in Figure 1.11.

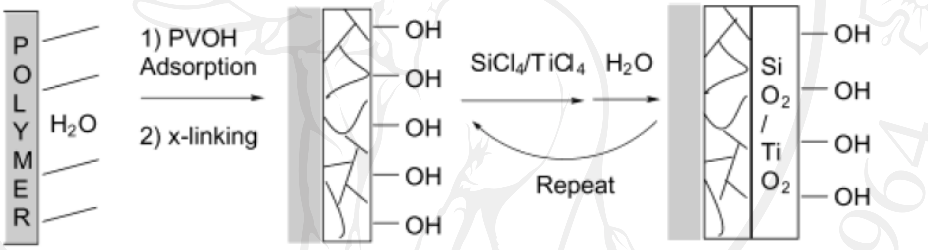

Figure 1.11 Schematic illustration of modification of polymer by adsorption of PVOH at interface of solid/liquid to introduce reactive hydroxyl groups [15].

It was found that the thickness of inorganic film and wettability were controlled by the number of repeating reactions between inorganic species and water. Chaimngoen *et al.* [16] developed superhydrophobic of electrospun PVOH fiber mats. The surface of PVOH fiber mats was firstly functionalized by formation of $SiO_2/SiOH$ and followed by silanization reaction with feeding dimethyldichlorosilane or methyltrichlorosilane in vapor phase. The processes are summarized in Figure 1.12.

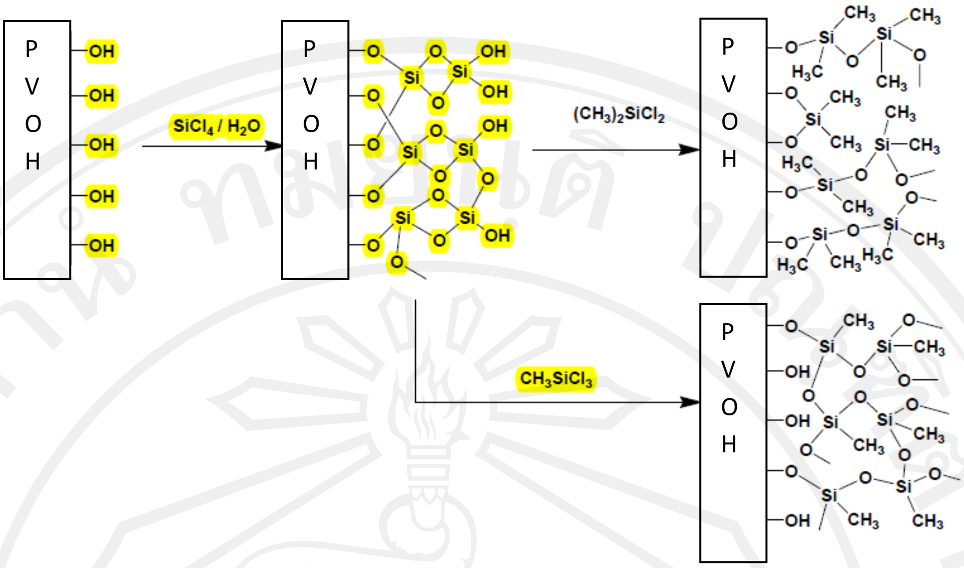

Figure 1.12 Schematic illustration of modification of PVOH fiber mats by silanization [16].

Yang and Deng [17] reported that superhydrophobic paper was developed by using multi-layer deposition of polydiallydimethylammonium chloride (polyDADMAC) and silica particles, followed by coating with 1H, 1H, 2H, 2H-perfluorooctyltriethoxysilane (POTS), in the close system, which is displayed in Figure 1.13.

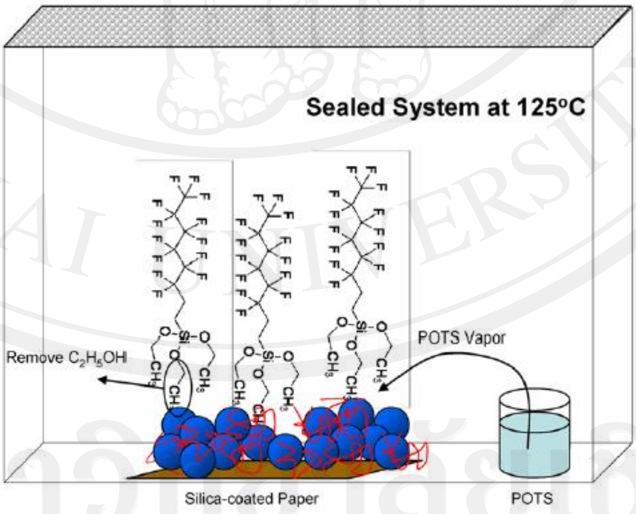

Figure 1.13 Schematic illustration of the surface modification on silica-coated paper surface [17].

It was found that in the superhydrophobic paper showed high hydrophobicity with water contact angle more than 150º and high water repelling property. Moreover, the prepared paper is also anti-bacteria. Wang *et al.* [18] modified a rectangular magnesium substrate to be superhydrophobic by chemical etching technique. The magnesium substrate was functionalized by immersion in sulfuric acid, hydrogen peroxide and ethanol solution containing stearic acid. The modified magnesium substrate obtained was superhydrophobic with water contact angle of 154º and sliding angle of 3º. Moreover, the charge transfer resistance of the modified magnesium substrate was higher than that of the bare magnesium substrate. A layer of flower-like superhydrophobic film was fabricated on pure Mg surface by chemical etching in H_2SO_4, H_2O_2 and subsequent immersion in stearic acid ($CH_3(CH_2)_{16}COOH$) ethanol solution. The superhydrophobic surface showed a static water contact angle of 154º with the sliding angle of about 3º. With scanning electron microscope (SEM), energy dispersive spectroscopy (EDS) and Fourier-transform infrared (FTIR) spectrometer, the microstructure and composition of the sample were analyzed. Results showed that the flower-like structure and the bonding of the $CH_3\,(CH_2)_{16}COO^-$ on Mg surface can be responsible for the superior water-repellent property. Electrochemical impedance spectroscopy revealed that the transfer resistance of superhydrophobic surface was increased about four times than bare Mg after one-hour immersion in 0.1 mol/L NaCl solution.

Bae *et al.* [19] prepared superhydrophobicity of cotton fabrics for self-cleaning. Cotton fabries were treated by silica nanoparticles and water-repellent agent that were found to be an excellent hydrophobic property with contact angle above 130º. Xu *et al.* [20] prepared superhydrophobicity of cotton fabrics by the incorporation of silica nanoparticles and subsequent hydrophobization with hexadecyltrimethoxysilane (HDTMS). They found that the wettability of cotton was hydrophobic property with water contract angle of 151.9º and 13º for water droplet of 5 and 15 μL, respectively. Janhom *et al.* [21] modified cotton fibers by coating PEI for investigation of the adsorption and desorption of lac dye onto cotton fiber. Moreover, they studied the effect of NaCl on dye adsorption and desorption onto cotton fibers for oil removal. As a result, the amount of lac dye adsorbed on cotton fiber increases with the present of NaCl. Alila *et al.* [22] modified cellulose fiber for removal of organic pollutant. The cellulose fiber was treated by using N, N’-carbonyldiimidazole as an activator and amino derivation as a grafting agent. It was found that the adsorption capacity toward organic compound dissolved water was enhanced by the chemical modified fiber.

1.6 Experimental Techniques

Many techniques have been used to characterize the structure and properties of cotton cloth for example; Fourier Transform Infrared Spectroscopy, Scanning Electron Microscopy and Energy Dispersion X-ray Spectroscopy, Water Contact Angle Analysis, and X-ray Diffraction Analysis.

1.6.1 Fourier Transform Infrared Spectroscopy

Fourier Transform Infrared (FTIR) spectroscopy is a technique used to determine qualitative and quantitative features of IR-active molecules in organic or inorganic solid, liquid or gas samples. It is a rapid and relatively inexpensive method for the analysis of solids that are crystalline, microcrystalline, amorphous, or films. Samples are analyzed on the scale of microns to the scale of kilometers and new advances make sample preparation, where needed, relatively straightforward. Another advantage of the IR technique is that it also can provide information about the "light elements" (e.g., H and C) in inorganic substances. FTIR is most useful for identifying chemicals that are either organic or inorganic. It can be utilized to quantitate some components of an unknown mixture. It can be applied to the analysis of solids, liquids, and gasses. The term Fourier Transform Infrared Spectroscopy (FTIR) refers to a fairly recent development in the manner in which the data is collected and converted from an interference pattern to a spectrum. Today's FTIR instruments are computerized which makes them faster and more sensitive than the older dispersive instruments. Infrared (IR) spectroscopy is a chemical analytical technique, which measures the infrared intensity versus wavelength (wavenumber) of light. Based upon the wavenumber, infrared light can be categorized as far infrared (4~400cm^{-1}), mid infrared (400~4,000cm^{-1}) and near infrared (4,000~14,000 cm^{-1}).

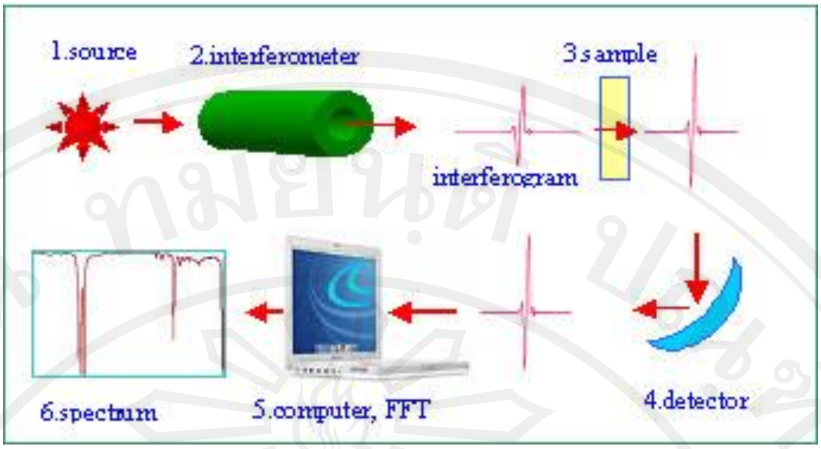

Figure 1.14 Schematic illustration of FTIR system [23]

FTIR can be used to identify chemicals from spills, paints, polymers, coatings, drugs, and contaminants. FTIR is perhaps the most powerful tool for identifying types of chemical bonds (functional groups). The wavelength of light absorbed is characteristic of the chemical bond as can be seen in this annotated spectrum. By interpreting the infrared absorption spectrum, the chemical bonds in a molecule can be determined. FTIR spectra of pure compounds are generally so unique that they are like a molecular "fingerprint". While organic compounds have very rich, detailed spectra, inorganic compounds are usually much simpler. For most common materials, the spectrum of an unknown can be identified by comparison to a library of known compounds. We have several infrared spectral libraries including on-line computer libraries. To identify less common materials, IR will need to be combined with nuclear magnetic resonance, mass spectrometry, emission spectroscopy, X-ray diffraction, and/or other techniques. Because the strength of the absorption is proportional to the concentration, FTIR can be used for some quantitative analyses. Usually these are rather simple types of tests in the concentration range of a few ppm up to the percent level. For example, EPA test methods 418.1 and 413.2 measure the C-H absorption for either petroleum or total hydrocarbons. The amount of silica trapped on an industrial hygiene filter is determined by FTIR using NIOSH method 7602.

Molecular bonds vibrate at various frequencies depending on the elements and the type of bonds. For any given bond, there are several specific frequencies at which it can vibrate. According to quantum mechanics, these frequencies correspond to the ground state (lowest frequency) and several excited states (higher frequencies). One way to cause the frequency of a molecular vibration to increase is to excite the bond by having it absorb light energy. For any given transition between two states the light energy (determined by the wavelength) must exactly equal the difference in the energy between the two states [usually ground state (E_0) and the first excited state (E_1)].

The energy corresponding to these transitions between molecular vibrational states is generally 1-10 kilocalories/mole which corresponds to the infrared portion of the electromagnetic spectrum.

Difference in Energy States = Energy of Light Absorbed

$E_1 - E_0 = h\ c\ /\ l$

Where [h=Planks consant, c=speed of light, l=the wavelength of light]

1.6.2 Scanning Electron Microscopy and Energy Dispersion X-ray Spectroscopy

Scanning Electron Microscopy (SEM) is a means of obtaining high-resolution, three dimensional-like images of solid samples. Variations in the surface topography of a material are depicted as variations in gray level of the image. Dynamic experiments can be documented with the aid of a conventional video recorder. The scanning electron microscope (SEM) uses a focused beam of high-energy electrons to generate a variety of signals at the surface of solid specimens. The signals that derive from electron-sample interactions reveal information about the sample including external morphology (texture), chemical composition, and crystalline structure and orientation of materials making up the sample. In most applications, data are collected over a selected area of the surface of the sample, and a 2-dimensional image is generated that displays spatial variations in these properties. Areas ranging from approximately 1 cm to 5 microns in width can be imaged in a scanning mode using conventional SEM techniques.

Figure 1.15 A typical SEM instrument, showing the electron column, sample chamber, EDS detector, electronics console, and visual display monitors [24]

Energy Dispersive X-Ray Spectroscopy (EDS) extends the usefulness of SEM in that elemental analysis can be performed within regions as small as a few cubic micrometers. EDS is an analytical technique used for the elemental analysis or chemical characterization of a sample. It relies on the investigation of an interaction of some source of X-ray excitation and a sample. Its characterization capabilities are due in large part to the fundamental principle that each element has a unique atomic structure allowing unique set of peaks on its X-ray spectrum.

An EDS spectrum is presented as the intensity of characteristic X-ray lines across the X-ray energy range. A spectrum in a range from 0.1 to about 10-20 keV can show both light and heavy elements because both K lines of light elements and M or L lines of heavy element scan be shown in this range. For example, Fig. 1.16 shows the EDS spectrum of a glass specimen containing multiple elements including Si, O, Ca, Fe, Al and Ba in an energy range up to 10 keV. Even so, EDS is an attractive technique for qualitative analysis of elements.

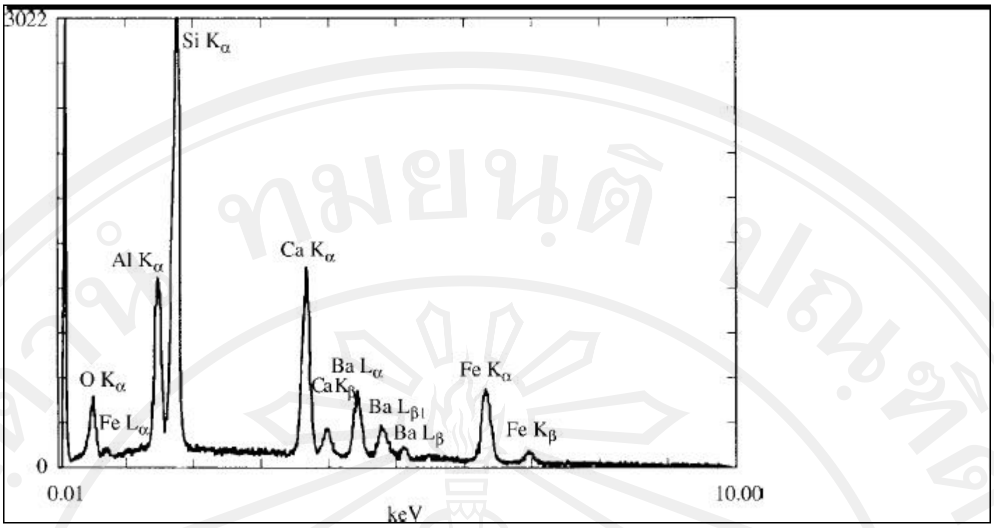

Figure 1.16 EDS spectrum of glass which includes Si, O, Ca, Al, Fe, and Ba [25].

The instrument used in this work was a Jeol JSM-5910LV Scanning Electron Microscope.

1.6.3 Water Contact Angle Analysis

The contact angle is an angle that a liquid creates with a solid surface or capillary walls of a porous material when both materials come in contact together. This angle is determined by both properties of the solid and the liquid and the interaction and repulsion forces between liquid and solid and by the three phase interface properties (gas, liquid and solid). Those interactions are described by cohesion and adhesion forces which are intermolecular forces. The balance between the cohesive forces of similar molecules such as between the liquid molecules (i.e. hydrogen bonds and Van der Waals forces) and the adhesive forces between dissimilar molecules such as between the liquid and solid molecules (i.e. mechanical and electrostatic forces) will determine the contact angle created in the solid and liquid interface. The traditional definition of a contact angle is the angle a liquid creates with the solid or liquid when it is deposited on it. A less traditional definition is the angle a liquid creates with the sides of a capillary when it rises in it to create a meniscus.

Contact angle, θ, is a quantitative measure of the wetting of a solid by a liquid. It is defined geometrically as the angle formed by a liquid at the three phase boundary where a liquid, gas and solid intersect as shown below:

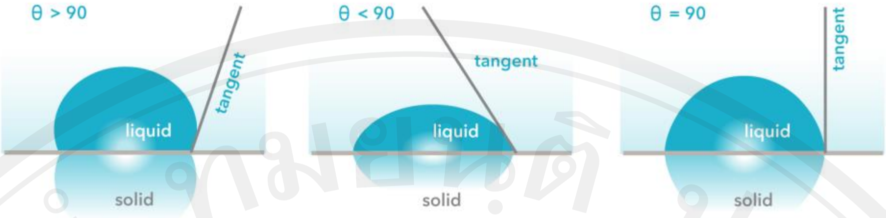

Figure 1.17 Schematic of a liquid drop showing the quantities [26].

Contact angles are extremely sensitive to contamination; values reproducible to better than a few degrees are generally only obtained under laboratory conditions with purified liquids and very clean solid surfaces. If the liquid molecules are strongly attracted to the solid molecules then the liquid drop will completely spread out on the solid surface, corresponding to a contact angle of 0º This is often the case for water on bare metallic or ceramic surfaces, although the presence of an oxide layer, or contaminants, on the solid surface can significantly increase the contact angle. Generally, if the water contact angle is smaller than 90º, the solid surface is considered hydrophilic and if the water contact angle is larger than 90º, the solid surface is considered hydrophobic. Many polymers exhibit hydrophobic surfaces. Highly hydrophobic surfaces made of low surface energy (e.g. fluorinated) materials may have water contact angles as high as ~120º. Some materials with highly rough surfaces may have a water contact angle even greater than 150º, due to the presence of air pockets under the liquid drop. These are called superhydrophobic surfaces.

In surface science, an instrument generally called a contact angle goniometer is used to measure the static contact angle, advancing & receding contact angles, and surface tension. The most frequently used is the goniometer-telescope measurement of sessile-drop contact angles. Commercial contact angle goniometers employ a microscope objective to view the angle directly. In the static method a drop is deposited on a surface and the contact angle can be measured by looking at the drop through a goniometer (an instrument that measures contact angles). The dynamic method is similar to the static one but the drop of liquid which is deposited on a surface is modified. The droplet is being deposited via a syringe and the droplet's volume is changed dynamically without increasing its solid-liquid interface area and this maximum angle is the advancing angle. Volume is then removed to produce the smallest possible angle, which is called the receding angle. The difference between those two measured angles is called contact angle hysteresis.


(A) (B)

Figure 1.18 (A) Surface scientists use a contact angle goniometer to measure contact angle, surface energy, and surface tension (B) The self-made contact angle meter captured image of deionized water and analyzed by using image analysis software [27].

Optical tensiometry can be used in many situations where force tensiometry cannot. You can use a great variety of solid substrates provided they have a relatively flat portion for testing, and can fit on the stage of the instrument. Substrates with regular curvature, such as contact lenses are also easily analyzed. Testing can be done using very small quantities of liquid. It is also easy to test high temperature liquids such as polymer melts.

1.6.4 X-ray Diffraction Analysis

X-ray diffraction (XRD) is one of the most important non-destructive tools to analyze all kinds of matter-ranging from fluids, to powders and crystals. From research to production and engineering, XRD is an indispensable method for materials characterization and quality control. X-ray powder diffraction is a rapid analytical technique primarily used for phase identification of a crystalline material and can provide information on unit cell dimensions. The analyzed material is finely ground, homogenized, and average bulk composition is determined.

Figure 1.19 Bruker's X-ray Diffraction D8-Discover instrument [28]

X-ray powder diffraction is most widely used for the identification of unknown crystalline materials (e.g. minerals, inorganic compounds). Determination of unknown solids is critical to studies in geology, environmental science, material science, engineering and biology.

The methods of X-ray diffraction analysis are used to study, for example, metals, alloys, minerals, inorganic and organic compounds, polymers, amorphous materials, liquids, gases, and the molecules of proteins and nucleic acids. X-ray diffraction analysis has been used most successfully to establish the atomic structure of crystalline substances because crystals have a rigid periodicity of structure and constitute naturally produced diffraction gratings for X-rays. The applicability of X-ray diffraction analysis to the investigation of a broad class of substances and industry’s need for such investigations stimulated the development of techniques for the analysis of structure.

Other applications include characterization of crystalline materials, identification of fine-grained minerals such as clays and mixed layer clays that are difficult to determine optically, determination of unit cell dimensions and measurement of sample purity. XRD can be used to determine crystal structures, modal amounts of minerals (quantitative analysis), characterize thin films samples and make textural measurements, such as the orientation of grains, in a polycrystalline sample.

1.7 Research Objectives

This research work is focused on the hydrophobicity enhancement on cotton cloth by pretreating with $SiCl_4$ followed by POTS, DMDCS, and SA. The main purposes of this study are;

a) To prepare the modified cotton cloth using $SiCl_4$ as a monolayer adsorbate

b) To enhance the hydrophobicity of the modified cotton cloth by chemical modification

c) To characterize the properties and also superhydrophobicity of the modified cotton cloth