# CHAPER I

# INTRODUCTION

Admicellar polymerization is a novel technique for thin film coating on substrates that was invented and patented in the 1980's (Harwell and O'Rear, 1988). Thin film coatings have become increasingly interesting in many areas including microelectronics, composites, and also textiles. Nowadays, coating in nanoscale is important for the development of surface of materials that can improve their properties for a variety of uses. Admicellar polymerization is a more recent technique for nano thin film coating by forming polymer film on substrate surface. Layers of only a few nanometers as analyzed by AFM have been reported for this technique (Yuan *et al*, 2001). The polymer film produced by this technique is made in the water phase without special equipment to polymerize both gaseous and liquid monomers onto many kinds of substrates, porous or nonporous materials, or ionic or nonionic surface materials. This technique has been successfully applied to several types of polymers and many kinds of substrates. In this work a textile material, i.e cotton, was coated by polystyrene film to form hydrophobic cotton.

The commercial water repellent cotton fabric is made by depositing a film of hydrophobic substance on the fabric. Silicone and fluorochemicals are examples of chemical used for this purpose. The common method is to apply a solution of water-repellent agents onto the fabric by the pad-dry-cure process to ensure uniform coating. There are several disadvantages in this method. The machine cost and energy requirement are high, and to ensure uniform coating, a relatively thick film has to be applied making the fabric stiff and heavy. Drawbacks to other methods include poor stability, expensive ingredients and an oily feel. Moreover, some processes raise serious environmental concerns such as the utilization of toxic transition metals.

To develop the good wear feeling of hydrophobic cotton, admicellar polymerization has been expected to give a product that would retain the unique quality of natural cotton and can be used as a water repellent garment product which is comfortable to wear.

In this work cotton, the porous organic substrate, was modified by admicellar polymerization to form very thin film of polystyrene on its surface. The appropriate conditions consisting of pH, counterion concentration, surfactant concentration, and the amount of styrene were investigated for the production of hydrophobic cotton. To complete the study in this work, the thin polystyrene film on cotton was characterized by FTIR, GPC, SEM, AFM, and XPS, and the wettability of the hydrophobic cotton was observed by using the drop test and Wilhelmy method. In addition to improving the film coating, types of initiator and cross-linking agent were chosen to exploit the development of film covering.

The fundamental knowledge for this study involves backgrounds in cotton, surfactant, wettability, and film characterization.
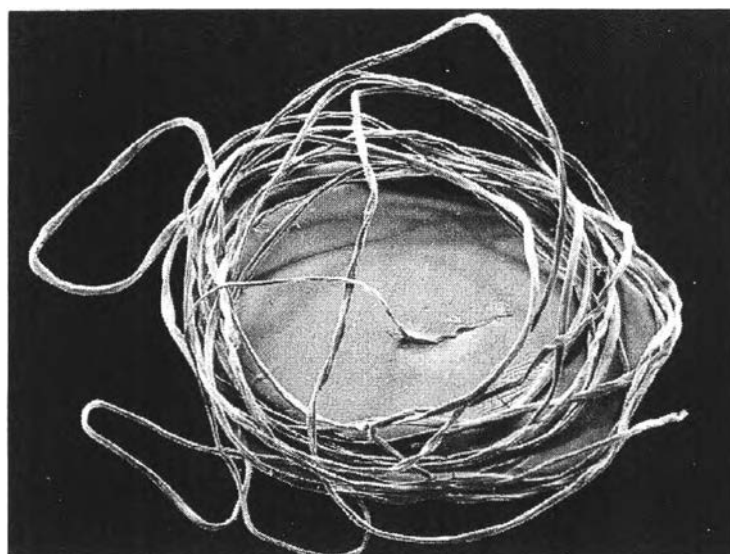
## 1.1 Cotton Fiber

Cotton fiber is the natural fiber from the seed of the plant in the genus Gossypium that is widely grown in warm climates (Grayson, 1984). It is the most important fiber in textile application and has the biggest market share compared with other natural and synthetic fibers. Fabric from cotton is comfortable to wear and can be dyed with a wide range of attractive colors. Its physical and chemical properties are described in the following sections.

### 1.1.2 Physical Properties

The relationship between the structure of cotton fiber and its properties is very important to its unique characteristics. Electron microscopy can create an image of the very small structure of cotton that is difficult to discuss with naked eye. The scanning electron micrograph of a coiled cotton reveals the clear difference between their dimensions, length and width, and the flattened, twisted areas as shown in Figure 1.1a and at a higher magnification of the fiber, the twists and wrinkles can be seen even clearer in Figure 1.1b. Length is the most significant dimension of cotton fiber and it is used to determine its quality and value. An experienced

classifier determines the length by parallelizing typical portions of fibers from pulls drawn from a sample.



(a)



(b)

Figure 1.1 Micrograph of cotton fiber

(http://msa.ars.usda.gov/la/srrc/cotton/cotupcl.html)

Diameter of the fiber is an innate characteristic that can be influenced by the conditions of soil and weather. The fiber dimension can be best observed in cross section of bundles of fine, medium, or coarse fibers. The typical shape has been described as resembling that of the kidney bean; however, the shape ranges from circular to elliptical to linear in most varieties (Grayson, 1984). The cross section of a bundle of cut fibers magnified at high level is shown in Figure 1.2. These fibers are twisted and aligned to form yarns as shown in Figure 1.3, and the yarns are woven into fabric. A typical plain weave fabric is shown in Figure 1.4. From the magnified images, cotton fibers are seen to be like the hollow tubes containing a lot of voids inside its structure to support its light weight and its unique property of good water absorption and air circulation that are the causes for feeling comfortable to wear beside its chemical structure.
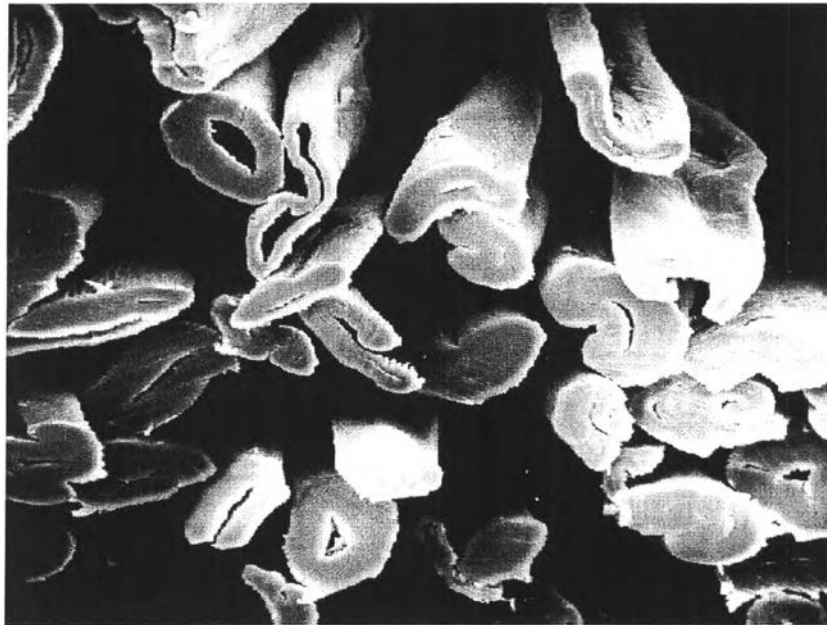
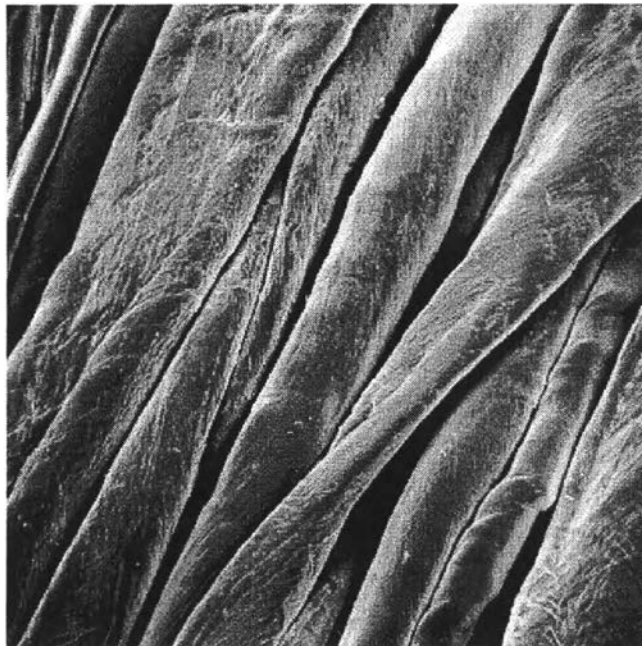

Figure 1.2 Micrograph of cross section of cotton bundle
(http://msa.ars.usda.gov/la/srrc/cotton/cotupcl.html)

Figure 1.3 Micrograph of parallel fibers in yarn of cotton fabric

(http://msa.ars.usda.gov/la/srrc/cotton/cotupcl.html)
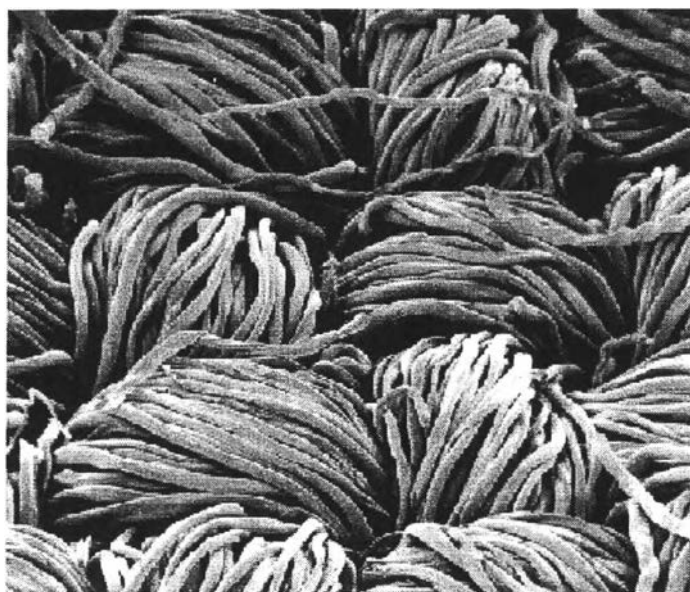


Figure 1.4 Micrograph of cotton fabric

(http://msa.ars.usda.gov/la/srrc/cotton/cotupcl.html)

### 1.1.2 Chemical Properties

Cotton fiber is mostly cellulose, a polymer with a repeat unit molecule of 1,4-D-glucose. Real cellulose may comprise 20,000 or more glucose residues. In cotton fiber, the noncellulosic materials, consisting mostly of waxes, pectinaceous substances, and nitrogenous matter, are located to a large extent in the primary wall; however, cellulose is essentially 95%. The compositions of typical cotton fiber are shown in Table 1.1 (Grayson, 1984).

Table 1.1 Compositions of Typical Cotton Fibers

| Constituent | Composition, % of dry weight | |
| --- | --- | --- |
| | Typical | Range |
| Cellulose | 94.0 | 88.0-96.0 |
| Protein (%N x 6.25)[a] | 1.3 | 1.1-1.9 |
| Pectic substances | 1.2 | 0.7-1.2 |
| Ash | 1.2 | 0.7-1.6 |
| Wax | 0.6 | 0.4-1.0 |
| Total sugars | 0.3 | |
| Pigment | Trace | |
| Others | 1.4 | |

[a] Standard method of estimating percent protein from content (% N).

Most of the pectin substances and wax in the cotton fiber, primarily in its wall, are totally removed by scouring with chemical treatment that does not change greatly the properties of the cotton. Although the cotton fiber, on drying, collapses from its round, never-dried shape (Figure 1.2) and much of its water is removed, moisture is retained intently in cotton. This moisture is expressed either as moisture content, amount of moisture as a percentage of original sample mass, or more commonly as moisture regain, amount of moisture as a percentage of oven-dry sample. Under ordinary atmospheric surroundings, moisture regain in cotton is 7-11% because it has such a high cellulose content.

As with most surfaces with no formal charge, cotton fiber acquires a negative charge when in water (Grancaric *et al*, 1991 and Aspland, 1991). This is a consequence of the fact that cations are usually more hydrated than anions and so have a greater tendency to reside in the bulk aqueous medium, whereas the smaller, less hydrated and more polarizing anions have the greater tendency to be specifically adsorbed (Shaw, 1992). Moreover, cotton also contains a small number of carboxylic acid groups (-COOH) which ionize to produce a negative charge in neutral solution. Bleaching, an oxidizing process normally results in fibers with a greater number of carboxyl groups (Stana-Kleinschek *et al*, 1999). The zeta potential of bleached cotton has been reported to be –16 mV and its point of zero charge is around pH 2–3 (Stana-Kleinschek *et al*, 1999 and Herrington *et al*, 1984).

## 1.2 Surfactant and Admicellar Polymerization

### 1.2.1 Fundamental of Surfactants

Surfactant, a contraction of surface-active-agent, consists of two different structural groups as shown in Figure 1.5. One is the hydrophilic head group and the other is hydrophobic tail group. This structure is known as an amphipathic structure, which causes concentration of surfactant at the surface, reduction of the surface tension of water, and also orientation of the molecule at the surface with its hydrophilic group in the aqueous phase and its hydrophobic group pointed away from the bulk liquid (Rosen 1989). Surfactants are one of the most unique chemical compounds that have the property of adsorbing onto surfaces or interfaces of the system and of altering to a marked degree the surface or interface free energies of these surfaces.

Hydrophilic
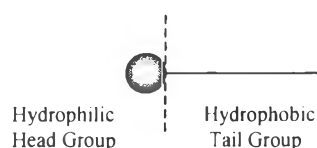Head Group

Hydrophobic
Tail Group

Figure 1.5 A surfactant molecule

In aqueous solution, surfactant molecules nucleate to form micelles at concentrations higher than the critical micelle concentration (CMC). The CMC is a specific characteristic of each surfactant. Surfactants can form at least three different types of aggregates: monolayer called hemimicelle or bilayer called admicelle at liquid-solid interface, micelle in solution, and monolayer aggregates at air-liquid interfaces as shown Figure 1.6.



A: Hemimicelle

B: Admicelle

C: Micelle

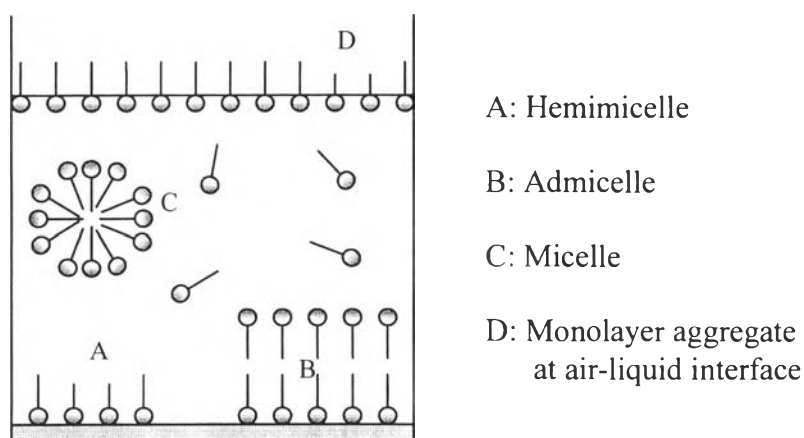D: Monolayer aggregate at air-liquid interface

Figure 1.6 Surfactant aggregates

Surfactant adsorbs onto the solid surface at the interface to form hemimicelle and admicelle aggregates that can be quantified by adsorption isotherm. Surfactant adsorption is one of its singularly important features in an oriented fashion. This property has been studied and applied in many areas, such as detergent to remove soil or dust from clothes and the adsorption polymerization process that has been increasingly utilized in nanocoated film of polymer onto substrates for various purposes.

1.2.2 Adsorption of Surfactant at Solid-liquid Interface

The adsorption of surfactant at solid-liquid interface is strongly influenced by three main factors: (1) the group of natural structure of solid surface — whether the surface contains highly charged sites or essentially nonpolar groupings, and the nature of atoms of which these sites or groupings are constituted; (2) the

molecular structure of the surfactant as the adsorbate — whether it is ionic or nonionic, and whether the hydrophobic group is long or short, straight-chain or branched, aliphatic or aromatic; and (3) the surroundings of the aqueous phase — its pH, its electrolyte content, the presence of any additives such as short-chain polar solutes, and its temperature. These factors can influence the mechanism of adsorption. Generally, there are many types of mechanisms of surfactant adsorption onto substrates involving single ions. These mechanisms consist of ion exchange, ion pairing, acid-base interaction, adsorption by polarization of $\pi$ electrons, and adsorption by dispersion forces (Rosen 1989).

In solid-aqueous system, the adsorption isotherm has been studied to comprehend the behavior of surfactant on solid surface and in solution. The amount of surfactant adsorbed per unit mass or unit area of solid adsorbent is a convenient way to indicate the amount of adsorbent covered in a constant-temperature system. In addition the measurement of surfactant concentration at equilibrium in the liquid phase is also required. The relationship between the amounts of adsorbed surfactant on substrate and surfactant at equilibrium in the liquid phase affect the surfactant formation both on the substrate surface in the form of hemimicelle or admicelle and in the supernatant solution in the form of micelle. This relationship has been plotted to give the adsorption isotherm curve, first reported by Somasundaran and Fuerstenau (1966) in their study of the adsorption of ionic surfactant onto an oppositely charged substrate. The amount of adsorbed surfactant can be calculated from the simple basic equation;

$$n_i^s = \frac{\Delta n}{m} = \frac{(\Delta C)V}{m} \qquad (1.1)$$

where    $n_i^s$ = the number of moles of adsorbed surfactant per gram of solid adsorbant at equilibrium,

         $\Delta n$ = the change in the number of surfactant molecules in solution,

         m = the mass of the adsorbant in grams,

$\Delta C$ = the change of the molar concentration of surfactant in solution,

V = the volume of liquid phase in liters.

From the number of moles of surfactant adsorbate per gram, $n_i^s$, the surface concentration, $C_i^s$, in mol/cm$^2$ of surfactant adsorbate can be calculated when the surface area per unit mass of solid adsorbant ( $a_s$ ), in cm$^2$/g, or the specific surface area is known. The calculation equation is;

$$C_i^s = \frac{(\Delta C)V}{a_s \, x \, m} \tag{1.2}$$

Either $n_i^s$ or $C_i^s$ can be chosen to plot the adsorption isotherm curve. The surface area per adsorbate molecule on substrate, $a_i^s$, in square angstroms, may be calculated from adsorption isotherm curve by the following equation,

$$a_i^s = 2\,x\,\frac{10^{16}}{NC_i^s} \tag{1.3}$$

The $a_i^s$ of completely formed admicelle can be obtained by using $C_i^s$ from the curve at CMC and N is Avogadro's number.

The typical adsorption isotherm curve is shown in Figure 1.7. The curve shows an S-shaped curve that can be divided into four regions by following the change in the slope that is related to the phenomena of surfactant adsorption at the solid interface. Region I is commonly referred to as the Henry's law region because there is a unique slope describing the adsorption under low concentration of surfactant. The equilibrium adsorption is proportional to the surfactant concentration in the solution. It is generally accepted that the surfactant/surfactant interactions are negligible in this region. Region II is characterized by a sharp increase of the slope. This slope of the isotherm indicates a cooperative effect of adsorption with the increase of surface coverage and an enhancement of the affinity of surfactant to the surface. At this concentration the surfactants start to aggregate on the substrate and the changing point from Region I to II is called "Critical Admicellar Concentration or CAC". Region III is characterized by a decrease in slope with the increase of
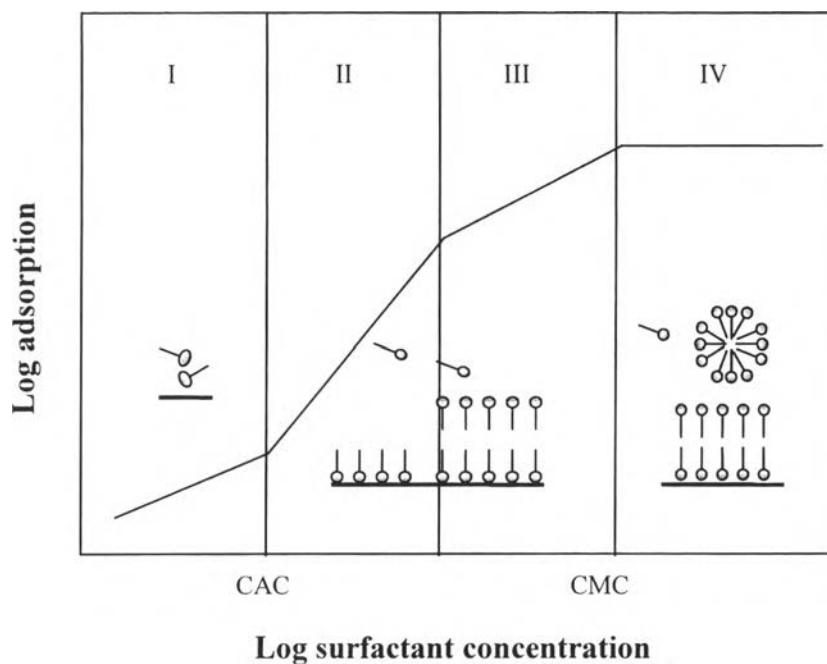
Figure 1.7 A typical adsorption isotherm of surfactant in solution

surfactant adsorption. According to Harwell (1985), a common explanation for adsorption behavior in this region is that with increasing adsorption of like-charged head groups on the surface, they begin to repel each other under the action of coulombic repulsion force. Another fine distinction may be expressed as the more energetic sites offering more favorable adsorption density in Region II than the less energetic sites in Region III. Since beside the electrostatic effect, there is always the hydrophobic interaction effect present in the tail-tail interactions of surfactant in both regions. In the final region, Region IV, the adsorption level is nearly constant while total surfactant concentration increases. In this region, the surface concentration of adsorbed surfactant has reached a saturation point so further addition of surfactant only distributes themselves to the bulk liquid. This plateau adsorption is due to the formation of micelles to account for the excess amount of surfactant added in the system. The concentration where micelle formation begin, or the changing point from Region III to IV, is called the "Critical Micelle Concentration or CMC". Surfactant surface coverage can be limited either by the attainment of CMC below bilayer coverage at low surface charge densities or by the attainment of bilayer

coverage below CMC at high surface charge densities (Scamehorn *et al*,1982). In either case, the adsorbed surfactants reach equilibrium in Region IV where the amount of surfactant adsorption remains constant with further increase in surfactant concentration.

The important parameters for surfactant adsorption are structure of the substrate surface, the molecular structure of surfactant, and the environment of the aqueous phase. The most critical parameter is the pH of the solution, relative to the pH at which the surface exhibits a net surface charge of zero (point of zero charge, or PZC). At pH values below the PZC, the surface becomes protonated and more positively charged; above the PZC the surface is negatively charged. Therefore, anionic surfactants adsorb well below PZC and cationic surfactants adsorb above PZC.

The adsorption of surfactant on substrate in Region III is important for complete admicelle formation on the substrate, particularly in the proper environment of pH and counterion to reduce coulombic repulsion force. The admicelle formation in this region is important as the organic monomer added in the system can transfer from the aqueous phase to its hydrophobic core. The solubilization of monomer into admicelle is called "adsolubilization." In general, the amount of adsolubilization rises with increasing surfactant adsorption and with increasing in the concentration of the adsolubilizate in the supernatant. However, saturation of the surfactant aggregates also occurs. The limiting ratio of surfactant adsorbed on substrates to adsolubilizate for saturated and aromatic hydrocarbon tested approaches values of 2:1. Much higher ratios are seen for alcohols at low coverage of surfactant (Lee *et al*, 1990). Adsorption and adsolubilization phenomena in the solid-aqueous system are fundamental to the admicellar polymerization process.

### 1.2.3 Admicellar Polymerization

Admicellar polymerization is the film-forming process based on admicelle formation. Like the mechanisms of emulsion polymerization from the Harkins mechanism and the Smith-Ewart theory (Dunn, 1997), the reaction of

adsolubilizate or monomer called adpolymerization occurs in admicelle (Wu *et al*, 1987), while polymerization of emulsion polymerization occurs in micelle. The film formation by this technique generally comprises three major steps, admicellar formation, monomer adsolubilization, and polymerization of monomer in admicelle as shown in Figure 1.8.

Step 1- Admicelle formation: Surfactants are adsorbed on substrate surface by controlling adsorption parameters such as pH and salt concentration. The best condition of surfactant concentration is in the Region III of the adsorption isotherm curve, particularly the point just lower CMC, to prevent micelle formation competitively in supernatant and avoid the emulsion polymerization. This process needs complete coverage and high density of admicelle to produce uniform formation of thin polymer film.

Step 2. Monomer adsolubilization:Monomers, nearly insoluble in water, are adsolubilized into the organic-like admicellar interior. This step can be carried out either after the formation of the admicelle or concurrently with surfactant adsorption. The process consisting of adsorption and adsolubilization, or a three-step process, is called "separate adsorption-adsolubilization (SAA)" process, and the process where adsorption and adsolubilization occur simultaneously, or a two-step process, is called "combined adsorption- adsolubilization (CAA)" process.

Step 3. Polymer formation: When the initiator, either ionic or organic matter, is added and heat or light is supplied in the system, the polymerization is accomplished for the in situ formation of very thin film of polymer. In this step, the initiation reaction is started in the aqueous phase as in the case of emulsion polymerization. The condition for the reaction normally relies on the types of initiator. More commonly, the initiators are azo-pompounds or peroxides that are decomposed to radicals through the application of heat, light, or a redox process. Many initiators have been listed and their kinetics and reactive conditions of polymerization described by Moad and Solomon (1995).

1) Admicelle Formation

Surfactant Solution

Solid Substrate
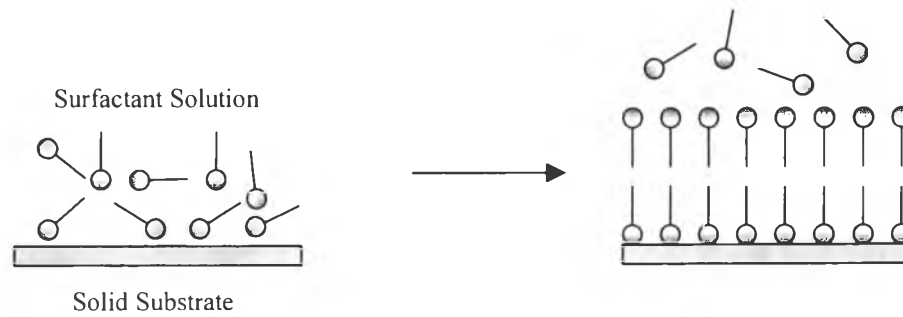
2). Monomer Adsolubilization

3). *In situ* Polymerization
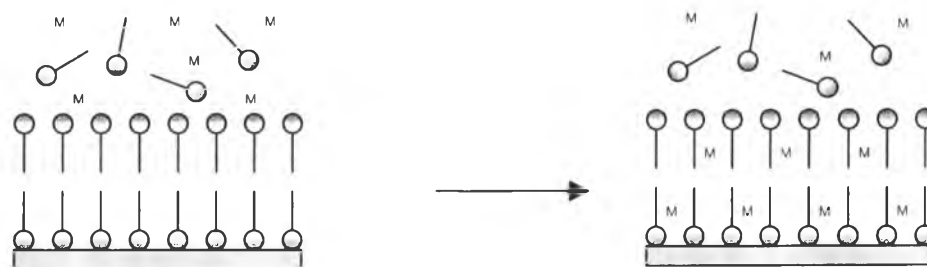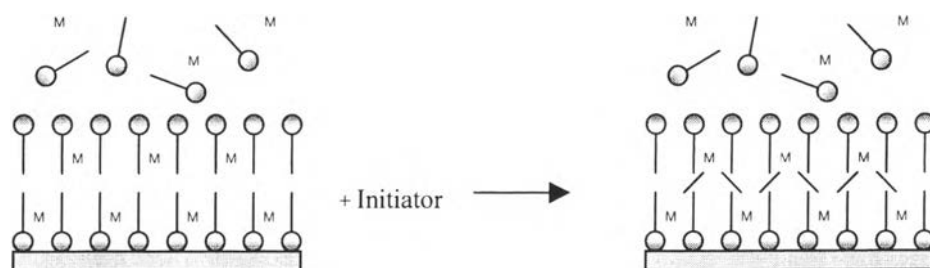
+ Initiator

Figure 1.8 Three-step process of admicellar polymerization

After the polymerization reaction is complete, the upper layer of surfactant could be removed by washing to expose the layer of polymer film on the substrate surface. With the various combinations of surfactant and monomer possible, a great variety of films with desirable characteristics can be obtained. The type of substrate also influences the choice of a surfactant for the system.

From the basic principle of admicellar polymerization, the procedure of this technique as applied to produce hydrophobic cotton in this study is shown in the diagram below:
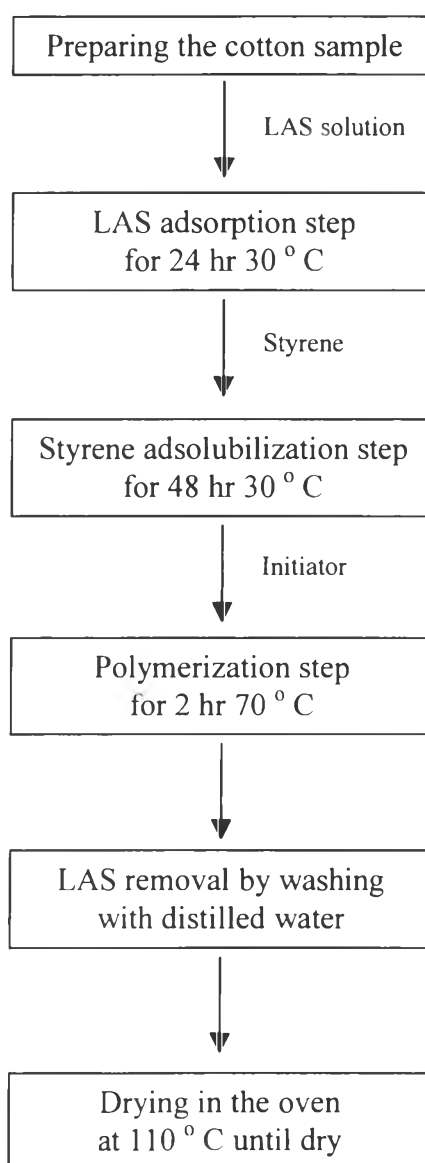
```
        ┌─────────────────────────────────────┐
        │     Preparing the cotton sample     │
        └─────────────────────────────────────┘
                          │  LAS solution
                          ▼
        ┌─────────────────────────────────────┐
        │        LAS adsorption step          │
        │         for 24 hr 30 ° C            │
        └─────────────────────────────────────┘
                          │  Styrene
                          ▼
        ┌─────────────────────────────────────┐
        │    Styrene adsolubilization step    │
        │         for 48 hr 30 ° C           │
        └─────────────────────────────────────┘
                          │  Initiator
                          ▼
        ┌─────────────────────────────────────┐
        │        Polymerization step          │
        │          for 2 hr 70 ° C           │
        └─────────────────────────────────────┘
                          │
                          ▼
        ┌─────────────────────────────────────┐
        │       LAS removal by washing        │
        │        with distilled water         │
        └─────────────────────────────────────┘
                          │
                          ▼
        ┌─────────────────────────────────────┐
        │         Drying in the oven          │
        │        at 110 ° C until dry         │
        └─────────────────────────────────────┘
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Figure 1.9 The procedure of admicellar polymerization
for hydrophobic cotton production

## 1.3 Wettability

Wettability is an important characteristic of materials indicating the hydrophobic or hydrophilic nature of the surface. Repellency or waterproof fabrics can be characterized by the interface characteristic between fabrics and water. Generally, water repellency can be defined as the ability of fabric to resist wetting or penetration by water under test environment. There are a wide variety of traditional methods to quantitatively measure the wettability of textiles. These methods aim at determining the extent to which the material is water-repellent or the degree to which water is not absorbed, with hydrophilicity mainly determined by the competitive effects of spreading among the fibers and absorption within fibers.

To illustrate and identify the wettability of textile, the contact angle and wicking of samples have been used in many researches in which the traditional techniques used for commercial repellent fabrics cannot measure the small differences. The measurements of repellency, traditional and developed techniques, and the wettability analysis are needed for the research to develop water repellent textiles. Some techniques for determining water repellency and wettability analysis are described below.

### 1.3.1 Test Methods for Water Repellency

The repellency test methods of commercial textiles can be divided into three main classes (Kissa, 1984);

*Class I*: Spray tests to simulate exposure to rain.

*Class II*: Hydrostatic pressure tests to measure the penetration of water as a function of pressure exerted by water standing on the fabric.

*Class III*: Sorption of water by fabric immersed in water.

Class I spray and sprinkling tests most frequently used are listed in Table 1.2. Almost all the tests are standard tests of textiles. The simplest and most widely used is the AATCC 22-1977 spray test developed by DuPont Co. This test not

only uses a simple apparatus, but also has the advantage that fabric and garment can be tested without cutting the samples.

Class II hydrostatic pressure tests measure water penetration under pressure, but the test results do not correlate with resistance to penetration by rain. The standard method is the AATCC 127-1977 by a Suter apparatus in which the sample is subjected to water pressure increased at a constant rate by increasing the length of the hydrostatic head (1 cm/sec). Class III absorption tests measure the weight increase of the sample immersed in water. The static absorption test, AATCC test method 21-1987, and dynamic absorption test, AATCC test method 70-1978, have different procedures (Kissa, 1984). Both tests report the weight increase as percent water absorbed to measure the hydrophobicity of the fibers and yarns in the fabric independently of the fabric construction.

There are many other methods developed to identify the wettability such as the vertical wicking test which measures the so-called "Saturated Value", and the determination of the time required for absorption of a certain volume (Drop Test, ATCC), as studied by J. J. De Boer (1980). Alternatively, water absorption by fabric can be observed by photographing the area wetted as liquid spreads from a water droplet placed on the surface (Kissa, 1981). All these are useful to interface study. The drop test is the simplest method to qualitatively identify the hydrophobic fabric by dropping water onto the fabric and measuring the time that the fabric can resist against water absorption inside its masses. In this work the fabric is judged hydrophobic when the time taken to resist the droplet absorbed is greater than 30 min. In addition, the shape of water droplet in contact with fabric surface can be used to identify the characteristic of fabric interface by observing the contact angle of the three-phase connection (Section 1.3.2). The contact angle measurement is used by researchers to study the characteristics of material interface by any of the several techniques (Adamson, 1990). The Dynamic Contact Angle (DCA) measurement, for example, couples slow movement of the three-phase line with a Wilhelmy plate system which uses a highly sensitive balance to determine the interaction forces between the surfaces of a solid and a liquid from which the contact angle can be found. The structure and scale of many porous materials poses a particular challenge to evaluating wettability.

Table 1.2 Water-repellency tests simulating exposure to rain (Kissa, 1984)

| Name of Test | References | | | Drop height (cm) | Water Volume (mL) | Method of evaluation |
|---|---|---|---|---|---|---|
| | AATCC Test Method | German Test DIN | AATCC Technical Manual, Vol 55 (page) | | | |
| Spray test | 22-1977 | | 264 | 15.2 | 250 | Wetting pattern. |
| Impact penetration | 42-1977 | | 262 | 61 | 500 | Water absorbed by blotter. |
| Rain test | 35-1977 | | 259 | 60-140 | | Water absorbed by blotter. |
| Bundesmann test | | 53 888 | | 150 | 0.8 mL/min. cm$^2$ | Water absorbed by fabric; penetration through fabric. |
| Drop penetration | | | | 173 | variable | Time needed for 10 mL water to penetrate. |

### 1.3.2 Interface Characteristic Analysis

The physical aspects of the interface are manifest in the phenomena of wetting and spreading, and measurement of surface free energies and contact angles can give a clearer understanding into the nature and effect of the forces that act at the interface. The majority of the practical applications involving the solid-liquid interface are concerned with two or more components in the liquid phase, and it is therefore necessary to consider the distribution of these components at the interface and the effect of this distribution on the macroscopic phenomena.

Wettability is the important feature to identify interface of material. The static dynamic contact angle and dynamic contact angle are the most well-known methods. By the droplet technique or "sessile drop", the most commonly used method, the contact angle can be directly measured for a drop of liquid resting on a flat surface of the solid as illustrated in Figure 1.9(a). This method can be further modified to study dynamic contact angle by swelling or shrinking the bubble to obtain receding or advancing angles (Adamson, 1990). Furthermore, in early study of liquid dropped on solid, Young in 1805 originally considered the equilibrium of liquid on solid and Dupre put it in mathematical terms in 1869 (Jaycock and Parfitt, 1981). The three-phase equilibrium in Figure 1.9(a) is to consider the forces that exist at the three-phase contact in Figure 1.9(b). Let the contact region move so that an additional square metre ($m^2$) of solid is wetted, then there is a surface free energy increase at the solid-liquid interface ($\gamma^{SL}$), a decrease at the solid-vapor interface ($\gamma^{SV}$) and an increase at the liquid surface ($\gamma^{LV} \cos\theta$ ).

The mathematical formation for contact angle using the three interface forces is given by the Young (or Young-Dupre) equation;

$$\gamma^{SV} = \gamma^{SL} + \gamma^{LV} \cos\theta \qquad (1.4)$$
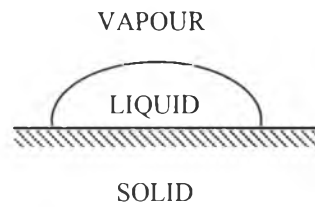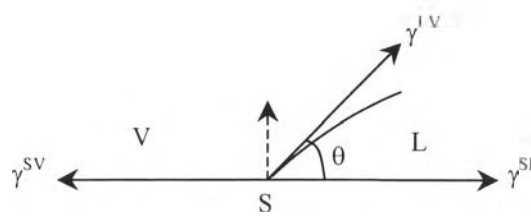
Figure 1.10 The shape of drop of liquid in contact with a solid surface (a)
and the forces that exist at the three-phase contact (b)

Practically, the wettability is presented in the terms of contact angle. If $\theta > 90^\circ$, the liquid does not wet the solid, and strictly only if $\theta = 0$ is wetting considered to occur. This method measures the contact angle in the horizontal direction. In addition, Neumann has developed the Wilhelmy slide technique to obtain contact angles to $0.1^\circ$ precision (Adamson, 1990). This technique measures the contact angle in the vertical direction as shown in Figure 1.10. This method can be simply applied to measure advancing and receding contact angle by moving the plate down and up, respectively.
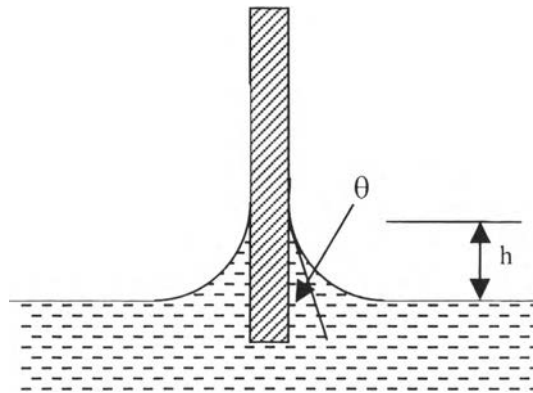
Figure 1.11 Wilhelmy technique

From Figure 1.10, the meniscus at a partially immersed plate rises to a definite height h if θ is finite. The equation is;

$$sin\theta = 1 - \frac{\rho g h^2}{2\gamma} = 1 - \left(\frac{h}{a}\right)^2 \qquad (1.5)$$

where ρ and γ are density and surface tension of liquid, h is the liquid distance climbing the surface of solid plate, and g is the gravitational acceleration, whereas a is the capillary constant.

However, the contact angle of smooth solid surface is difficult to reproduce in different laboratories. This arises is from the preparation of solid surface that is very important to a subsequent determination of contact angle. The effects of wettability measurement not only depends on temperature, but also on the nature of the solid surface particularly the roughness and heterogeneity of the surface. From these surface properties, the contact angle hysteresis, the different values of advancing and receding contact angles, is well demonstrated (Adamson, 1990).

In textiles and powders, the phenomenon of capillary rise will occur in the wettability tests. The wicking method has been applied in these porous materials. The wicking is the displacement of a material-air interface with a material-liquid interface by the spontaneous flow of a liquid into the porous substrate, driven by

capillary force (Kissa, 1996). Capillary flow in textile and other porous substrates has been examined by several techniques and a mathematical model of capillary flow has been applied to help interpret the effects of geometrical and material parameters (Rajagopalan *et al*, 1989). The kinetics of capillary rise usually follows the Lucas-Washburn equation that is noted for textile and porous material (Washburn, 1921). This equation can be used to estimate the contact angle by observing the wicking rate from following the distance liquid travels inside the porous solid as a bundle of round capillary tubes shown in Figure 1.11 and the cross section of bundle of arranged cylinders in Figure 1.12.

The Lucas-Washburn equation is shown below:

$$\frac{dh}{dt} = \frac{r\gamma_L}{4\eta h}\cos\theta + \frac{r^2\rho g}{8\eta}\cos\beta \qquad (1.6)$$

where h is the distance traveled by the liquid from the reservoir, r is the effective pore radius, $\eta$ is the viscosity of liquid, $\beta$ is the angle between the direction of flow and the gravitational acceleration g. When penetration is horizontal ($\beta = 90^0$) or when r is very small ($\leq 10$ µm), the second term in equation 1.6 can be ignored, leaving:

$$\frac{dh}{dt} = \frac{r\gamma_L}{4\eta h}\cos\theta \qquad (1.7)$$

The integration subject to the initial conditions in which h = 0 at t = 0 gives:

$$h^2 = \left(\frac{r\gamma_L}{2\eta}\cos\theta\right)t \qquad (1.8)$$

The equation to calculate the contact angle from Wilhelmy technique is:

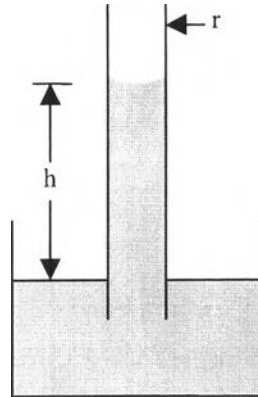$$\cos\theta = \frac{h^2}{t} x \frac{2\eta}{r\gamma_L} \qquad (1.9)$$
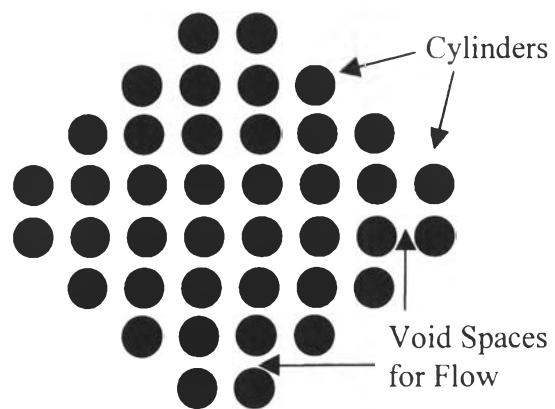
Figure 1.12 Capillary rise



Figure 1.13 Cross section of bundle

Assuming a uniform cross section area, A, of a bundle of sample, equation 1.9 can be expressed as follows:

$$cos\theta \quad = \quad \frac{w^2}{(A\rho)^2 t} x \frac{2\eta}{r\gamma_L} \qquad\qquad (1.10)$$

or

$$cos\theta \quad = \quad \frac{w^2}{t} x \frac{\eta}{\rho^2 \gamma_L C} \qquad\qquad (1.11)$$

where C is the dimension constant of the sample. Equation 1.9 is the most commonly seen form of Washburn equation. The term $w^2/t$ is obtained from experimental data by observing the wicking rate with electronic microbalance (Chen and McMorran, 1999).

## 1.4 Film Characterization

Characterization of unmodified surface of a solid is important for assessing the change in the modified surface. Moreover, it is desirable to carry out qualitative and quantitative analysis of the polymer coating on the surface. There are many analytical instruments to identify the types of polymer covering, to measure the amount of covering, and to study the morphology of modified solid surface.

### 1.4.1 Polymer Characterization

In general, molecular weight is one of the basic properties of polymer that needs to be investigated. Gel permeation chromatography (GPC) (Cooper, 1989) is the analytical technique that can be used for the determination of average molecular weight (MW) and molecular weight distribution (MWD) of polymer.

To identify the types of polymer, infrared (IR) spectrophotometer and ultraviolet (UV) spectrophotometer are common techniques that can be used. The other more advanced techniques for identification are mass spectrometry (MS), NMR spectrometry, etc., (Sandler *et al*, 1998, and Silverstein *et al*, 1991).

IR spectrophotometer is reasonable in cost and easy to use. Its resulting signals are also easy to interpret to determine the types of polymer. Its signals involve the absorption of electromagnetic radiation in the infrared region of the spectrum, which results in the changes in the vibrational energy of molecule. All molecules have vibrations in the form of stretching, bending, etc., which absorb the energy levels associated with these. From these results, each and every functional group has its own vibrational energy, the IR spectra can be seen as their fingerprints. A newer technique named Fourier Transform Infrared (FTIR) spectroscopy is becoming increasingly important. This technique has the instrumentation similar to the previous one, but it combines a computerized mathematical manipulation known as "Fourier Transform" performed on the data at each wavelength.

### 1.4.2 Solid Surface Characterization

Characterized surface can be obtained by morphology study to illustrate the surface feature in very small scale, nano-scale levels, through specialised techniques that are the advanced microanalysis techniques. The information can be accomplished by light transmitted or reflected from matter such as Scanning Electron Microscopy (SEM) Transmission Electron Microscopy (TEM), etc, or by probe scanning technique measuring the surface on the atomic scale such as Atomic Force Microscopy (AFM), Scanning Tunneling Microscopy (STM), etc. The instrumentation of all these techniques is complicated. SEM and AFM are the two popular techniques used for morphology study.

In SEM technique, an electron beam is focused onto the sample surface kept in a vacuum by electron-magnetic lenses. The beam is then rastered or scanned over the sample surface. The scatted electron from the sample is then fed to the detector and then to a cathode ray tube through an amplifier, where the images formed give the information of the surface of the sample. The sample should be conducted or coated with a thin layer of gold for SEM For AFM, a sharper probe, or a very fine, is used to scan the surface of the sample with much lower force to obtain the topography and morphology information (Miles, 1994).

Nowadays, X-ray Photoelectron Spectroscopy (XPS) is also an important surface characterization technique used to identify the elements or chemical compound on solid surface. This technique can be used for both qualitative and quantitative analysis. The instrument consists of a radiation source of primary X–ray, a monochromator, an energy analyzer (to resolve the electrons generated from samples by energy), and a detector (to measure the intensity of the resolved electron). This technique is mostly referred to as Electron Spectroscopy for Chemical Analysis (ESCA) to study the ejected electrons. For the qualitative identification, the chemical environment around the atoms, based on the chemical shifts, can be estimated to determine the valence states of atoms present in various moieties in a sample. Quantitative measurement can be made by determining the intensity of the ESCA lines of each element (Desimoni and Zambonin, 1993, and Briggs, 1994).

## 1.5 Surface Area Measurement

The experimental methods to determine the surface area of porous material can be done by applying the Brunauer-Emmett-Teller (BET) theory. This method measures the volumetric adsorption of an inert gas on the surface and is called volumetric method. However there are other two methods, one monitors the adsorption by gravimetric means and the other employs the continuous flow of an inert gas and adsorbate through an adsorbent bed. They are called the gravimetric method and the dynamic method respectively.

In this study, the surface area of cotton fiber was determined by BET technique to obtain and estimate the adsorption of LAS on cotton surface. Surface area can be estimated by using various equations, such as Langmuir equation, Recasting equation, or the BET equation depending on the types of adsorption of a gas by a solid. The monolayer volume can then be obtained to calculate the specific surface area (Thomas and Thomas, 1997). Normally, the surface area will be automatically calculated and recorded by the machine.