

CHAPTER II

LITERATURE SURVEY

This work relates to many areas with the aim of producing hydrophobic cotton. The properties of modified cotton and the improvement of covered film on cotton are two important aspects of this work. The literature survey for this work follows the manuscripts of published papers and proceedings in Chapter 3-7. The admicellar polymerization is the main technique used to modify cotton and is chiefly mentioned in Chapter 3-5, whereas the wettability, which is the primary property of surface character for hydrophobic and hydrophilic surface needed to demonstrate the change in the cotton surface, is described in Chapter 6. In addition, in Chapter 7, the improvement of film covering was studied by adding the cross-linking agent in the polymerization step and the coated film was analyzed to determine the effect of the cross-linking agent.

2.1 Admicellar Polymerization Application

Currently, admicellar polymerization has been successfully applied in many studies. Some successful examples of admicellar polymerization process are presented below.

Wu *et al.* (1987a, 1987b, and 1988) coated polystyrene on alumina surface by using sodium dodecyl sulfate (SDS) as surfactant in water/ethanol solution. Either persulfate or AIBN was added as initiator. The results confirmed that admicellar polymerization occurred. It was found that the polymerization of styrene in the admicelle followed the case 1B model in the Smith-Ewart theory. The characterization of the alumina surface coated with styrene was analyzed. Film thickness ranged from 1.8 to 0.4 nm while BET surface area decreased from 94.7 to 57.8 m²/g. The alumina surface changed from hydrophilic to hydrophobic while retaining the basic pore structure.

Esumi *et al.* (1989) studied polymerization on alumina powder by using sodium 10-undecenoate, a polymerizable surfactant. Polymerization was carried out in the bilayer of surfactant by UV radiation. Dispersion of alumina particles was

studied by means of mean particle size. Because hydrophilic groups of the surfactant in the second layer were in contact with the aqueous solution, the alumina particles were dispersed due to electric repulsion. The results also showed that purging with nitrogen gas enhanced this polymerization.

O'Haver *et al.* (1994) coated polystyrene on precipitated silica. Many types of surfactants consisting of cationic surfactant (CTAB), nonionic surfactant (MACOL), and water-insoluble surfactant (ADOGEN) were used. Two kinds of polymerization, thermal and REDOX polymerization, were used. The results showed that CTAB adsorbed less than SDS and ADOGEN but greater than MACOL. When using AIBN as an initiator, the ratio of initiator to monomer was necessarily high. One explanation was that ethanol used to dissolve AIBN may consume many of the radicals formed. For REDOX system this ratio was lower but it took longer to complete the reaction. The reduction in the molecular weight of the extractable polymer, as well as the increase in dispersity, was expected. As the chain length of the polymer increases, they should become more entangled in the surface and more difficult to extract.

Lai *et al.* (1995) studied the formation of polytetrafluoroethylene (PTFE) on aluminum oxide by admicellar polymerization. Ammonium persulfate was used as initiator. Sodium bisulfate (NaHSO_4) and ferrous sulfate (FeSO_4) were used as initiator regulators to improve the initiator effectiveness at low temperature. The results showed that a main factor in the control of adsolubilization of the gaseous monomer tetrafluoroethylene into surfactant bilayers was pressure. The concentration of the initiator also affected polymerization indicating that this factor must be taken into consideration during the analysis of kinetic data. Polytetrafluoroethylene was successfully coated on both aluminum oxide powder and chips. Frictional behavior seemed to be related with film thickness and continuity.

Sakhalkar *et al.* (1995) attempted the formation of polystyrene films on glass fiber surface. This work used cationic surfactants, which were dodecyl trimethylammonium bromide (DTAB) and cetylpyridinium chloride (CPC). The concentration of styrene used and testing method of treated fiber were tested the same as in the work of Wu *et al.* (1987), except that, in this work, treated fiber was examined by SEM. The results showed that polystyrene can be coated on glass fiber

surface but the SEM micrographs revealed a nonuniform coating on the surface. This experiment also showed that polymerization was not restricted to the admicelles and that some polymerization occurred in the supernatant.

Grady *et al.* (1998) and Barraza *et al.* (2001) produced coated glass cloth with styrene-isoprene copolymer by admicellar polymerization for use in composite manufacture. SDS was used as the surfactant. A soluble inorganic salt (potassium persulfate) and an organic azo-initiator (AIBN) were used to initiate polymerization. The composite made from the admicellar-treated cloth with polyester was studied to show the improvement of interfacial adhesion to the same level as in commercial, or silane-treated cloth. Then Barraza studied the wetting behavior in terms of “contact angle” as measured by Wilhelmy method and characterized its morphology by AFM.

Cho *et al.* (2000) coated ultrathin polypyrrole (PPy) films on alumina particles using adsorbed hexanoic acid as a template at various pH values. Ammonium persulfate was used to initiate the polymerization of pyrrole in the system. The pH level of 4 was the optimum condition of this work. AFM was used to study the morphology of the resulting PPy on alumina particles. The results showed multigranular alumina particles were completely coated by PPy films. The contact conductivity of these PPy is more than three times that of a pure polypyrrole powder, even with a very low amount (121 wt%) of polypyrrole onto alumina.

Yuan *et al.* (2001) produced the electrically conducting polypyrrole (PPy) thin films on mica and alumina in aqueous solution with surfactant (or admicellar polymerization process) and without surfactant. On alumina, PPy thin films were deposited by using SDS or CTAB as surfactant and using ammonium persulfate (APS) or iron trichloride hexahydrate (ITC) as initiator. The deposited films were studied by AFM to measure film thickness and surface fractal dimensions. The results show that the films from surfactant solutions are smooth, well connected, and as thin as 30-60 nm, while those from non-surfactant solutions are thicker than 150 nm and full of wrinkles.

2.2 Wettability in Yarn

The studies of wettability in yarn have been carried out to explain the water absorption by capillary force. The wicking technique is the formal technique to calculate the contact angle in many observations. The mathematical model is also one of the interested studies in this area.

Washburn (1921) studied the dynamics of capillary flow. This work has been the principal and original theory of capillary flow that has been widely mentioned in many researches. The penetration of liquids into cylindrical capillaries was mathematically demonstrated as the equation in terms of penetration rate (dl/dt). The experiment was observed on the static method of capillary rise.

De Boer (1980) studied the wettability of scoured and dried cotton fabrics. Several techniques, such as the vertical wicking test, the determination of "Saturation Value", the drop test, and the immersion test, were used to investigate the phenomenon of hydrophobicity. The competitive effects of spreading among the fibers and absorption in the fibers were mainly determined and discussed from those methods. The results can be concluded that liquid penetrated into a fabric can be taken up in two sides, in the capillary space between the fibers and inside the fiber.

Kissa (1981) measured the sorption of a liquid drop on fabric or paper as a function of time by photographing simultaneously the spreading liquid and the time. The empirical equation to predict the area covered by the spreading liquid was also investigated in this work.

Kissa (1996) reviewed the fundamentals of wetting and wicking to explain and define the difference of those behaviors. Wetting is the displacement of a fiber-air interface with a fiber-liquid interface, while wicking is the spontaneous flow of a liquid in a porous substrate driven by capillary force. According to fiber-liquid interface, the wicking process can be divided into four categories: (1) capillary penetration only, (2) simultaneous capillary penetration and imbibition by the fibers (diffusion of the liquid into the interior of the fiber), (3) capillary penetration and adsorption of a surfactant on fiber, and (4) simultaneous capillary penetration, imbibition by the fiber, and adsorption of a surfactant on fibers.

Delker *et al* (1996) studied the dynamics of capillary rise of water in porous media. It was found that, at the early time data, the classical Washburn equation (Washburn, 1921) was well used to describe the capillary rise in a column of tube filled with porous media. At later time, the dynamics is governed by the randomness of the capillary force on the air-water interface.

Takahashi *et al* (1997) used the dynamic spiral nuclear magnetic resonance (NMR) imaging technique to investigate the water imbibition into cellulose fiber matrices. The NMR imaging data obviously demonstrated that water imbibition into a fiber matrix consists of two different processes: water penetration into capillaries between fiber and water diffusion into the cellulose fibers. The qualitative analysis from this technique can be determined by the water capillary flow and can be described by the Washburn equation. The effects of pore morphology, tortuosity, and surface heterogeneity on the water absorption process were also described.

Perwuelz *et al* (2000) studied the capillary flow in polyester and polyamide yarns and glass fibers using a technique by images taken during the capillary rise of colored liquid in yarns. The result showed that the kinetics of capillary rise always followed the Lucas-Washburn equation, but the great dispersion along the yarns is attributed to the yarn heterogeneity of the interfilament space.

Rajagopalan *et al* (2000) established the mathematical models of capillary flow in the complex geometries, e.g. flow in the void spaces between a regular array of cylinders. The computational fluid dynamics (CFD) simulations were also developed for this flow and compared with the results to analytical models. These models were used to understand the effect of geometrical and material parameters on moisture transport that is the important factor of textile yarn and fabrics. A detailed CFD models of surface tension driven flow consists of conservation equations and boundary conditions, which are solved using a suitable numerical method.

2.3 Cross-Linking Polymer

The development of polymer film covering on cotton fabric was also of interest in this work. Making a network polymer is one of the ways that may improve the covering and hydrophobicity of the proposed product. Some researches relating

to the cross-linking of styrene with divinylbenzene (DVB) are described below.

Hayashi *et al* (1987) produced styrene-divinylbenzene cross-linking copolymer in the presence of fine poly(vinyl chloride) (PVC) powder and studied its dynamic mechanical properties and morphology. The effect of polymerization temperature on the properties of composite was mainly investigated. The systems were polymerized at the temperature of 65, 80, and 110°C with initiator. The results showed that the increased DVB diffusion into PVC particles decreased the cross-linking density of P(St-DVB) phase, though the copolymerizability of the second double bond of DVB increased at a higher polymerization temperature.

Matsutomo *et al* (1999) studied the network formation by using Flory-Stockmayer gelatin theory in free-radical cross-linking copolymerization of styrene with m-divinylbenzene (m-DVB). The reactions of styrene and m-DVB as a most typical monovinyl-divinyl system were discussed under specific conditions where the occurrence of a thermodynamic excluded volume effect and intramolecular cross-linking as the primary and secondary factors, respectively. The molecular weight distribution (MWD) curves were also observed with the conversion as a result of occurrence of intermolecular cross-linking reaction governed by F-S theory.

Downey *et al* (1999) studied the mechanism of poly(divinylbenzene) in the precipitation polymerization. The experimental results from this work indicated that particle growth during precipitation polymerization of DVB in acetonitrile occurs by an entropic precipitation mechanism where soluble oligomeric species were captured from solution by reaction with vinyl groups on the particle surface. This was in contrast to the enthalpic precipitation mechanism commonly observed.

Jang and Kim (2000a and 2000b) synthesized and characterized crosslinked styrene-alkyl acrylate copolymers for oil absorbency application and studied the effects of polymerization conditions on oil absorbency. Crosslinked copolymers were synthesized by adding divinylbenzene (DVB) as crosslinking agent. The copolymers were characterized by FTIR, ¹H-NMR, DSC, and a solubility test. The effects of various polymerization conditions (crosslinking agent concentration, initiator concentration, monomer concentration, and polymerization temperature) were studied through oil-adsorption tests using kerosene oil. The oil absorbency was influenced mainly by the degree of crosslinking and the hydrophobicity of the

copolymer units. Oil absorbency was increased by incorporation of hydrophobic acrylate units. Too much concentration of acrylate, however, introduced the side reaction of crosslinking and resulted in the slight drop in oil absorbency.

These are some of the research work in the areas relating to the present study, admicellar polymerization, wettability, and crosslinking polymerization. They help to understand the investigations carried out in this work.