

CHAPTER II LITERATURE SURVEY



2.1 Admicellar Polymerization

Admicellar polymerization is the technique for coating very thin film on many kinds of substrate. This technique consists of 3 main steps to produce the thin film of polymer on the substrate surface (Figure 2.1).

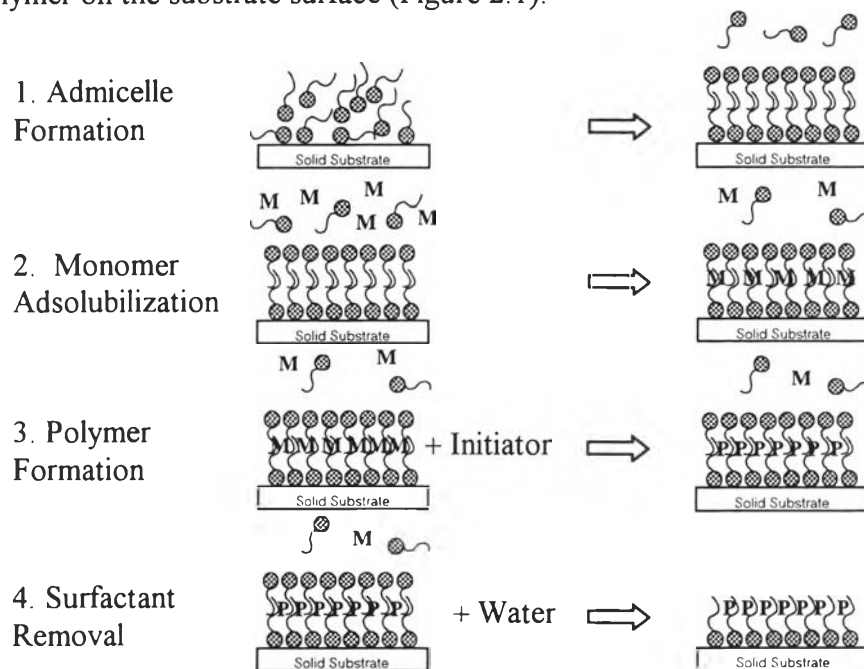


Figure 2.1 Steps in admicellar polymerization process.

Step 1 consists of admicellar formation. Adsorption of the surfactant from an aqueous solution to the surface is the prevalent phenomenon. The initial feed concentration of surfactant is generally chosen close to or equal to the critical micelle concentration (CMC) to avoid emulsion polymerization in the micelle and to maximize admicelle formation. This is the concentration in region III of the typical adsorption isotherm of ionic surfactant on substrate (Figure 2.2). The point of zero charge (PZC) of the surface influences the choice of surfactant. At pH below PZC, the surface becomes positive but it becomes negative at pH above PZC. Added salt can reduce the repulsion between head groups of surfactant and causes the surfactant molecules to come closer together, hence admicelle formation is enhanced.

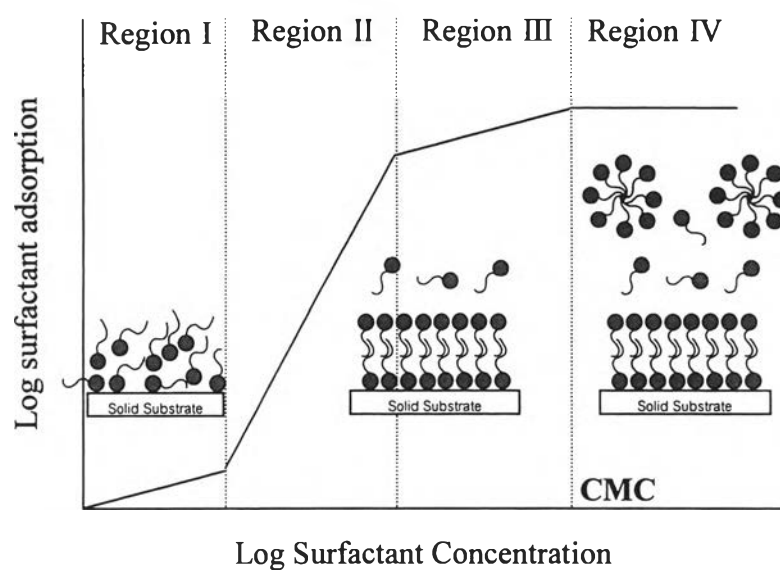


Figure 2.2 Typical adsorption isotherm of ionic surfactant on a substrate.

Step 2 is the monomer adsolubilization. The solubilization of the monomer occurs in the bilayer micelle. The monomers will diffuse from aqueous solution and solubilize in the hydrophobic interior of the admicelle.

Step 3 is the polymer formation. The polymerization of the monomer takes place in the admicelle. Once the initiator is added, the polymerization is initiated in the admicelle that acts as two-dimensional reaction solvent for polymerization. The polymerization mechanism is similar to that occurs in the conventional emulsion polymerization.

After the polymerization reaction is complete, the upper layer of surfactant can be removed by washing to expose the thin layer film of polymer on the substrate surface.

Admicellar polymerization has been used to produce a thin film on many materials. Conducting polymers have been successfully coated on many materials by admicellar polymerization.

2.2 Cotton and Polyester Fabrics

Textile materials represent an interesting class of materials that can benefit greatly from the process of admicellar polymerization. Polymer modified coated

textiles constitute a very diverse range of materials with extremely wide applications. Textiles can be modified to enhance electrical conductivity, water-repellency, soil-resistance and flame retardancy. Among these, modified-coated cotton has by far the highest share of all the coated textiles. Cotton is a natural cellulosic fiber with 1,4-D-glucose as its repeat unit. As with most surfaces with no formal charges, the fiber acquires a negative charge when in water. 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. In addition, cotton also contains a small number of carboxylic acid groups which ionize to yield an anionic charge in neutral solution. Another type of fabric of interest is polyester fabric. It has good resistance to weak mineral acids, even at boiling temperature, and most strong acids at room temperature, but it dissolves with partial decomposition by concentrated sulfuric acid. Strong alkalies can etch the fiber surface and reduce the strength of the fabric. Polyester displays excellent resistance to oxidizing agents, cleaning solvents and surfactants. The common polyester that is used in textile industry is poly(ethylene terephthalate), PET. Figure 2.3 shows the molecular structure of cotton and PET.

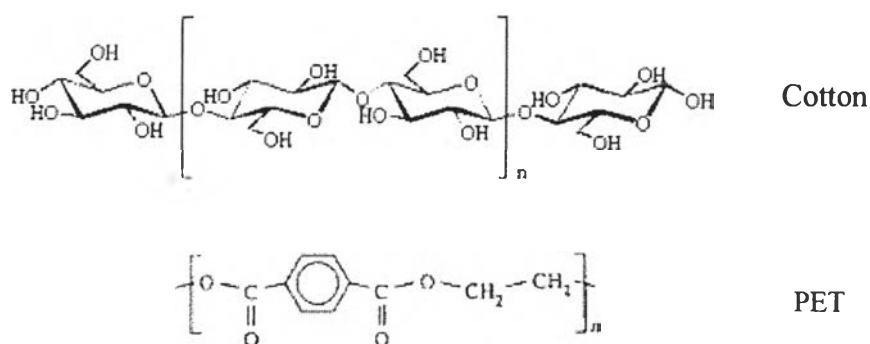


Figure 2.3 Molecular structure of cotton and PET.

2.3 Thin Film Coating by Admicellar Polymerization

Admicellar polymerization has been used to produce thin film on many materials including the coating of conducting polymers on suitable substrates.

Wu *et al.* (1987) studied the polymerization of styrene in sodium dodecyl sulfate (SDS) bilayers adsorbed on alumina surface. After 25 minutes, 75% and higher conversion of adsolubilized monomer to polymer are found. The uniform films of 3.4-3.6 nm thickness are formed on the alumina oxide layers on glass slides for reaction time 30-45 min. Under varying conditions, film thickness of 13 nm is also obtainable.

O'Haver *et al.* (1994) studied the formation of polystyrene in adsorbed surfactant bilayers on precipitated silica. Results from the polymerization in cetyltrimethylammoniumbromide (CTAB), octylphenoxypoly(ethoxy) ethanol and methyltri(C₈-C₁₀) ammonium chloride bilayers show effective conversion of adsolubilized styrene monomer to polystyrene. The process has been demonstrated effective with amorphous precipitated silica substrates having a variety of surface areas and with two types of initiation schemes, AIBN and tert-butyl hydroperoxide. The extractable polymer has been characterized using FTIR, UV and GPC. Only approximately 25% of the polymer is extractable after refluxing for 4 hours in THF.

Lai *et al.* (1995) studied the polymerization of tetrafluoroethylene (TFE) within the adsorbed surfactant bilayer, which formed fluorocarbon thin film on alumina oxide powder. Pressure variation was found to be a main factor in the control of TFE adsolubilization into surfactant bilayer. The concentration of the initiator that has an effect on polymerization of TFE is in the range from 0.25-2.5 wt%, indicating that this factor must be taken into consideration during the analysis of kinetic data. The measurement of FTIR, friction coefficient and contact angles verify that thin PTFE films are formed on alumina plates.

The study of solubilization and adsolubilization of pyrrole by anionic surfactant, sodium dodecyl sulfate (SDS), was reported by Funkhouser *et al.* in 1995. The solubilization of pyrrole was measured by semiequilibrium dialysis and the highest solubilization constant, K , is 2.85 M^{-1} in the absence of salt while the minimum K is 1.95 M^{-1} at 0.1 M of salt. For the study of adsolubilization of pyrrole, pyrrole (0-0.16 M) caused a decrease in surfactant adsorption but the adding of salt about 0-1.5 M improved pyrrole adsolubilization. The result of pyrrole polymerization in the system that did not have SDS, polypyrrole film could form on alumina surface but this film did not occur by pyrrole adsorbed before

polymerization, so it was not well adhered to the surface. The result of resistance measurements showed that, in the system that has pyrrole and SDS, polypyrrole film did not form on the alumina surface.

Thin polystyrene film has been coated on glass fibers (Sakhalkar *et al.*, 1995). The thin film polymerization process occurs in three steps, namely, the formation of surfactant admicelles, the partitioning of the styrene monomer into the admicelles, and the *in situ* polymerization of the adsorbed monomer. In the third step of polymerization, polymer formation is not restricted to the surface aggregates as originally thought, but a fraction of the polymerization occurs in supernatant as well. The SEM micrograph showed a nonuniform coating on the fiber surface. It is also clear that polymer formation definitely occurred, although the formation of a uniform polymeric coating was not achieved.

Genetti *et al.* (1998) prepared nickel-filled low-density polyethylene composites involving coating the nickel-flake with polypyrrole by admicellar polymerization. The particle-particle contact and the tunneling resistance of this material were reduced because the polypyrrole molecules form chain entanglements at high filler loading. The product containing the nickel particles with polypyrrole was obtained with increase in conductivity. The thermal and the mechanical properties of the coated material did not change.

Vidanapathirana *et al.* (1999) reported the galvanostatical polymerization of electro-active poly N-methyl pyrrole (PNMP) films under a range of conditions. The influence of the conditions used in electropolymerization, such as electrolyte concentration, current density, type of doping anion and temperature during polymerization on the electrical conductivity has been investigated. The conductivity was measured by the in-situ method using a specially prepared two-band microelectrode. The current density used during the polymerization has a considerable influence on the conductivity, as earlier observed for polypyrrole in non-aqueous electrolytes. The conductivity changes with the size of the anion and the concentration of the electrolytes as well as on the temperature at which the polymerization was carried out. Polymer films formed at relatively higher temperatures had lower conductivities and were not able to insert as many counterions, indicating that the films formed were less perfect. At higher

temperatures the increased rates and numbers of side reactions may be competing with the ideal one-dimensional polymerization process.

Chemical deposition of electrically conducting polypyrrole (PPy) thin film on mica and alumina was carried out in aqueous solution with and without surfactant (Yuan *et al.*, 2001). Examination of film morphology and thickness by atomic force microscopy (AFM) indicated a strong dependence of structure on the preparation method. Films grown in the absence of surfactant were thicker than 150 nm with wrinkles present, indicating the overcoming of film-substrate adhesion by internal film cohesion. Oxidative polymerization with surfactant allowed reproducible synthesis of very thin films (50 nm thickness) with improved adhesion and suppressed formation of wrinkles. Experimental results are discussed within the context of a Stranski-Krastanov model of film growth. Film thickness and surface dimensions were derived from AFM. Analysis of PPy films on alumina helped discern their presence on the microscopically rough substrate and quantitatively expressed the changes in sample color by surface roughness.

Irina *et al.* (2001) investigated the in-situ polymerized polyaniline films on glass surface. They focused on the film formation of polyaniline. Polyaniline films were produced on glass surface immersed in the reaction mixture during the oxidative polymerization of aniline. Glass supports placed in the reaction mixture at the start of the oxidation were gradually removed during the reaction. The thickness of polyaniline films produced on glass, assessed by optical absorption, was followed as a function of reaction time. The progress of polymerization was monitored by temperature changes. In another experiment, glass supports were successively inserted into the polymerization mixture. The formation of polyaniline films on glass, which had been already pre-coated with polyaniline, was also investigated. The proposed model of film formation is based on the concept of the primary and secondary nucleation. Oligoaniline cation radicals adsorbed on the glass surface nucleate the primary growth of polyaniline film, the secondary nucleation occurs on the produced polyaniline layer.

Cotton was coated with 3,4-dichloro-1-butane and sodium styrene sulfonate by admicellar polymerization to improve its thermal stability and dyeability (Pisuntornsug, 2001). SEM microscopy showed that cotton was very well coated.

Moreover, dyeing process of treated cotton can be done at room temperature without addition of salt.

Polyelectrolyte multilayers containing electrochemically active polythiophenes have been constructed on ITO/glass substrates using the layer-by-layer adsorption deposition technique (Zotti *et al.*, 2001). Electrochemically active layers of poly(cyclopentadithienyl-alkylsulfonate), poly(cyclopentadithienyl-alkylammonium), and α,ω -bis(carboxyhexyl)sexithiophene were deposited with nonelectroactive layers of polyallylamine and polystyrenesulfonate. The first sequential adsorption of multilayers in which both the polycation and the polyanion are based on the same polythiophene is reported. UV-vis spectroscopy and cyclic voltammetry indicate a linear dependence of the amount of deposited polymer on the number of deposition cycles. The rate of deposition depends on the oxidation state of the polythiophene, being three times lower for the oxidized polycationic polymer. Atomic force microscopy characterization of the layers has shown that flat monolayers are deposited with a progressive increase of roughness. Interposition of multiple nonelectroactive layers between the electrode and a single external electroactive polythiophene layer interpenetrates the confining layers up to a three-layer distance. The conductivities of the multilayers along the surface and perpendicular to it are anisotropic depending on the layer alternation. The photoluminescence properties of the α,ω -bis(carboxyhexyl)sexithiophene multilayers are the same for vacuum-deposited polycrystalline layers.

Polythiophene (PT), poly(3-chlorothiophene) (PCT), and poly(3-methylthiophene) (PMeT) have been electrochemically deposited on mirrorlike stainless steel (SS) electrode surfaces by direct oxidative polymerization of corresponding monomers in boron trifluoride diethyl etherate (BFEE) solution (Shi *et al.*, 2002). The doping levels of as-grown thin films have been determined electrochemically. The results demonstrated that PTs were formed nearly in neutral state initially and their doping levels increased during electrochemical growth processes. Monomer structure and electrolyte have strong effects on the doping levels of PTs with a given thickness. Raman spectroscopic studies also confirmed these findings. Furthermore, it is found that the oxidized species of polythiophene and poly(3-chlorothiophene) are mainly present in radical cations, while dications are

avored to be formed in poly(3-methylthiophene) with a doping level higher than ca.5%.

Han *et al.* (2002) performed the chemical oxidative polymerization of aniline in a micellar solution of dodecylbenzene sulfonic acid (DBSA, anionic surfactant) to obtain conductive nanoparticles with enhanced thermal stability and processability. DBSA was used to play both the roles of surfactant and dopant. The polymerization kinetics and optimum polymerization conditions were determined by UV-VIS spectra. As the DBSA content increased, the polymerization rate increased due to lower pH value and enhanced micelle formation. The green colored colloidal dispersions have a good long-term colloidal stability and exist as stable dispersions without precipitation over 1 year. The optimum aniline to oxidant ratio for polymerization reaction was 0.5 and the optimum aniline to DBSA ratio was almost 1. Excess amount of DBSA caused doping level to decrease, which seems to be due to the competition between adjacent DBSA molecules, making it difficult to perform doping and moving into the core of the micelle with polymerization of aniline. The reaction model was proposed on the basis of the roles of DBSA. The electrical conductivity varied with the molar ratio of DBSA to aniline and the highest conductivity of particles was 24 S/cm. The layered structure due to PANI backbone separated by long alkyl chains of DBSA was observed and it seems to facilitate the electrical conduction. The doping level of particle was fairly high and was dependent on the preparative conditions. The average size of the PANI particles determined by Guinier plot of small-angle X-ray scattering (SAXS) measurement was 20-30 nm, which was well coincidence with scanning electron microscopy (SEM) results. The particle showed relatively well-ordered layered structure when aniline, APS and DBSA were used proper molar ratios.

2.4 Coating of Conducting Polymers on Fabrics

Various techniques have been studied to deposit conducting polymers onto different kinds of fiber and textile. Their properties and applications have also been investigated.

The conductive fabrics were prepared by oxidative polymerization of polypyrrole and polyaniline (Kuhn *et al.*, 1990). The electrical conductivity of the fabrics depends on the kind of the conductive polymers, thickness of the polymer film and doping agents. The reaction rate can be lowered for more ordered conductive polymers by lowering the reaction temperature, by lowering reactant condition, by using different oxidizing agents, by increasing pH, and by incorporating additives in reaction system. The electrical resistivities of the fabrics at 70°F and 50%RH are measured. The treated fabrics should have the resistivity below 10^6 ohms per square, preferable 500 to 5,000 ohms per square.

By aniline diffusion and chemically oxidative polymerization, polyaniline (PANI) was adherently deposited on PET fibers and Nylon fabrics (Jin *et al.*, 1996). PANI-PET fibers and PANI-Nylons fabrics doped with HCl have an electrical conductivity as high as 0.42 S/cm and 0.45 S/cm respectively. With p-toluenesulfonic acid (p-TSA) and dodecylbenzene sulfonic acid (DBSA) and 5-sulfosalicylic acid (SSA) as dopants, the conductivity and final composites are one or two orders of magnitude lower than that with HCl. A washing test was designed to investigate the interfacial adhesion of PANI on textiles. Results showed that the conductivity and interfacial adhesion of composites improved greatly by preliminary aniline diffusion treatment of textiles. Further investigations by SEM and WAXS and DSC showed that the improvement in properties of composite textiles is mainly attributed to the increased interaction of macromolecules at the interface caused by the diffusion of PANI chains in the surface layer of the substrates.

Collins *et al.* (1996) studied the conductive polymer-coated fabrics for chemical sensing. A novel sensing format for the detection of toxic vapors uses thin films of conductive polymers, polypyrrole or polyaniline, coated onto poly(ethylene terephthalate) or nylon threads woven into a fabric mesh. Chemical sensing on fabrics offers the opportunity of using the large surface area for improved sensitivity and expanded dynamic range. The resistivity of these materials was monitored following exposure to several toxic gases. Detection limits in parts per million (ppm) were demonstrated for various pollutants and chemical warfare simulants, including dimethyl methylphosphonate (DMMP), ammonia, and nitrogen dioxide. The effect of humidity on the detection capabilities of these materials was also characterized.

Polymeric overcoats including polyethylenimine and fluoropolyol were evaluated as a means of introducing selectivity and sensitivity with respect to the adsorption of particular classes of gas analytes. The chemical deposition of the polypyrrole and the polyaniline results in a smooth even overlayer on the PET thread, although regions do exist where the polymer aggregated during polymerization. The fabric weave consists of a series of overlapping conductive polymer-coated threads, which results in a much more complicated chemical sensor substrate than that found for films grown on chemiresistor devices, quartz crystal microbalances or field-effect transistors, for example.

In the same year, Bhadsni et al. (1996) prepared conductive natural fibers by coating polypyrrole on fibers such as silk, cotton and wool. The electrochemical polymerization was used as the coating process. The polymer was found on the fiber surfaces. The weight percent gain and conductivity of fiber increased monotonically with time of electrolysis. However, the conductance did not increase with the increase in current levels. The conductivity of the fibers was in the range 0.2-1.5 s/cm depending on the kind of fibers.

The adsorption at the liquid-solid interface of the conductive textiles based on polypyrrole was investigated (Kuhn *et al.*, 1997). The reaction worked very well when relatively low concentration of pyrrole (0.01-0.02 M) was used. The degree of conductance and degree of stability were affected by different doping agents. After treating, there was no fiber-to-fiber bonding so the mechanical properties of the fabric did not change. In addition, the surface resistance of the treated fabric was in the range 10 to 10,000 ohms per square depending on the amount of pyrrole and weight and construction of the fabric.

Graft copolymerization of polyaniline and poly(o-toluidine) onto poly(ethylene terephthalate) fiber was conducted by using peroxydisulfate as initiator under nitrogen atmosphere at various experimental conditions in aqueous hydrochloric acid medium (Anbarasan *et al.*, 1999). The grafting of polyaniline and poly(o-toluidine) onto poly(ethylene terephthalate) was verified by recording cyclic voltammetry of the grafted fiber, conductivity measurements, and thermal analysis. The conductivity value of polyaniline-grafted poly(ethylene terephthalate) backbone is higher than that of poly(o-toluidine)-grafted poly(ethylene terephthalate)

backbone at $1.50\text{M ohm}^{-1}\text{cm}^{-1}$ and $3.30\text{G ohm}^{-1}\text{cm}^{-1}$ respectively. Graft parameters such as % grafting, % efficiency and the rate of grafting show the same trend for both grafting. Grafting was always accompanied by homopolymerization. The rate of homopolymerization was also followed in all experimental conditions.

Oh *et al.* (1999) compared two methods of obtaining electrically conductive fabrics by *in situ* polymerization of aniline. Conductive fabrics were prepared by immersing the nylon 6 fabric in 100% aniline or an aqueous hydrochloride solution of aniline followed by initiating successive polymerization in a separate bath (DPSB) or in a mixed bath (DPMB) of oxidant and dopant solution with aniline. In each case, the polymerization conditions were optimized to obtain the maximum quality of polyaniline on the fabrics. The higher conductivity of composite fabrics, whose value reached up to 0.6×10^{-1} s/cm, was obtained by the DPMB process. Moreover, this method induced the least decrease in the degree of crystallinity as compared to the DPSB process. The serviceability of the polyaniline-nylon 6 composite fabrics was also evaluated. No significant changes in the conductivity were observed after abrading the composite fabrics over 50 cycles and multiple acid and alkali treatment. The stability of conductivity was significantly decreased by less than 1 order after exposure to light for 100 h, but it was significantly decreased after washing with detergent.

Tessier *et al.* (2000) studied polypyrrole coated polyester fabric prepared by the 3-step method for biomedical applications. In the first step, the fiber surface was activated using phosphorous trichloride. Then, 1-(3-hydroxypropyl) pyrrole was grafted to the phosphorous trichloride. Finally, the pyrrole-grafted fibers were dipped in FeCl_3 catalyst and exposed to pyrrole monomer vapor for the final polymerization. The surface resistivity of the treated fabric was in the range 10^4 - 10^5 ohms/square. The contact angle of water on polypyrrole-coated fabric was between 103 - 105° while on untreated fabric, it increased with time because of the less stable hydrophobic surface of the fabric.

Anbarasan *et al.* (2001a) examined the chemical grafting of polyaniline onto nylon 66 fiber in two different media, hydrochloric acid and p-toluene sulfonic acid (PTSA), using peroxodisulfate (PDS) as an initiator. The results indicated that aniline could be better grafted onto nylon 66 fiber using PTSA as a reaction medium and the

percent grafting and percent efficiency values revealed the same relationship. Anbarasan and coworkers (2001b) also reported the use of peroxy salts such as potassium peroxydisulphate (PDS) and potassium peroxomonosulphate (PMS) to initiate graft copolymerization of aniline onto rayon fiber, including the kinetics approach of grafting. From the kinetic study the following conclusions are made. (1) Grafting copolymerization occurs with simultaneous homopolymer formation. (2) Both R_h and R_g showed first-order dependence on [aniline], [PDS], or [PMS] and amount of rayon fiber. (3) FTIR spectroscopy, cyclic voltammetry (CV), weight loss study and conductivity measurements confirm the chemical grafting of aniline onto rayon fiber. The conductivity value of polyaniline-grafted rayon fiber increased with % grafting. The conductivity value of the polyaniline-grafted rayon fiber also depends on the nature of initiator used. Here, PMS is a stronger oxidizing agent than PDS, which leads to the formation of a quinoidal structure rather than a benzenoidal structure due to over oxidation. This PMS-initiated system showed very low conductivity value when compared with PDS when used as initiator. (4) A probable mechanism has been proposed to explain the experimental results obtained.

Oh *et al.* (2001a) studied the thermal stability of conductive polyaniline (PANI)-nylon 6 composite fabrics doped by a mixture of hydrochloric acid (HCl) and various organic aryl sulfonic acids such as benzenesulfonic acid (BSA), dodecylbenzenesulfonic acid (DBSA), and p-toluenesulfonic acid (TSA). Conductive fabrics are prepared by immersing nylon 6 fabric in an aqueous hydrochloric solution of 0.5M aniline and by initiating successive polymerization with an oxidant in various doping solutions. When the same molar ratio of HCl in the diffusion bath and various protonic acids in the polymerization bath are mixed and serve as the dopant for polyaniline, the highest fabric conductivity is obtained with HCl/BSA (3.122×10^{-2} S/cm), HCl/TSA (2.726×10^{-2} S/cm), HCl/DBSA (2.144×10^{-2} S/cm), and HCl/HCl (1.733×10^{-2} S/cm) in decreasing order. The conductivity of all doped PANI-nylon 6 composite fabrics decays at elevated temperatures in air. Among the various dopants, HCl/DBSA shows the best thermal stability, followed by HCl/TSA > HCl/BSA > HCl/HCl in decreasing order. In addition, the thermal stability of conductivity increases as the molecular weight of the dopant increases, since dopants

higher molecular weight can not be easily liberated during heat treatment.

The effect of plasma treatment on the surface characteristics and conductivity of polyaniline-nylon 6 composite fabric was investigated by Oh *et al.* in 2001(b). Plasma surface modifications with oxygen, ammonia, and argon were performed on nylon 6 fabric to improve the adhesion and rate of polymerization. The surface morphology of the fiber was observed with scanning electron microscopy, and functional groups introduced onto the surface of nylon 6 fibers by various plasma treatments were characterized by X-ray photoelectron spectroscopy. With oxygen plasma treatment, the fiber surface was effectively etched; polar groups such as $-OH$ and $-OOH$ were introduced onto the surface of nylon 6 fiber, and they increased surface activity, promoted oxidation polymerization, and resulted in higher add-on and electrical conductivity. However, the introduced amine and amide groups with ammonia treatment caused a reduction in conductivity. Argon did not significantly alter the surface characteristics of the nylon 6 fiber. In addition, to control fabric conductivity and cover as a wide range of conductivity as possible, they observed the effects of the monomer concentration and number of deposits on the fabric conductivity. The results showed that fabric conductivity increased as the monomer concentration increased up to $0.5M$ and then leveled off, and further increases were achieved with an increase in the number of multiple deposits. Fabrics with log conductivity in the range -2.2 to -1.6 S/cm could be reached in a single deposit, -1.9 to -1.4 S/cm could be reached in two deposits, and -1.6 to -1.1 S/cm could be reached in three deposits.

Electrically conductive polyaniline(PANI) / Nomex [poly(m-phenylene isophthalamide)] composite fabric was prepared by *in situ* polymerization of aniline doped by a mixture of hydrochloride (HCl) and various sulfonic acids such as benzenesulfonic acid (BSA), sulfosalicylic acid (SSA) and dodecylbenzenesulfonic acid (DBSA); their effects on conductivity and physical properties were then investigated (Kim *et al.*, 2002). (PANI)/Nomex composite fabrics doped by a mixture of protonic acids exhibits higher conductivity than those doped by other single dopants such as camphorsulfonic acid (CSA), p-toluenesulfonic acid (TSA), BSA, SSA and HCl. The conductivity of PANI/Nomex fabrics especially doped by a mixture of HCl and DBSA was evenly maintained up to $100^{\circ}C$ without depression of

mechanical properties of Nomex. Their conductivity was also maintained under extension of the composite fabric. In addition, electrical conductivity of PANI/Nomex fabric was highly increased by ultrasonic treatment, which facilitated better diffusion and adsorption of aniline by cavitation and vibration.

Polypyrrole (PPy) was polymerized chemically and electrochemically in sequence on a polyester (PET) woven fabric, giving rise to PET fabric/PPy composite with high electrical conductivity (Kim *et al.*, 2002). In the chemical polymerization, pyrrole dissolved in an aqueous solution without or with polyvinyl alcohol as a surfactant was first sprayed on the PET fabric and oxidized by spraying an aqueous solution of an oxidant and a dopant. Electrochemical polymerization was carried out in an aqueous electrolyte solution by applying a constant current density to the PET fabric coated with chemically polymerized PPy and a stainless steel plate as the working and the counter electrodes, respectively. They investigated the effects of the chemical or the electrochemical polymerization conditions on the properties of the resulting composite such as surface morphology, electrical conductivity, environmental stability, and electromagnetic interference shielding effectiveness (EMI SE). They found that the composite shielded EMI by absorption as well as reflection and that EMI shielding through reflection increased with the electrical conductivity. The specific volume resistivity of the composite prepared in this study was extremely low at $0.2 \Omega \text{ cm}$ and EMI SE was in the practical useful range of about 36 dB over a wide frequency range up to 1.5 GHz.

Dhawan *et al.* (2002) studied shielding behaviour of conducting polymer-coated fabrics in X-band, W-band and radio frequency range. Electromagnetic interference response of conducting polyaniline-coated fabrics in the microwave range, W-band, RFI range as well as in UV-Vis-NIR range has been studied. In the radio frequency range from 100 to 1000 MHz, conducting polyaniline-coated fabrics shows a shielding effectiveness in the range 30-40 dB. Shielding effectiveness of the conducting fabrics in W-band region at 101 GHz shows an attenuation of 35.61 dB. The microwave reflectance studies of the coated fabrics in 8-12 GHz range shows that conducting fabrics gives shielding effectiveness value of -3 to -11 dB. The reflectance studies of conducting polyaniline-coated fabric shows that 98% of the energy is absorbed in the UV-Vis-NIR range and 2% is reflected back. In

polypyrrole-coated fabric 96% of energy is absorbed and 4% is reflected back, whereas in substituted polythiophene-coated fabric, 82% of the energy is absorbed and 18% is reflected back.

2.5 Volume and Surface Resistivity Measurements of Fabrics

A fundamental property of insulators is resistivity. The resistivity may be used to determine dielectric breakdown, dissipation factor, moisture content, mechanical continuity and other important properties of a material. Because of such large magnitudes, measuring the resistivity of insulators can be difficult unless proper test methods and instrumentation are used. One test method often used for measuring resistivity of insulators is ASTM D-257, "DC Resistance of Conductance of Insulating Materials." Instruments called electrometers are used to make this measurement because of their ability to measure small current.

The basic equation that governs electrical conductivity, σ , is

$$\sigma = nq\mu \quad (2.1)$$

where n is number of charge carriers per unit volume, q is charge per carrier and μ is mobility of the carrier (Warner, S.B., 1999). This equation simply states that conductivity is due to a concerted motion of charge carriers. Conductivity is the reciprocal of resistivity, ρ :

$$\sigma = 1/\rho \quad (2.2)$$

The resistivity of an insulator is measured by sourcing a known voltage, measuring the resulting current and calculating the resistance using Ohm's law. From the resistance measurement, the resistivity is determined based on the physical dimensions of the test sample.

Volume resistivity is a measure of the leakage current directly through a material. It is defined as the electrical resistance through a one-centimeter cube of insulating material and is expressed in ohm-centimeter. When measuring the volume resistivity, the fabric is placed between two electrodes and a potential difference is applied between them. As a result, the current is distributed through the volume of the test sample and is measured using sensitive ammeter or electrometer. The surface

resistivity is defined as the electrical resistance of the surface of an insulator. It is measured by placing two electrodes on the surface of the test sample, applying a potential difference between them and measuring the resulting current. The resulting current is primarily in a thin layer of moisture or some semiconductor material that is on the surface of the test sample. Both volume and surface resistivity values are obtained by converting resistance measurements to resistivity by taking geometric considerations into account. To account for the geometry, electrodes with convenient dimensions should be used, such as Model 6105 Resistivity Adapters. These electrodes are made of stainless steel and are based on the ASTM D257 standards. The basic measurement techniques for the volume and surface resistivity measurements using the Models 6105 are shown in Figure 2.4.

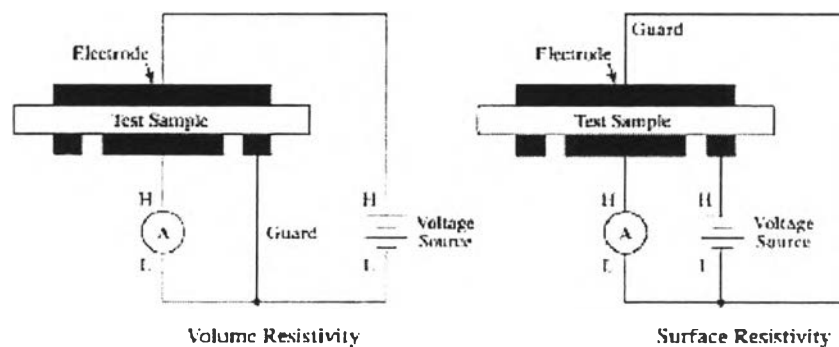


Figure 2.4 Resistivity measurements

The volume resistivity is measured by applying a voltage across the sample and measuring the resulting current. The resistivity is calculated from the geometry of the electrodes and the thickness of the sample. Once the resistance is measured, the volume resistivity can be calculated.

The volume resistivity, ρ_v , can be determined from the following equation:

$$\rho_v = \frac{AV}{tI} \quad \text{ohm-centimeter} \quad (2.3)$$

where V is the applied voltage, I is the measured current, A is the effective area of the guarded electrode for the particular electrode arrangement in cm^2 and t is the average thickness of the test sample in cm .

Using the Model 6105 Resistivity Chamber, the following calculation is used:

$$\rho_v = \frac{22.9V}{tI} \quad \text{ohm-centimeter} \quad (2.4)$$

The surface resistivity is measured by applying a voltage across the surface of the sample, between the bottom two electrodes. The resulting current is measured and the resistivity is calculated. The surface resistivity, ρ_s , can be calculated from the following equation:

$$\rho_s = \frac{PV}{gI} \quad \text{ohms} \quad (2.5)$$

where V is the applied voltage, I is the measured current, P is the effective perimeter of the guarded electrode for the particular electrode arrangement used and g is the distance between the electrodes

If using the Model 6105 Resistivity Chamber, the formula is:

$$\rho_s = \frac{53.4V}{I} \quad \text{ohms} \quad (2.6)$$