

## **CHAPTER I INTRODUCTION**

Electrically conductive polymers have been widely investigated since last two decades. The development of the researches of these polymers has been growing due to their outstanding properties and applications. The conducting polymers have been utilized in several fields such as electronic devices, and electrochemical sensor. There are many approaches to produce the conducting polymer in various forms like films and powders. However, The limitation of the conducting polymers in their properties such as poor mechanical properties and poor processibility is required to improve in order to achieve the satisfactory applications. Many researches have analyzed the electrically conductive polymers in various approaches for example electrochemical, plasma and diffusive. The new method applied to the conducting polymers is a thin film via surfactant template (TFST) technique or well known as an admicellar polymerization.

The admicellar polymerization has been improved over last several years. The method involves the formation of ultrathin polymer films on charged surface by using surfactants. Polypyrrole (PPy) film on a solid substrate such as nickel or alumina produced by in this method has been used in very technological works such as conductive adhesive, reinforcing fillers, electrodes and sensor. Moreover, their properties have been enhanced in processability, flexibility, high corrosion resistance and high conductivity.

In this study, attempt was made to employ admicellar polymerization to produce a thin film of conducting PPy coating on the latex particles. Thus this brings two advantages significantly, first processing of PPy can be facilitated and electrical conductive properties of latex is enhanced. Due to its

well-established process, high interaction and stability with several surfactants, the Natural Rubber (NR) latex was chosen as the substrate for PPy coating. Admicellar polymerization required that the monomer, pyrrole, in surfactant bilayers was adsorbed onto the surface of latex particles. The initiator was added, therefore, polymerizable monomer was governed by partition onto adsorbed surfactant layer, and the excess surfactant was washed away with water to obtain the thin polypyrrole coating onto the latex surfaces.

The mechanism of surfactant adsorption and the pyrrole adsolubilization were studied in order to get the formation of thin film of polymer with good performance in their applications. The polymer film on latex surface was also characterized to assure the success of admicellar polymerization.

## 1.1 Theoretical Background

### 1.1.1 Surfactant

A surfactant or surface active agent is a chemical substance which has a characteristic property on the surfaces or interfaces of the system in order to encourage the surface or interfaces free energies when the surfactant presents at low concentration. The interfacial free energy means the less work used to create an unit area of surface or interface. The structure of the surfactant molecules known as an amphipathic is classified into two distinct groups: lyophobic (hydrophobic) group and lyophilic (hydrophilic) group. When surfactants are dissolved in a suitable solvent such as water, the lyophobic group exhibits in the interior of the water and causes the distortion of the water. Consequently, the less work is required to create unit area of surface or interface from surfactant molecule than that from water molecules. On the other hand, the lyophilic group inhibits the solvent phase apart from the surfactant. Concisely, the amphipathic property is to accumulate lower free energies at the interfaces and to arrange the molecules with lyophilic group in the aqueous phase and lyophobic group leaving away from that aqueous phase. There are many effects on the amphipathic structures of lyophobic group and lyophilic group such as solvents properties and system conditions. For example, in highly polar solvents such as water, the lyophobic group is usually a hydrocarbon or fluorocarbon or siloxane chain. Normally, The lyophobic group is a long-chain hydrocarbon chain and the lyophilic group is an ionic or highly polar group.

The variety of the lyophilic groups is used to classify surfactants into four important categories.

1. Anionic surfactant: Negative charge of the surfactant molecules is exhibited on the hydrophilic group, for example  $\text{RC}_6\text{H}_4\text{SO}_3\text{Na}^+$  (alkylbenzene sulfonate).

2. Cationic surfactant: Positive charge of the surfactant molecules is exhibited on the hydrophilic group, for example  $\text{RN}(\text{CH}_3)_3\text{Cl}^-$  (quarternary ammonium chloride).

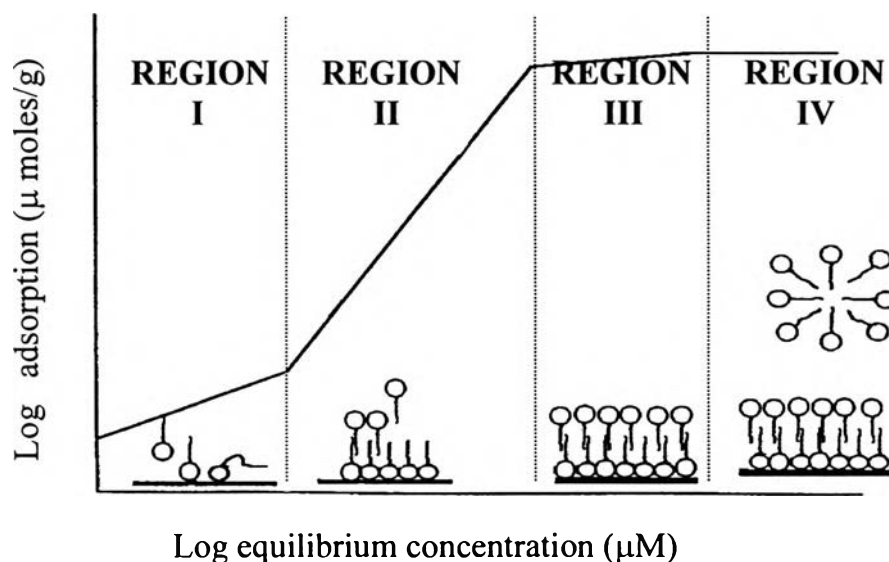
3. Zwitterionic surfactant (referred to amphoteric): Negative charge and a positive charge of the surfactant are carried on the hydrophilic group, for example  $\text{R}^+\text{NH}_2\text{CH}_2\text{COO}^-$  (long-chain amino acid).

4. Nonionic surfactant: No ionic charge on the hydrophilic group appears for example  $\text{RC}_6\text{H}_4(\text{OC}_2\text{H}_4)_x\text{OH}$  (polyoxyethylenated alkylphenol).

### 1.1.2 Mechanism of the Surfactant Adsorption

Many literatures have been reported the adsorption of surfactant on high surface area solids such as metal or glass. Somasundarn and Fuerstenau (1966) were the first to introduce the adsorption isotherm shape obtained for surfactant on alumina. Figure 1.1 illustrates an adsorption isotherm for an ionic surfactant adsorbed on an oppositely charged hydrophilic surface. The characteristic adsorption isotherm plotted on a log-log scale of the adsorbed surfactant versus the equilibrium surfactant can be classified into four regions. Region I referred to as Henry's Law region is the surfactant adsorption on solid surface at low surface coverage. The line is linear and has a slope of 1. In region II, The substantially increase in the adsorption is found in this region than that of first region. The region I/II transition is the onset of surfactant aggregate on the surface. The concentration of the surfactant is described by the HMC (hemicelle concentration) (Scamehorn, 1985) or the CAC (critical admicelle concentration) (Harwell *et al.*, 1985). The name 'hemicelles' was proposed by Gaudin and Fuerstenau (1955) and was defined as the formation of

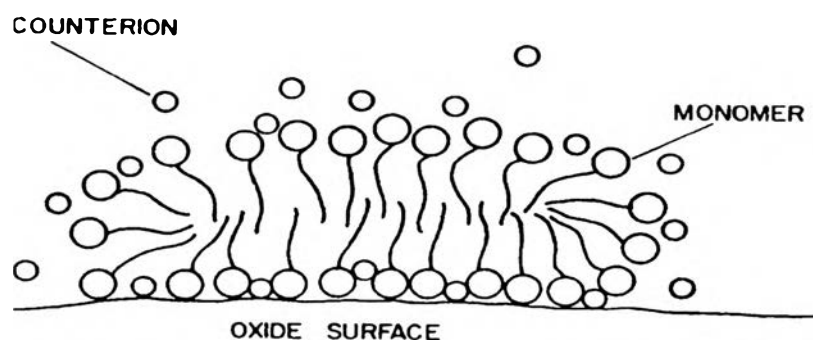
surfactant aggregate structures at the solid-liquid interface having its hydrophilic groups oriented towards the solid surface and its hydrophobic groups in the solution. These aggregates act as local monolayers. When surfactant presents at high concentration, these aggregates change to bilayer structures (named as 'admicelles') on the surface where the hydrophilic groups of the outer layer are directed to the solution. The adsorption of surfactants in this region can be whether the monolayer form or bilayer form. In region III, the adsorption increases more slowly than that in region II. As the surfactant aggregates at the surface, the surface becomes charged as the surfactant, therefore the surfactants at the surface tend to repel each other. The region III/IV transition occurs at the critical micelle concentration (CMC) of the surfactant. Some authors believed that it is the completion of bilayer coverage of the surfactant. Region IV is the plateau adsorption that has the concentration of surfactants above CMC



**Figure 1.1** Illustration of surfactant adsorption isotherm.

### 1.1.3 Admicellar Polymerization Technique

An admicellar polymerization technique is based on the physically adsorbed surfactants onto the substrate, so called admicelle. The feasibility of the phenomena of admicelle formation and adsolubilization to form polymerized and organized ultrathin film of molecular dimension on substrates has been investigated continually for several years. Wu *et al.* (1993) was the first to propose the formation of styrene-sodium dodecyl sulfate (SDS) on alumina by this polymerization. Clearly, the bilayer structure of this polymerization is shown in Figure 1.2



**Figure 1.2** The formation of a sodium dodecyl sulfate admicelle on the alumina surface.

### The four-step for the formation of ultrathin polymer film by admicellar polymerization

The mechanism of this method is classified into four steps as shown in Figure 1.3.

#### Step 1 Admicelle formation

In step 1, The formation of an admicelle (Harwell *et al.*, 1985) is occurred by the adsorption of a surfactant bilayer at the solid/aqueous solution interface. The surface aggregate formation at the surfactant concentration below the critical micelle concentration (CMC) is manipulated by the solution pH, counterion concentration and surfactant structure

(Scamehorn *et al.*, 1982). The most parameter may be used to facilitate the admicelle formation is the solution pH at which the substrate surface exhibits a net surface charge of zero (the point of zero charge, or PZC). At pH value below the PZC, the surface becomes positively charged. At pH value above the PZC, the surface is negatively charged. The PZC is benefit for the wide selection of surfactant type to adsorb on substrate. Anionic surfactants can be adsorbed on the surface below the PZC and cationic surfactants are adsorbed on the surface above the PZC. For example, Wu *et al.*, 1988 studied the adsorption of anionic surfactant, sodium dodecyl sulfate, on the solid surface of alumina. The PZC of alumina was pH 9.5 at 30 °C, thus the solution was adjusted to the pH 4.0 to be suitable for anionic surfactant.

#### Step 2 Monomer adsolubilization

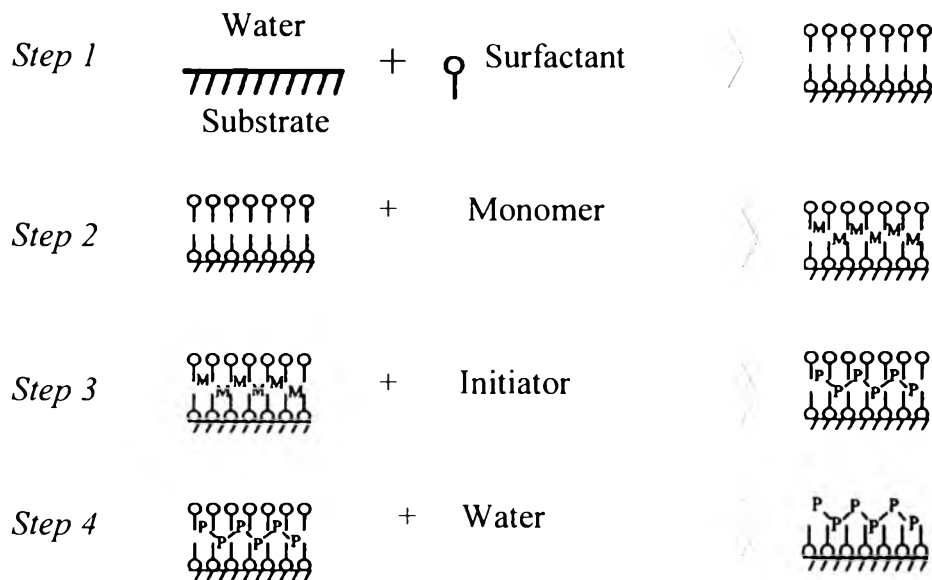
The adsolubilization is described as the solubilization of monomer into the admicelle. The adsorption of a surfactant bilayer at the solid/aqueous solution interface (step1) acts as a two-dimension solvent. Consequently, the hydrophobic monomer is adsolubilized or partitioned into the adsorbed surfactant aggregates.

#### Step 3 Polymerization of adsolubilized monomer

The monomer concentrated at the surfactant bilayers (step 2) is reacted with a water-soluble initiator. The polymerization is occurred and the monomers are transferred to polymer.

#### Step 4 The washing of the substrate to remove the excess surfactant

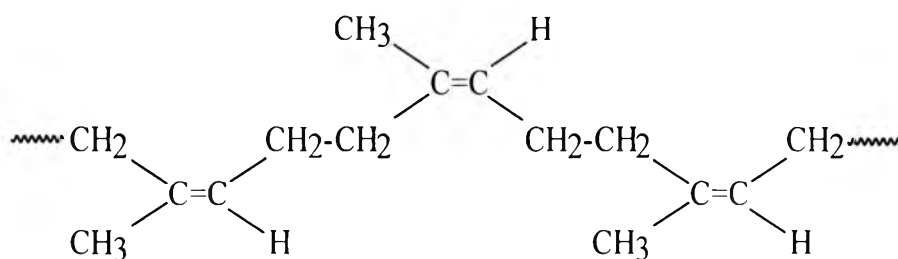
In order to obtain the ultrathin polymer film, the excess surfactant is removed by washing with water.



**Figure 1.3** Formation of a thin film by admicellar polymerization.

#### 1.1.4 Natural Rubber

Natural rubber is discovered from the plants at least 2000 species the entire world. The most significant species is the para rubber tree, *Heavea brasiliensis*. Figure 1.4 illustrates the structure of this rubber, which is cis1-4-polyisoprene.



**Figure 1.4** Typical structure of NR latex from *Heavea brasiliensis*.



In general, natural rubber is known as the natural rubber (NR) latex. The latex appears in the bark outside the cambium layer in ducts spiralling from the left to right as the latex ascends the tree. These ducts are found in concentric rings around the cambium and are really more concentrated near the cambium (Cole O.D., 1958 and Martin G., 1961.).

The procedure to obtain the latex called tapping is to make a spiral cut that is made downwards from left to right through the bark of the tree. This cut is manipulated to promote the latex to flow into the receptacle such as a plastic, glass, or earthenware cup. The fresh latex coagulates rapidly after tapping, especially in the ambient temperature. The fresh latex has pH of 7.0. Bacteria decomposes the sugar substances of latex, therefore the stability the latex decreases continually as the pH decreases. Bacteria come from various places such as the atmosphere, the bark and the tapping. The preservation of NR latex was first introduced by Johnson and Norris (1853). They suggested to use ammonia as the anticoagulant to the latex. The ammonia acts as an alkali to increase the pH of the fresh latex, thus the bacteria remains inactive and the stability of latex improves. In addition, the electrophoretic mobility of rubber tends to be negatively charged in the base environment. Fresh NR latex exuded from tree has dry rubber content 33 %wt. In industry, the latex is concentrated to about 60 %wt, which is economical and uniform in quality. There are several processes to concentrate latex: (1) evaporation, (2) creaming, (3) centrifuging.

The freshly-tapped NR latex is a whitish fluid of density between 0.975 and 0.980 g.m-1, and pH from 6.5 to 7.0. Its viscosity is variably.

The composition of latex is defined below:

total solids content	36%
dry rubber content	33%
proteinous substances	1- 1.5%

resinous substances	1- 2.5%
ash	up to 1%
sugars	1%
water	ad.100%

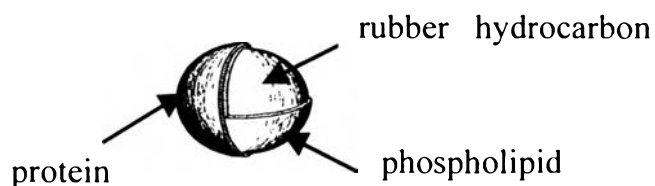
Hauser (1962) found that rubber particles were quite pear-shaped rather than spherical, and consisted of a tough, hard elastic shell which enclosed a viscous liquid. However, many literatures have reported that the rubber particles were spherical in shape, especially the latex from young trees. There are also suggestions that the shape of the latex depends on the age and type of tree.

The structure of the *Hevea brasiliensis* latex is :

Rubber hydrocarbon	86 %
Water (dispersed in the rubber hydrocarbon)	10 %
Proteinous substances	1 %
Lipid substances	3 %

Trace metals such as magnesium, potassium and copper are included with the rubber particles about 0.05 %.

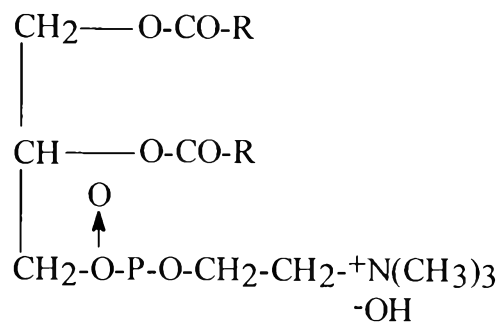
Figure 1.5 shows the structure of the NR latex particle. The NR consists of the protein structure at the outer layer of the surface. The adsorbed layer of protein determines the charge on the particle, electrophoretic mobility, and coacervation characteristics. The lipids associated with rubber particles are sterols and sterol esters, fats and waxes, such as eicosyl alcohol and phospholipids. They are found in the bulk of latex particle. They may be dissolved in rubber hydrocarbon. The phospholipids are adsorbed on the particle and are associated with the protein which are anchored on to the rubber.



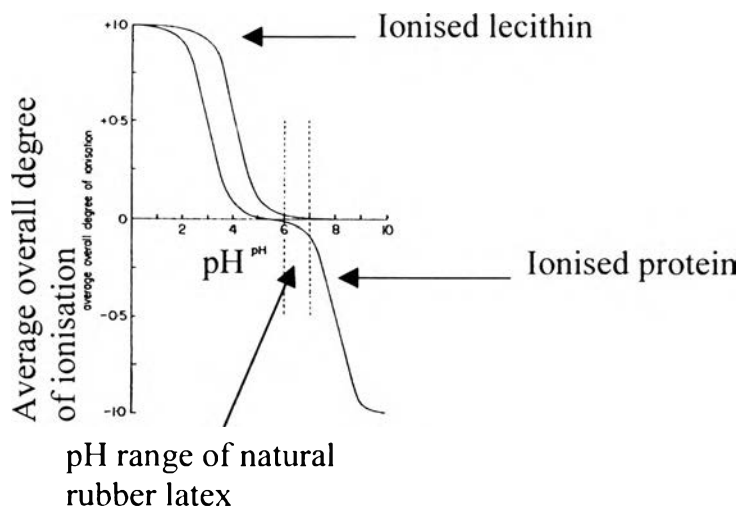
**Figure 1.5** Schematic representation of structure of NR latex particle.

The structures of phospholipids mostly found are lecithin. Figure 1.6 shows the example of one of lecithin structures whose R groups are hydrocarbon radicals of the heptadecyl ( $C_{17}H_{35}$ ) or heptadecenyl ( $C_{17}H_{33}$ ) types. The lipid layer exhibits positive charge, while the protein and lecithin offer negative charge. Figure 1.7 illustrates the effect of pH change on the ionic states of two species, protein and lecithin. At low pH value, protein and lecithin are positively charged. At high pH value, the charge of both species decreases where the effect to protein is more than that of the lecithin. If the pH is still increased, the charge of the protein may be reversed. On the other hand, the lecithin has the basic function as permanently ionised quaternary ammonium group so its charge is more difficult to change. The ammonia-preserved latex changes some compositions of fresh latex. The ammonia is used for hydrolysis of protein and phospholipid. The protein is degraded to polypeptide and amino acid and phospholipid is displaced by glycerol, fatty acid anion, organic bases and inorganic phosphate. The fatty acid anions are adsorbed at the particle interfaces. Therefore, the rubber particles of the ammonia-preserved latex

consist of proteinate ions and the fatty acid anions to improve the stability of the latex.



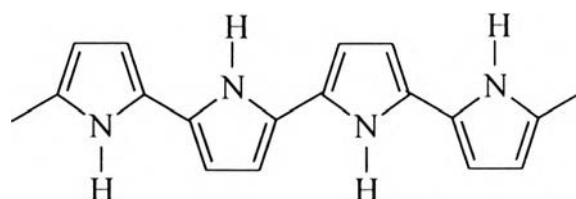
**Figure 1.6** The lecithin structure of phospholipid.



**Figure 1.7** The effect of pH on ionic charge of protein and lecithin.

### 1.1.5 Polypyrrole

Polypyrrole (PPy) is a heterocycle structure as shown in Figure 1.8. PPy was reported to be a conducting polymer by Dall'Olio *et al.* (1968). It was prepared by oxidation in sulfuric acid as black powder at ambient temperature. It presented with the conductivity of  $8 \text{ Scm}^{-1}$ . This polymer was continually studied at IBM with the electrochemical polymerization. PPy was synthesized in various approaches such as electrochemically and chemical polymerization.



**Figure 1.8** Structure of polypyrrole.

PPy has been mostly investigated in electrically conductive polymer. It is remarked with high conductivity, good stability in air and water. Additionally, It can be used in special applications such as antistatic coating, conductive paints, and electromagnetic shielding. However, there are several limits for conventional use as a conducting polymer. It suffers from poor mechanical properties e.g. brittleness, low procesability, and is hardly obtained with a controlled conductivity.

In this work, the thin conductive films of the conducting PPy onto the submicronic particles substrate by admicellar polymerization were studied. In this respect, the NR latex was used as a substrate.