CHAPTER I
INTRODUCTION

Conducting polymers have been utilized in several fields, such as electronic devices and sensors. Polypyrrole (PPy) is one of the most studied conducting polymers because of its good electrical conductivity, environmental stability and relative ease of synthesis (Omastova M. *et al.*, 2003). PPy can be prepared by electrochemical or chemical oxidation of pyrrole in various organic solvents and in aqueous media. Chemically synthesized PPy have been subjected to intense structural, physical, and electrical studies over last two decades because the ease of synthesis, environmental stability, and mass productivity are very attractive features that could facilitate large-scale industrial utilization. To prepare a large quantity of PPy, the chemical polymerization is the better method, for it is free from the restriction of an electrode shape (Kudoh Y., 1996). However, the flexibility of PPy is limited by the nature of oxidizing reagents used and the reaction conditions employed. The limitations of PPy, such as poor mechanical properties e.g. brittleness and poor processibility, must be addressed in order to achieve satisfactory utility. Several attempts have been made to improve the processibility of conducting polymers through the molecular design, copolymerization and functionalized organic dopants.

Natural rubber (NR) contains 93–95% cis-1,4-polyisoprene. It is an unsaturated elastomer with some good properties, such as high strength, outstanding resilience, and high elongation at break. However, NR is very sensitive to heat oxidation because of the carbon–carbon double bonds in its chains. Furthermore, NR has low tensile strength and tensile modulus and poor creep characteristics unless highly vulcanized. These drawbacks have been improved by some methods, such as modification of NR by graft copolymerization with a vinyl monomer (Nakason C. *et al.*, 2005).

One method to overcome the limitations of PPy and NR is the thin-film technique referred to admicellar polymerization (Bunsomsit K. *et al.*, 2002). Admicellar polymerization is, by design, a fine-coating technique that leads to the formation of ultrathin polymer films on charged surfaces by using surfactant bilayers

as a reaction template. Thin-film coatings have become increasingly important in many areas including, microelectronics, and composites. Several new methods have been invented and intensively studied for thin-film coating on many kinds of substrates. More recently, a new method for thin-film coating by admicellar polymerization has been invented. Layers of only a few nanometers in thickness have been reported for this method. Application of a thin PPy coating to a moldable latex might improve its utility by overcoming the poor processibility of neat PPy from its solubility and melt properties.

In this research, the objectives of the work are to study admicellar polymerization technique of polypyrrole coated on natural rubber particles by using dodecylsulfate sodium salt as surfactant and to observe the conductivity and processibility of admicelled natural rubber. The scope of work is to study the effect of pyrrole monomer on the morphology and conductivity, the effect of amounts of oxidant on the polymerization yield and the effect of salt concentration on the adsorption isotherm.

After admicellar polymerization, the following work is to analyze and characterize the film coated on natural rubber particles. This research focuses on the influence of pyrrole, initiator and salt content on the morphology, conductivity, mechanical properties, thermal properties and resistance to environment. This effort has two possible advantages: the processing of PPy might be facilitated and the electrical conductivity of the latex might be improved.

1.1 Theoretical Background

1.1.1 Surfactant

A surfactant or a surface active agent is a chemical substance that is the most versatile product in the chemical industry. It is used in automobiles, detergents pharmaceuticals, and also applied to many high technology areas. In a system with low surfactant concentration, the surfactant tends to adsorb at a surface or interface.

The molecular structure of a surfactant is called an amphipathic structure (Figure 2.1) because it consists of a lyophobic and a lyophilic group (a

hydrophobic and a hydrophilic group, respectively in the case of aqueous solution). In general, the molecules at the surface or interface have higher potential energy than that in the interior because the interaction between the same substance is stronger than that between different substances. When the surfactant is dissolved in a solvent, the lyophobic group of the surfactant in the interior of the solvent causes an increase in free energy of the system. Therefore, displacement of the surfactant molecules to the surface or interface is easier than that of the solvent molecule. From these reasons, the amphipathic structure of the surfactant is the cause of (1) high concentration of surfactant at the surface, (2) reduction of the surface tension of water and (3) orientation of the surfactant molecules at the surface or interface. The chemical structure of surfactant molecule must have an amphipathic structure in the solvent under the condition used for good surface activity in a particular system. The lyophobic group of surfactant is usually a long-chain hydrocarbon while the lyophilic group is an ionic or highly polar group.

The surfactant can be divided into 4 types. It depends on the nature of the hydrophilic group.

1. Anionic surfactant: The hydrophilic group consists of negative charge, for example, $RC_6H_4SO_3^-Na^+$ (alkylbenzene sulfonate).

2. Cationic surfactant: The hydrophilic group consists of positive charge, for example, $RNH_3^+Cl^-$ (salt of long chain alkyl amine).

3. Zwitterionic surfactant: The hydrophilic group may give both negative and positive charges, for example, $RNH_2^+CH_2COO^-$ (long-chain amino acid).

4. Nonionic surfactant: The hydrophilic group does not contain any ionic charge, for example, $RCOOCH_2CHOHCH_2OH$ (monoglyceride of long-chain fatty acid).
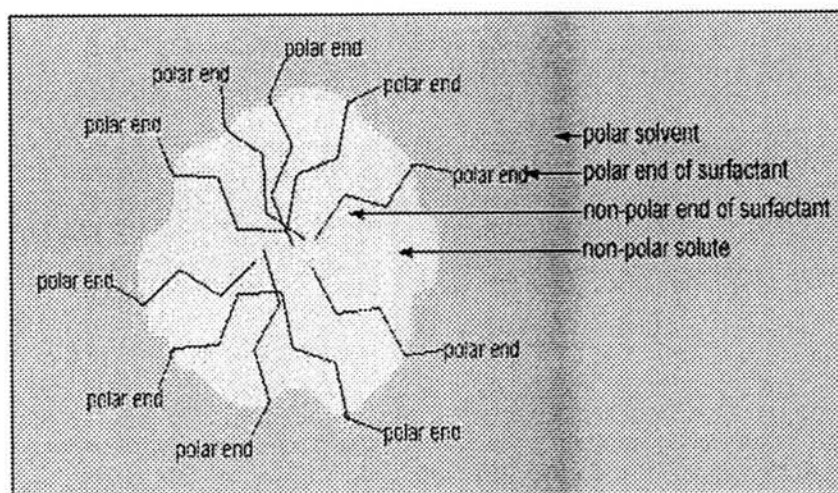
Figure 1.1 Molecular structure of a surfactant.

1.1.2 Surfactant Adsorption

The adsorption of surfactant is influenced by a number of factors:

1. The nature of the structural groups on solid surface (e.g. polar group, or nonpolar group).

2. The molecular structure of the surfactant (e.g. anionic, cationic, or nonionic surfactant).

3. The environment of the aqueous phase (e.g. pH, electrolyte content and temperature).

The point of zero charge (PZC) or the net surface charge of zero is the most critical parameter to manipulate the surfactant adsorption (Figure 1.2). The point of zero charge is specific for a substrate. It is known from the intersection of the electrophoretic mobility curve and the zero axis. When the solution pH is equal to PZC, the substrate surface has zero charge. At pH value below the PZC, the substrate surface exhibits a positive charge, while pH value above the PZC, the charge of the surface becomes negatively. The PZC value can determine the type of surfactant adsorbed on the substrate surface. Anionic surfactants are adsorbed below PZC, while cationic surfactants are adsorbed above the PZC.
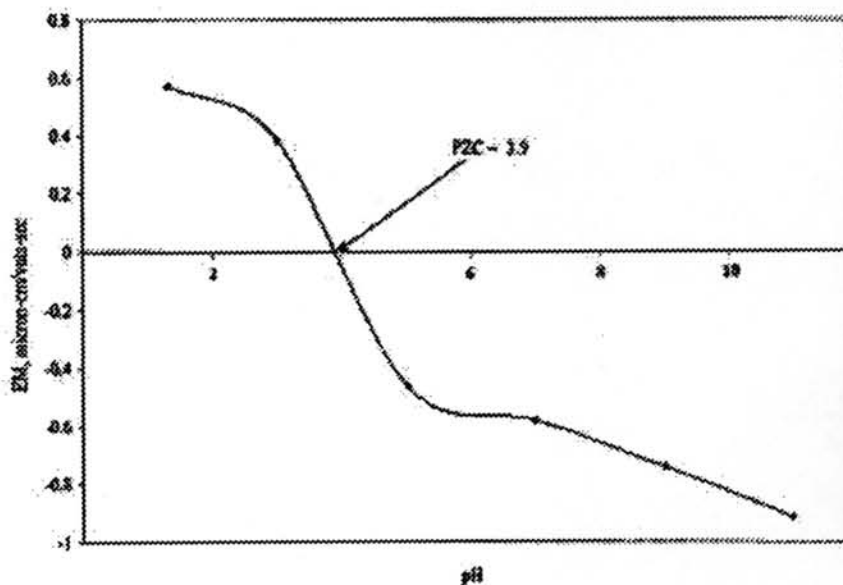
Figure 1.2 The point of zero charge on natural rubber surface (Bunsomsit. K. *et. al.*, 2002).

Furthermore, surfactant absorption is interesting to determine; (1) the amount of surfactant adsorbed per unit mass or unit area of the solid adsorbent, i.e. the surface concentration of the surfactant at the given temperature, since this is a measure of how much of the surface adsorbent has been covered and hence changed by the adsorption. (2) At the liquid-solid interface, the adsorption isotherm is used to help to explain the mechanism of surfactant adsorption. The adsorption isotherm curve is the plot between the log of adsorbed surfactant and the log of equilibrium concentration of surfactant in the bulk solution.

The shape of an adsorption isotherm curve can be classified into 2 types depending on the adsorbent.

1. Adsorption isotherm of surfactant from aqueous solution onto strongly charged site adsorbents.

The adsorption isotherm curve is typically an S-shape curve and can be separated into four regions as shown in Figure 1.3.

Region I | Region II | Region III | Region IV

CAC

CMC
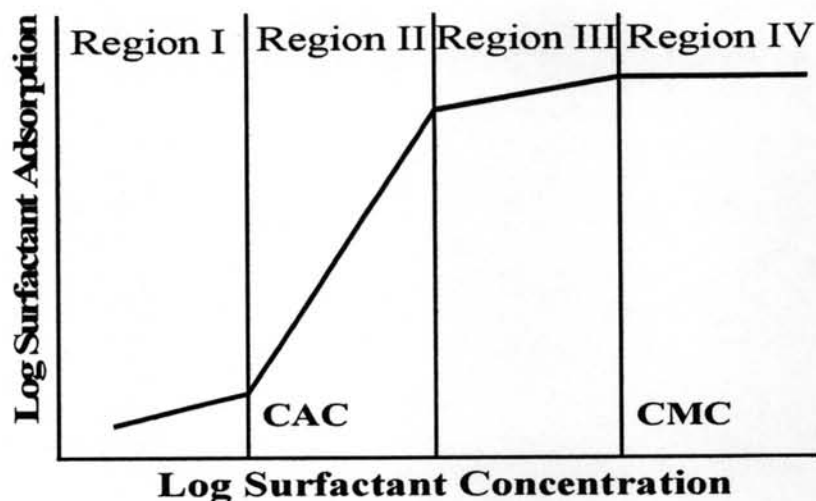
Figure 1.3 Adsorption isotherm of surfactant from aqueous solution onto strongly charged site adsorbents (Pongprayoon. T. *et. al.*, 2002).

In region I, the surfactant adsorbs mainly by ion exchange. In region II, it is a marked increase in adsorption, resulting from interaction of the hydrophobic chain of oncoming surfactant ions with those of previously adsorbed surfactant and with themselves. In region III, the slope of isotherm is reduced because adsorption now must overcome electrostatic repulsion between the oncoming ions and the similarly charged solid surface. In region IV, adsorption is usually completed when the surface is covered with a monolayer or bilayer of the surfactant and micelles are initiated.

2. Adsorption isotherm of surfactant from aqueous solution onto nonpolar, hydrophobic adsorbents.

The adsorption isotherm curve is in the form of Langmuir type or L-shape curve as shown in Figure 1.4.
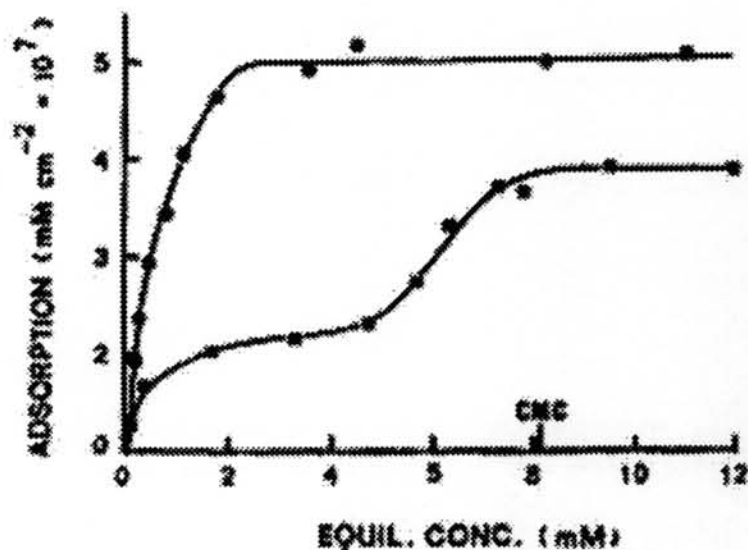
Figure 1.4 Adsorption of sodium dodecyl sulfate onto Graphon at 25°C: ■, from pure water; •, from aqueous 0.1M NaCl (Rosen. M.J. *et. al.*, 2004).

The hydrophobic tails of surfactant are adsorbed on the solid surface, so the orientation of the molecules of surfactant is mostly parallel to the surface. When the molecules of surfactant continue to adsorb on the surface, the orientation is more and more perpendicular to the surface. The inflection point may be from the change of orientation from parallel to perpendicular.

1.1.3 Admicellar Polymerization Technique

An admicellar polymerization technique is based on the physically adsorbed surfactant onto the substrate, so called admicelle. The feasibility of the phenomena of admicelle formation, adsolubilization to form polymerized and organized ultra thin film of molecular dimension of substrates has been investigated continually for several years.

Admicellar polymerization consists of four steps (showed in Figure 1.5)
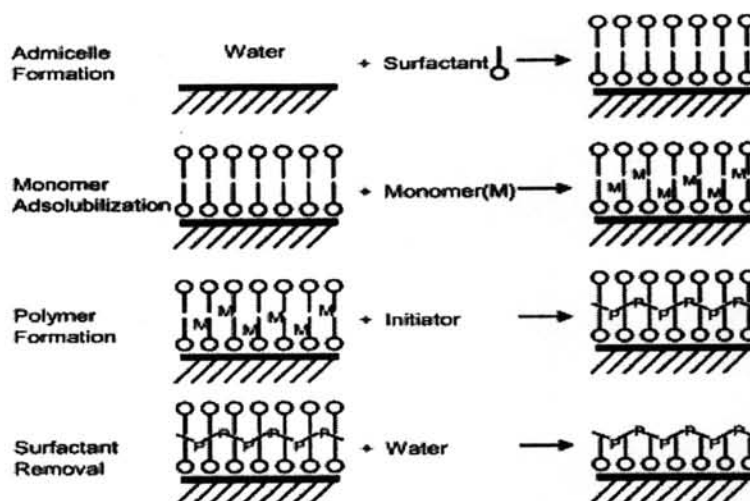
**Figure 1.5** Step of the four steps of admicellar polymerization technique (Rungruang P. *et al.*, 2006).

Step I Admicelle formation

The formation of an admicelle 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. 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). The PZC is benefit for the wide selection of surfactant type to adsorb on substrate.

Step II Monomer adsolubilization

The partitioning of organic solutes from aqueous solution into interior of adsorbed surfactant aggregates is termed "adsolubilization". The suggested definition of adsolubilization is "the incorporation of a compound into surfactant surface aggregates, which compound would not be in excess at the interface without surfactant". This phenomenon is analogue of solubilization, with adsorbed surfactant bilayer playing the role of micelles as showed in Figure 1.6.

Solubilization
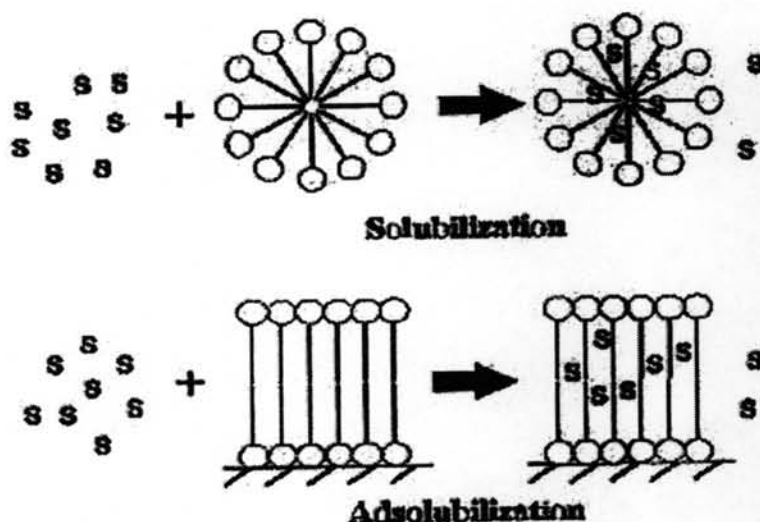
Adsolubilization

Figure 1.6 Phenomena of solubilization and adsolubilization (Arayawongkul. S. *et. al.*, 2002).

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

Step III Polymer formation

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

Step IV Solvent removal

In order to obtain the ultra thin polymer films, the excess surfactant is removed by washing with water.

1.1.4 Natural Rubber

Natural rubber is discovered from the plants at least 2000 species in the entire world. The most significant species is the para rubber tree, *Heavea brasiliensis*. Figure 1.7 illustrates the structure of this rubber, which is cis-1,4-polyisoprene.
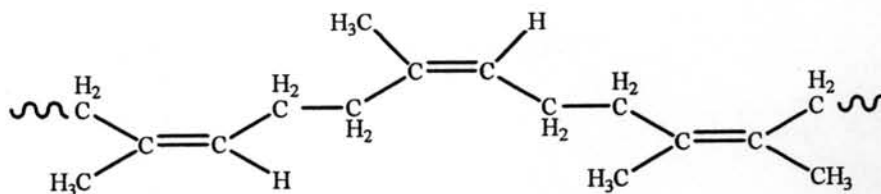
Figure 1.7 Typical structure of NR latex from *Heavea brasiliensis*.

In general, natural rubber is known as the natural rubber (NR) latex. The latex appears in the bark outside the cambium layer in ducts spiraling 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.

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 decompose the sugar substances of latex, therefore the stability of 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-shape 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 suggested that the shape of the latex depends on the age and type of tree.

The structure of the *Heavea 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%.

rubber hydrocarbon

**protein**

phospholipid
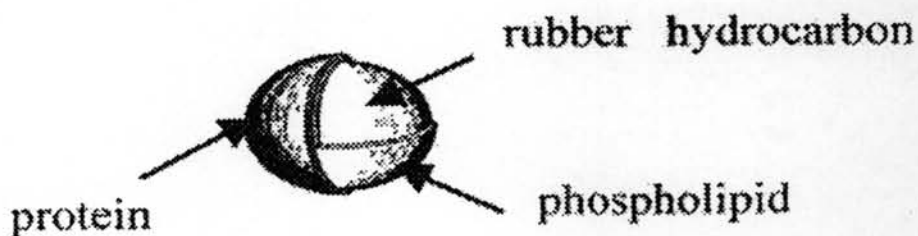
Figure 1.8 Schematic representation of structure of NR latex particle.

Figure 1.8 shows the structure of the NR latex particles. 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.

1.1.5 Polypyrrole

Polypyrrole (PPy) is a heterocycle structure as shown in Figure 1.9. 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 S.cm^{-1}. This polymer was continually studied at IBM with the electrochemical polymeriazation. PPy was synthesized in various approaches such as electrochemicaly and chemical polymerization.
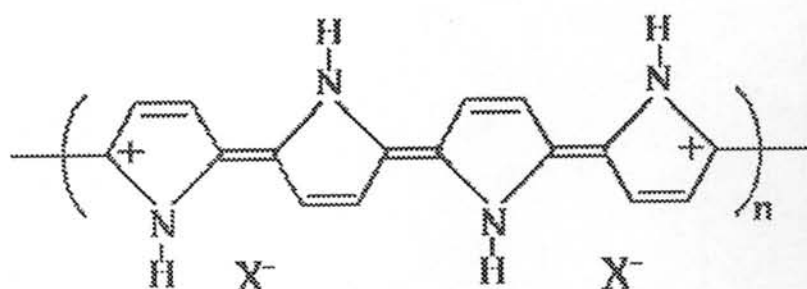
Figure 1.9 Structure of polypyrrole.

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, conducting paints, and electromagnetics shielding. However, there are several limits for conventional use as a conducting polymer. It suffers from poor mechanical properties e.g. brittleness, low processibility, and is hardly obtained with a controlled conductivity.