

CHAPTER I

INTRODUCTION

Numerous applications of conductive polymers have been proposed. The objective is mainly to combine their favorable electrical properties with the processability of polymers. Polypyrrole (PPy) is known to be a good conductive polymer, however, its processability is relatively poor due to its brittleness (5% in elongation at break and 24 MPa in tensile strength (Li, Y. and Ouyang, J., 2000) and strong cohesive strength. Thus, several investigations have been carried out to blend PPy with other polymers, both plastics and rubbers, to make PPy composites. The composites typically show improved thermal resistance and conductivity compared to pure polymer matrices. The new application of latexes is used in electronic chip production as ceramic and metal powder dispersants, allowing for thin film application. Moreover, a thin film via surfactant template (TFST) technique, which is known as admicellar polymerization, has been recently applied to produce various conductive polymers. The recent technique involves the formation of ultra thin polymer film on charged surface by using surfactants.

Polymer films coated on a solid substrate such as nickel or alumina are also prepared by TFST method but their higher melt temperature preclude processing possible with a softer substrate such as latex. The most promising conductive polymer should demonstrate good solution or melt processability, in addition to environmental stability, mechanical integrity, and controllable conductivity. These materials will be useful when the unique properties of a conductive polymer are important, e.g. elasticity in composites, electrochromic behavior, and chemical reactivity in sensor applications. Thermoplastics are commonly used to make electronic enclosures and cabinetry. The advantages of the attributes of thermoplastics are cost effectiveness, lightweight, appearance, and ease of processing. Development efforts in recent years have resulted in commercially available conductive thermoplastic compounds that are acceptable as shields against electromagnetic interference (EMI).

Admicellar polymerization in this work is based on soft polymer substrate, i.e. natural rubber latex particles. The surfactant bilayer was deposited on the surface of these particles and initiator (oxidant) was added to allow polymerization of pyrrole monomer associated with the surfactant bilayer. The outer layer of surfactant was washed away by water at last.

From the previous research, admicellar polymerization had been used for the preparation of conductive PPy coating on natural rubber (NR) latex particles using anionic surfactant sodium dodecyl sulfate (SDS). Surfactant adsorbed on the particle surface to form the surfactant layer after adjusting pH below the point of zero charge (PZC) of the latex. It was found that pyrrole (10-20 mM) caused a decrease in SDS adsorption at equilibrium. Surfactant adsorption and pyrrole adsolubilization increased in the presence of salt (NaCl) (0.3-0.6 M). The morphology of the film was observed by Optical Microscopy and the conductivity of the film was also investigated. The dried films of PPy coated onto latex exhibits lower conductivity than that distributed in an aqueous suspension of latex particle. The film of PPy coated NR latex containing salt gives higher conductivity than the one containing only SDS.

The attempts of this study were composed of two parts in order to incorporate polymerization to produce a conducting thin film of natural latex particles at various amounts of polypyrrole. Therefore, two advantages that are also the aims of this work will be obtained: firstly improve processability of PPy and, secondly, enhancement in conductivity properties of the latex. Moreover, the mechanical properties of the samples are investigated. The mechanism of surfactant adsorption and the pyrrole adsolubilization will be considered to get the thin film formation of polymer with better performance in their applications. The method to characterize the morphology also changed by using SEM instead of Optical Microscopy in the previous work. However, coating has limitation at 10 and 20 mM pyrrole (little increase in pyrrole adsolubilization from 10 to 20 mM) therefore admicelled latex particles (particles with PPy admicellar polymerization) were mixed with pyrrole at different weight%. Mixing methods were called one and two-step polymerization respectively. One-step polymerization is similar to admicelled latex but the amount of latex particles and pyrrole in wt% was calculated to obtain the desired

composition. In order to embed latex particles in PPy matrix; two-step polymerization was preferable because of much greater amount of pyrrole incorporated in the mixture. The samples obtained from two-step polymerization called admicelled/PPy composite prepared by mixing admicelled latex with pyrrole, then polymerizes them together. So, two-step polymerization was chosen anyway, some samples were selected for testing because of its brittleness.

1.1 Theoretical Background

1.1.1 Natural Rubber Latex

The only rubber plant that has been of commercial interest for the past 60 years, since the period of World War II, is the *Hevea brasiliensis*. It may be tapped from the Brazilian rubber tree for latex by gouging the bark with a tapping knife. *H. brasiliensis* belongs to the family of *Euphorbiaceae* (Mooibroek, H. and Cornish, K., 2000) with species which are well known for the milky suspension of rubber globules (latex). The rubber material obtained from the latex produced by certain plants and trees especially cis-1,4-polyisoprene was the only rubber of any commercial significance until the 1930s, and still is one of the most important, primarily due to its molecular structure and high molecular weight. The molecular weight of fresh raw rubber typically has a number average value of about 5 million, in addition, freshly tapped rubber contains crosslinked microgel. This rubber has high performance properties that cannot easily be mimicked by artificially produced polymers. These high performance properties include resilience, elasticity, abrasion resistance, efficient heat dispersion (minimizing heat build-up under friction), and impact resistance. However, *H. brasiliensis* has strict climate requirements, limiting its cultivation to specific tropical regions. The composition of the *Hevea* Latex varies quite widely but the following may be considered to be a typical composition. Figure 1.1 illustrates the structure of cis-1,4-polyisoprene.

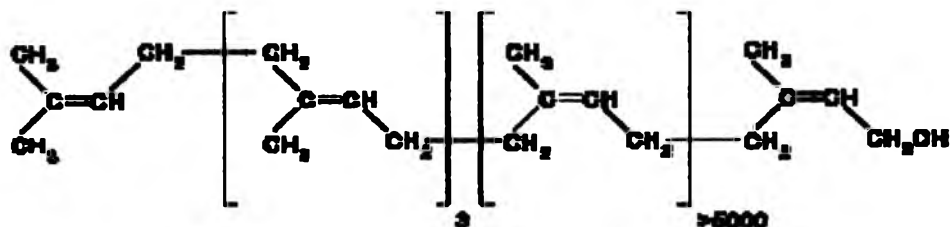


Figure 1.1 Structural formula of cis-1,4-polyisoprene in natural rubber.

Table 1.1 Typical composition of *Hevea* latex

Total solids contents	36% (including dry rubber content, DRC, of 33%)
Proteinous substances	1-1.5%
Resinous substances	1-2.5%
Ash	less than 1%
Sugar	1%
Water	0.60%

The latex may then either be concentrated to about 60% DRC, usually by centrifuging or evaporation, or alternately coagulated and dried.

The overall structure of rubber particles is similar in all species examined so far, they contain a homogeneous rubber core surrounded by an intact monolayer membrane (Irving and Cornish, 1997). The membrane is made up of a highly species-specific complement of lipids and proteins (Siler *et al.*, 1997). Normally, cis-1,4-polyisoprene is amorphous but crystallizes on cooling to below 0°C so that natural rubber hardens on storage at low temperatures. This may be arrested in anti-crystallizing rubber. Crystallization can also be induced by stretching and is responsible for the high tensile strength of natural rubber. At ambient temperature, linear raw rubber is a weak material becoming sticky at about 60°C and fluid at about 120°C. Natural rubber is still of major importance due to its low cost, low hysteresis, high strength, high resilience, excellent dynamic properties and fatigue resistance despite competition from the recently developed synthetic rubbers, e.g. SBR, polybutadiene, and polychloroprene, etc. The proximity of the

methyl group to the double bond in natural rubber results in more reactive at both the double bond and at the α -methylene position than polybutadiene, SBR, and particularly, polychloroprene.

1.1.2 Polypyrrole

Conducting polymers have been of interest for more than two decades and one of the current interests in researching is polypyrrole (PPy). It has been attached much interest since it offers reasonably high conductivity and has fairly good environmental stability. However, PPy is insoluble in ordinary solvents and infusible because it decomposes before melting like many other conductive polymers. Moreover, it has poor processability and low mechanical strength.

Polypyrrole can be easily prepared by electro-chemical or chemical polymerization. The chemical oxidative polymerization can occur in four ways: 1. at an interphase of two immiscible solutions (Nakata, M. *et al.*, 1992); 2. in a homogeneous solution (Machids, S. and Miyata, S., 1989), 3. in the vapor phase (He, F. *et al.*, 1993; Baik, D.H. *et al.*, 1998), and 4. at the solid-liquid interface (Bunsomsit, K. *et al.*, 2002).

The poor processability of PPy can be overcome by different methods such as latex-based coatings (Brown, R. A., *et al.*, 1989) by the preparation of core-shell latexes, composites fabrication, copolymerization method, and admicellar polymerization, etc.

Conductivity is not the only important property of PPy. Other interesting properties are charge storage and ion exchange ability, visible light absorption, and transparency to X-rays.

Admicellar polymerization of PPy coated on NR latex particles was carried out in this study in order to produce ultra thin PPy film on latex particles. Mechanical strength and processability of PPy will be examined.

1.1.3 Admicellar Polymerization

The *in situ* polymerization of the absorbed monomer with surfactant or Admicellar Polymerization technique has been the object of intense study in recent years because of the wide variety of possible applications of these films. The process

for the formation of ultra thin films on substrates include four major steps, which is based on the formation of micelle-like aggregates of adsorbed surfactants at a solid-solution interface. This technique is reported to be quite versatile and is applicable to a variety of surfaces. Thin film formation process can be classified into 4 basic steps described briefly below:

Step 1. *Admicelle formation*

The well-known phenomenon of surfactant aggregation at solid-liquid interfaces to form bilayers (admicelles) via adsorption from an aqueous solution occurred below the critical micelle concentration (CMC). The critical parameter to be concerned in order to obtain admicelle formation is the pH of the solution relative to the surface charge of the substrate (referred as the point of zero charge, PZC). Generally, anionic surfactants adsorb below the PZC and cationic surfactants adsorb above the PZC. Adsorption is accomplished through the use of a suitable surfactant under appropriate system conditions. In this study, NR latex particle with a negatively charged surface was used as substrate, it typically has a PZC in the acidic pH range. (There is not a high surface charge density for NR latex.)

Step 2. *Monomer adsolubilization*

The solubilization of monomer into the admicelle is called adsolubilization. Generally, adsolubilization can be defined as the excess concentration of species at an interface that would not exist in the absence of admicelles. This process can occur after the formation of the admicelles or concurrently with surfactant adsorption.

Step 3. *In situ polymerization of adsolubilized monomer*

In this step, initiators begin the polymer formation, probably by the mechanisms similar to those occurring in conventional emulsion polymerization technique. In this study ammonium persulfate was used as the initiator or oxidant. To reduce polymerization in the bulk solution, the study of adsorption and adsolubilization isotherms is made to ensure that the system equilibrates with the

surfactant concentration in the bulk solution below the critical micelle concentration (CMC).

Step 4. Surfactant washing

The treated substrate is washed to remove the outer surfactant layer as much as possible so as to expose the thin polymer film.

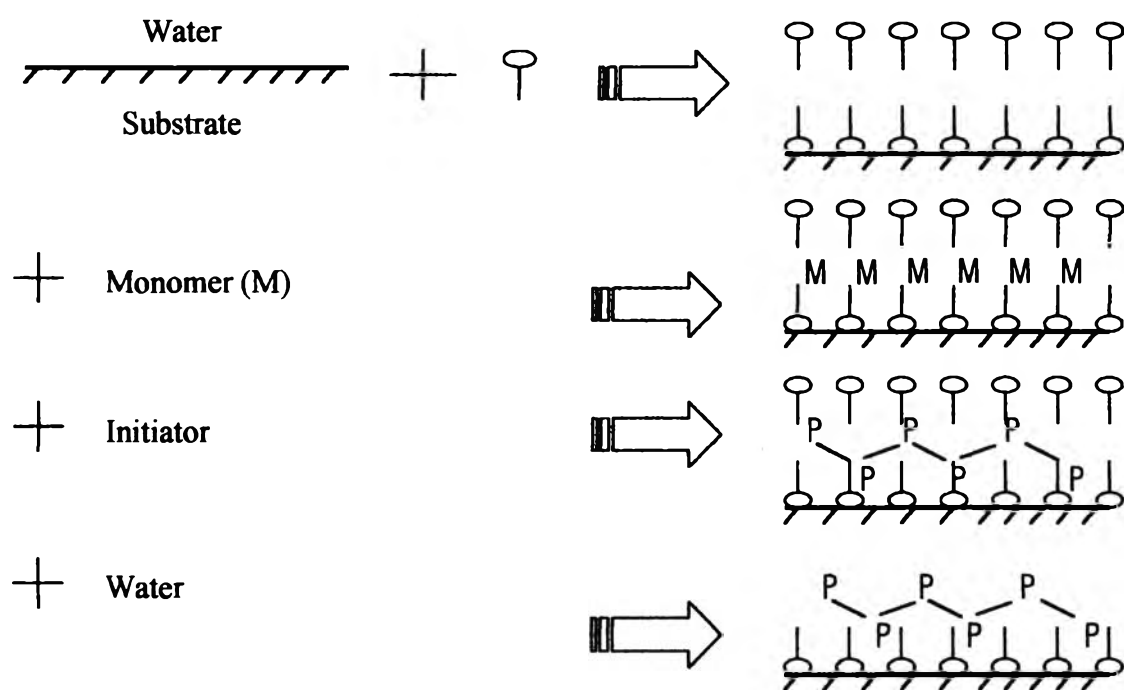


Figure 1.2 Schematic representation of thin film formation step.