



CHAPTER I

INTRODUCTION

Rubbers are usually electrically insulating. Rubber can be rendered conductive by the incorporation of the adequate loading of carbon black as low as 20 parts per 100 parts (by weight) of the raw rubber. Although conductive rubber has been known since the late of the nineteenth century, it was not of major interest until 1930. The particle size of carbon black ranges from 10 to 300 millimicrons, formed by burning or cracking hydrocarbon oil or gases. These particles tend to form themselves into chains, instead of being individually dispersed. The carbon chain gives rise to the conductivity of rubbers. The values of resistivity may lie between 1 ohm.cm and 10^{15} ohm.cm. (Norman, 1970)¹

Conductive rubbers may be used instead of metallic conductors because the soft materials have the obvious advantage of flexibility and their ability to absorb mechanical shock. Both soft and rigid organic materials have the following advantages over metals (Tasakorn, P.1999)²:

- (i) Ease of shaping, flexible
- (ii) Low density, light weight
- (iii) Wide range of electrical conductivity
- (iv) Low thermal conductivity
- (v) Corrosion resistance

Currently, many works are devoted to the synthesis of conducting polymers for use in a variety of applications, mainly for electronic and optical devices as well as for various industrial applications, eg. semi-conductive textiles, including yarns and fabrics, and military applications, i.e. radar-absorbing materials, camouflage netting, microwave antennas, etc. Moreover, composites of electrically conductive particles in a non-conducting polymer matrix are materials with increasing importance as resistors in microelectronic devices, electrochemical devices, optical switching devices, mechanical actuators and display devices, batteries, molecular electronics, nonlinear optics, electrical magnetic shields, microwave-absorbants, polymer light

emitting-diodes (PLED), heating elements, electrically conductive adhesive, film and foams, or plastics dissipating static charges, and so on. (Gordon, G. 2003)^{3,13}

Several attempts have been made to improve the processibility of conducting polymer through molecular design, copolymerization, and functionalized organic dopants. Usually, blending the nonconductive polymers with conductive polymers is a common and simple route to improve the processability and mechanical properties. This approach often results in a lowering of conductivity, and it is not easy to control the compatibility between two polymers. A number of conducting polymers, such as polyaniline(PANI), polypyrrole(PPy), and polythiophene(PTH) (Figure1.1) in an aqueous or organic medium, can be blended with the insulating polymer, eg. rubber to produce conducting polymer composites with good conductivity and superior mechanical properties.

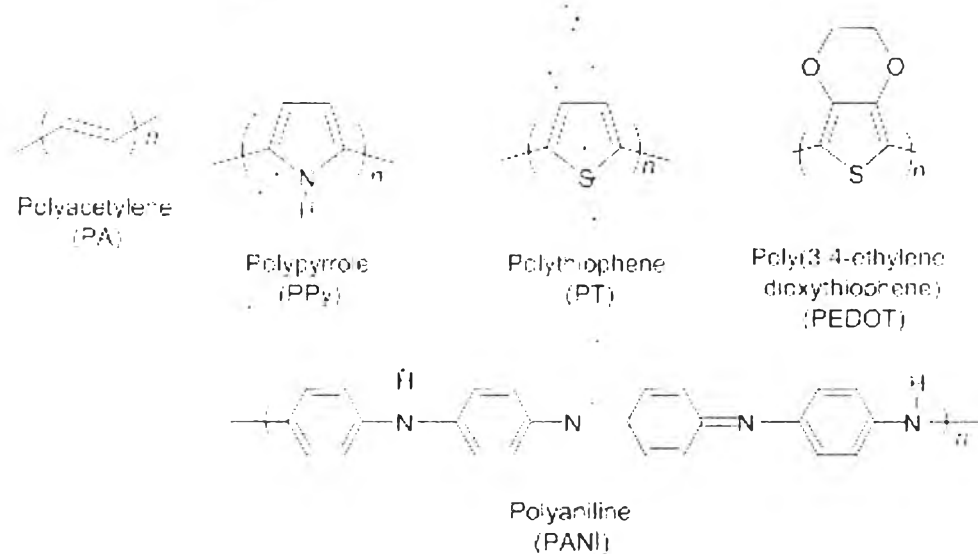


Figure 1.1 Chemical structures of common conductive polymers: polyacetylene, polypyrrole, polythiophene, poly(3,4-ethylenedioxythiophene), and polyaniline^[4].

Conductive polymers (CPs) exhibit good stability, conductivities, and ease of synthesis [4-6]. Table 1.1 lists a broad range of different CPs and their conductivities.

Table 1.1 Conductivity of common CPs^a

Conducting polymer	Maximum conductivity (S/cm) ^b	Type of doping
Polyacetylene (PA)	200–1000	n,p
Polyparaphenylene (PPP)	500	n,p
Polyparaphenylene sulfide (PPS)	3–300	P
Polyparavinylyene (PPv)	1–1000	P
Polypyrrole (PPy)	40–200	P
Polythiophene (PT)	10–100	P
Polyisothionaphthene (PITN)	1–50	P
Polyaniline (PANI)	5	n,p

^a Reproduced from [7]

^b S=Siemens.

Polypyrrole is one of the most studied conductive polymers because of its good electrical conductivity, good environmental stability, biocompatibility, and relative ease of synthesis. Polypyrrole exhibits a wide range of surface conductivities ($10^{-3} \text{ Scm}^{-1} < \sigma < 100 \text{ Scm}^{-1}$) depending on the functionality and substitution pattern of the monomer and the nature of the counter ion or dopant (Nalwa,1997)⁸. PPy can be prepared by the electrochemical or chemical oxidation of pyrrole in various organic solvents and in aqueous media. Chemical polymerization is one of the best methods to prepare a large quantity (Bunsomsit,2002)⁹. However, the flexibility of PPy is limited by the nature of the oxidizing reagents used and the reaction conditions employed. The limitations of PPy, such as poor mechanical properties (e.g. brittleness and poor processability) have to be addressed in order to achieve satisfactory utility.

Organic dopant is one of the most important factors that can affect the properties of the conducting polymers. It has been demonstrated that one-step electrochemical polymerization of a conducting polymer in the solubilized polyelectrolyte is an extremely convenient preparation technique (Pongprayoon,2002)¹⁰. Electro-

chemically polymerized PPy deposited on the electrode surface has been reported; the morphology and structure can be altered by the use of polymeric anions (Tasakorn, 1996)¹¹.

Recently, Chantarak. S. (2006)¹² reported the success of material polypyrrole (PPy) coated on the surface of natural rubber particles by admicellar polymerization using Dodecyl Sulfate Sodium salt (SDS) as a surfactant at various pyrrole concentration. This work encourages the further study of the conductive polymer composites made electrochemically. Its advantages are shown in the Table 1.2.

Table 1.2 Comparison of chemical and electrochemical CP polymerization^{[4],[13]}

Polymerization approach	Advantages	Disadvantages
Chemical polymerization	<ul style="list-style-type: none"> • Larger-scale production possible • Post-covalent modification of bulk CP possible • More options to modify CP backbone covalently • High yield • Ordered structure • Faster reaction 	<ul style="list-style-type: none"> • Cannot make thin films • Synthesis more complicated
Electrochemical polymerization	<ul style="list-style-type: none"> • Thin film synthesis possible • Ease of synthesis • Entrapment of molecules in CP • Doping is simultaneous • Efficiency to control on the polymerization and doping level • Reduce the stickiness problem • Don't need an initiator • Don't need control temperature 	<ul style="list-style-type: none"> • Difficult to remove film from electrode surface • Post-covalent modification of bulk CP is difficult

Objectives of the research

The main objective of this study is to investigate the possibility of using electrical synthesized conductive polymers in natural rubber structure as admicelled polymerization. In this study, natural rubber particles were coagulated together with electrochemical synthesized PPy and PTh on the anode. The composites of polypyr-

role or polythiophene with natural rubber were prepared by electrochemical synthesis with SDS as surfactant.

Scope of the research

This research focuses on the influences of pyrrole content and thiophene content, pH, time, and voltage on the morphology. Furthermore, it also studies the mechanical properties, thermal properties, and conductivity to compare properties between the electrochemical method and the previous research method (chemical) of both conductive polymers.