CHAPTER VII
EFFECT OF DOPING WITH IODINE INTO CONDUCTIVE RUBBER BY ADMICELLED TECHNIQUE

7.1 Abstract

A novel electrical and optical properties of a non-conjugated elastomer, cis-1,4-polyisoprene (natural rubber), upon treatment with admicelled technique has been studied. Pyrrole and Thiophene polymer prepared via this technique at different ratio. A significant improvement of the conductivity of the iodine-doped natural rubber latex was estimated one order (from 7.18×10^{-15} to 7.25×10^{-14}) of magnitude higher than of nondoped. Examination of FTIR studied reveals the formation is accompanied by transformation of the outer charge transfer complexes from C=C bond to the dopant molecule. A comparison of the doping with non doping is studied in their different properties such as mechanical properties, thermal stability, and conductivity. This also indicated morphology by using SEM to explanation the changing of properties.

7.2 Introduction

In past few decades, the synthesis and characterization of conductive polymers have become one of the most importance research areas in polymer science. Traditionally these polymers are synthesized via chemical and electrochemical polymerization. Conjugated double bond sequences are one of a prerequisite for electrical conductivity in polymer. Rubber having isolated double bonds with no conjugation has been widely components in conducting composites or copolymers together with conjugated polymers, such as polyacetylene. Such composites have improved physical properties (solubility, fusibility and meltable) compared with most conjugated conducting polymers. The discovery, in 1988, that "Iodine-doped" rubber can conduct electricity attracted a great deal of interest. Thakur discovered that the conductivity of cis-1,4-polyisoprene (natural rubber) can be increased by 10 orders of magnitude upon doping with iodine. This observation generated a great deal of interest from both theoretical and experiments point of view. Since then, various other polymers containing isolated double bonds, such as trans-1,4-polyisoprene has been found to become dark in color and conductive when doped with iodine in the solid state. Surprisingly, however, cis-1,4 polybutadiene does not change color or become conductive upon I_2-doping. Dai, L.(1995) reported that I_2-doping of cis-1,4-polyisoprene produces conjugated sequences of unsaturated double bonds in the polymer backbone, which confer the conductivity.

Doping can be accomplished in several ways depending on the polymer natural and its intended application. The initial discovery of the ability to dope conjugated polymers involved chemical doping by charge transfer redox chemistry (E.J.Louis ,1977)[134,135]. Oxidation (p-doping) was accomplished by exposing the polymer to iodine vapors whereas reduction (n-doping) involved treatment with sodium napthalenide (Figure 7.1).
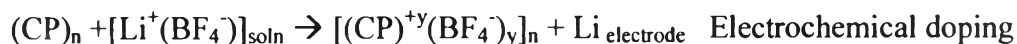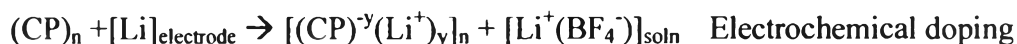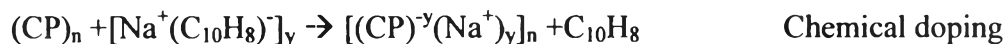
a) p-type doping

$(CP)_n +3/2\ ny(I_2) \rightarrow [(CP)^{+y}(I_3^-)_y]_n$ Chemical doping

$(CP)_n +[Li^+(BF_4^-)]_{soln} \rightarrow [(CP)^{+y}(BF_4^-)_y]_n + Li_{electrode}$ Electrochemical doping

b) n-type doping

$(CP)_n +[Na^+(C_{10}H_8)^-]_y \rightarrow [(CP)^{-y}(Na^+)_y]_n +C_{10}H_8$ Chemical doping

$(CP)_n +[Li]_{electrode} \rightarrow [(CP)^{-y}(Li^+)_y]_n + [Li^+(BF_4^-)]_{soln}$ Electrochemical doping

Figure 7.1 Doping methods in conjugated polymers demonstrated for chemical and electrochemical doping.

Generally, the molecular backbone configuration of natural rubber were divided into 2 types, which are shown in Figure 7.2. The relevant properties of natural rubber are listed in the Table7.1. Dai, L.(1995)[136].
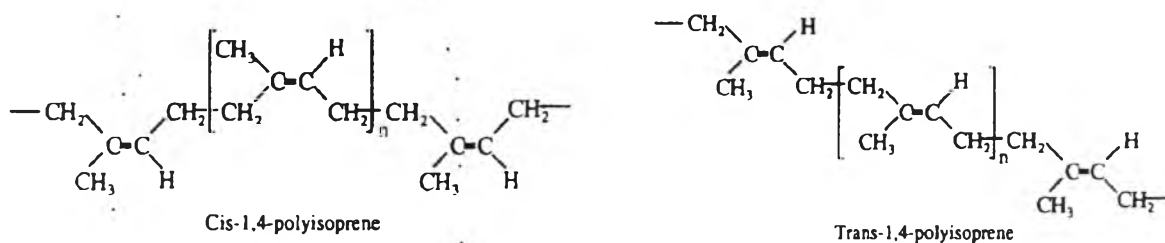

Figure 7.2 Molecular structure of the natural rubber.

Table7.1 Molecular characteristics of the natural rubber

Sample	Percentage content of isomer	Mol wt (M_w)
Cis-1,4 polyisoprene	97% cis	800,000
Tran-1,4 polyisoprene	100% trans	410,000

Doped intrinsically conductive polymers have been authoritatively recognized as the "Hottest thing in modern physics". Organic polymers are generally recognized insulators of electrical current flow and are generally complex mixtures of microscopic crystalline and disordered or amorphous elements with no free electrons to carry charges through them. Recent discoveries of polymers having unsaturated carbon to carbon double bonds in the "mers" or repeating groups which are alternative with or "conjugated" in the known polymers, such as polyacetylene,

poly(paraphenylene) and poly(p-phenylene sulfide) when treated or "doped" with electron donors or electron acceptor (dopants) have been found to produce conductive polymers.

The initial reduction to practice of this invention came about through the successful doping of natural rubbers (polyisoprene). Polyisoprene is the principal rubbery component of natural rubber. Isoprene has been used extensively in the synthesis of synthetic rubbers. Earlier attempts in our initial research to dope polybutadiene rubber established little or no success. This polymer is understood to have the basic "mer" structure: $(--CH_2 --CH=CH--CH_2 --)_n$

Note the exclusive hydrogen substitution of the double bond.

An initial survey of the electrical conductive properties of natural and synthetic rubbers having established the improvement in stability upon exposure to oxygen and water over an extended period of time and the promising improvement in electrical conductivity upon doping with the halogen, iodine, of other natural and synthetic rubbers available from commercial sources were studied. Germany had produced artificial rubber on a commercial scale from dimethylbutadiene, commonly called methyl rubber. If one methyl group appeared to be significant, reason suggested two would be of theoretical interest. Samples were obtained. These methyl rubbers of commerce were subjected to doping with iodine (limited facilities prevented use of more toxic dopants). It was found that methyl rubber, or di-methyl rubber, to define over polyisoprene rubber, not only developed a higher level of conductivity upon doping, but developed it upon shorter exposure than had been the case with polyisoprene.

Recently, our research group success with synthesize of material PPY/PTh-coated on the surface of natural rubber particle by admicelled polymerization technique. The typical conductive polymers are summarized in Figure 7.3. Among conductive polymers, polypyrrole(PPy) and polythiophene(PTh) have been particular interest because of their high electrical conductivity, good environmental stability and the possibility of their application in emerging technologies. The main objective of this study is to investigate the possibility of using electrical synthesized conductive polymers in natural rubber latex by admicelled polymerization with doping Iodine. In this study, natural rubber particles were coagulated together with

electrochemical synthesized PPy and PTh on the anode. The composites of polypyrrole or polythiophene with natural rubber were prepared by electrochemical synthesis with SDS as surfactant. This research focuses on the influences of Iodine doping to the materials. It also studies the properties such as conductivity, mechanical, thermal properties and morphology.

Name	Structure	Name	Structure
trans-Polyacetylene		Poly(phenylene ethynylene)	
cis-Polyacetylene		Polyselenophene	
Polypyrrole		Polyfuran	
Polythiophene		Poly(N-substituted aniline)	
Poly(p-phenylene)		Poly(N-substituted pyrrole)	
Poly(phenylenevinylene)		Poly(diphenylamine)	
Polyaniline		Poly(indole)	
Poly(thienylenevinylene)		Poly(thieno[3,2-b]pyrrole)	
Poly(furylenevinylene)		Poly(fluorene)	
Poly(phenylenesulfide)		Polypyridine	

Figure 7.3 Typical conducting polymers.

7.3 Experimental

7.3.1 Materials

In this research, the natural rubber latex used as the substrate for electrochemical polymerization was provided by Rubber Research Institute, ~60% DRC. The anionic surfactant, selected for this experiment was Sodium Dodecyl Sulfate (SDS). A schematic of the chemical structure of SDS is shown in Figure 3.1. SDS was purchased from Aldrich Chemical Company, Ltd. with 99% purity[89]. According to Rosen (1996) the CMC of SDS was determined to be ~1.58 x 10^{-3} mol/dm^3 at 25 °C. Hydrochloric acid used as doping and adjust PH. The pyrrole monomer (Aldrich) was first purified by distillation at 131°C and stored and refrigerated at 4°C before using in polymerization. Pyrrole monomer: purum 97% GC, Mr =67.06, bp =120-131 °C, d^{20}_4=0.970. Thiophene monomer: purum 98% GC, Mr= 84.14, bp=82-84°C, d^{20}_4=1.063 contain 0.2% benzene. Iodine (I$_2$) was a reagent grade which was stored over silica gel in desiccator.

7.3.2 Equipments

NR latices were purified by centrifugation at 10000 rpm/20 min with two cycles at 20 °C by centrifugator, Hermle Z383K. The density was tested by Sartorius approach, model: YDK01. Functional groups were determined by Fourier Transform Infrared Spectroscope (FTIR) (Nicolet 670, HATR flat plate system with 45°C ZnSe crystal) PERKIN ELMER 1760X. Particle Size Analyzer (Mastersizer X) was used to measure the particle size of NR latex particles (45 mm lens, active beam length 2.4 mm). Thermogravimetric-Differential Thermal Analyzer (Perkin Elmer, Pyris Diamond) was used to study the thermal stability and the decomposition temperature. The morphology of the admicelled latex films were observed by Scanning Electron Microscopy (JOEL 5200) and Transmission electron microscope (JEOL JEM-2100). Tensile testing was carried out using Lloyd LRX Universal Testing Machine under ASTM D882-91 and Instron Universal Testing Machine under (ASTM638M-91a).The hardness shoreA and ShoreD was observed by Lever Loader, model 716. Surface and volume resistivity were measured by using Resistivity Test Fixture (Keithley Model 8009) and Electrometer/High Resistance Meter (Keithley 6517A).

7.3.3 Purification of the Natural Rubber Latex

The rubber latex has a 60%wt dried solid content (DSC). Rubber latex (4-8 g) was mixed with 50 ml distilled water and centrifuged two times at 20oC, 10000 rpm for 20 minutes to removed dissolved impurities. The 25 g of latex was separated in 10 ml dilute water. Then the rubber latex was mixed with surfactant solution, SDS, 16 mM, in 490 ml dilute water to obtain a 500 ml total volume, then using HCl to maintain the pH of the solution at 3.0, which is the pH below the point of zero chart.

7.3.4 Polymerization of Pyrrole onto Latex Particles

1) dope NR with Iodine

The iodine doping reaction is carried out by dissolving the polymer sample and iodine at a determined ratio of $[C=C]/I_2=31$ (Dai.L et al.,1994)[136]. The purified solution was added Iodine 1-3%wt (table A3 in the appendix) with various monomer concentration from 0-800 mM. Then, it is stirred a day at 60°C (Atilla cihaner.2004)[138] to over night to let the surfactant molecules form the bilayer at the surface of rubber particles (Figure 7.5 a). Its color will be changed from white to white-orange.

2)Preparation of conductive natural rubber by electrochemical method

Pyrrole/Thiophene solution (20-800 mM, 0.69–27.66 ml) was added and left for an hour (Figure 7.5 b). Next, the apparatus for electrolysis was set up, and the aqueous solution was poured into the reaction bottle. Then, an additional current was passed though the solution containing the pyrrole/thiophene monomer at various voltages (Figure 7.5c). While the current was applied across the cell, polypyrrole polymerized on the rubber latex solution by forming the admicellar structure, and conductive natural rubber occurred on the cathode electrode, (the copper has a diameter around 3x10 cm), as shown in Figure 7.4.

After the electro-polymerization has started, the pH and mass on the electrode are checked every hour and the electrode was replaced. The pH was adjusted to 3.0 by HCl. The dark solid rubber on the working electrode was washed with water, followed by drying in a vacuum oven at 70°C for 12 hours to obtain a black sheet with a constant weight. The solution changed from white to black and finally to clear. After the polymerization was complete, the upper layer of surfactant was removed by washing with distilled water (Figure 7.5 d).
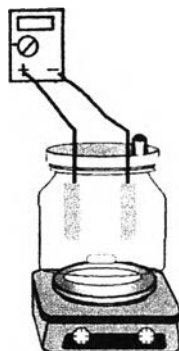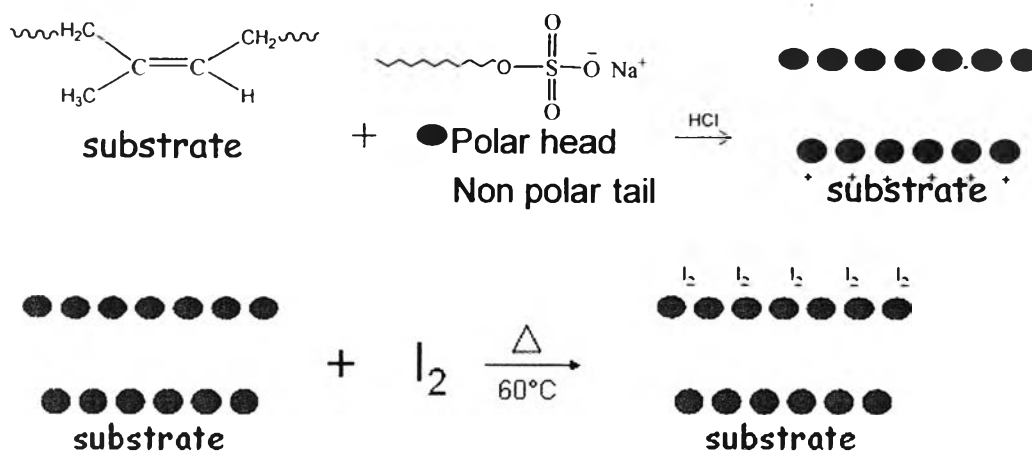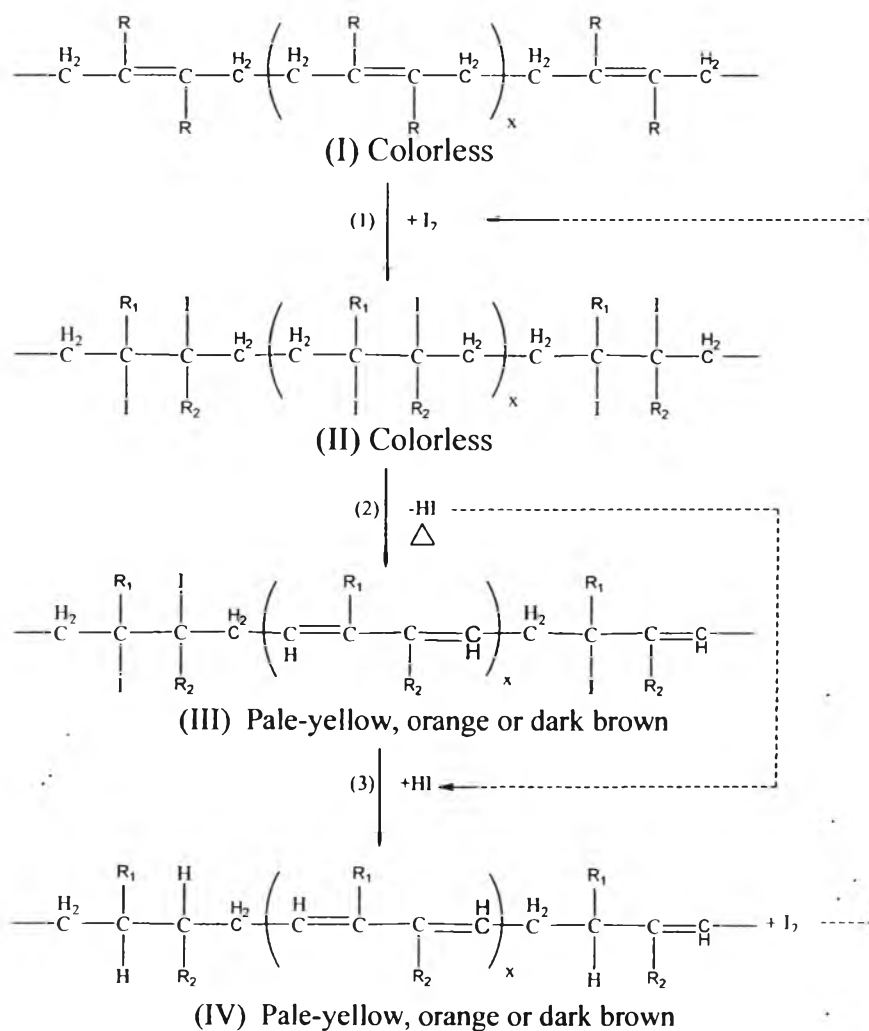
Figure 7.4 Apparatus for admicelled polymerization with electrolysis. It consists of a reaction bottle and cover, cathode and anode electrodes, a voltmeter, an ammeter, a current supply, a hot plate and a magnetic stirrer.
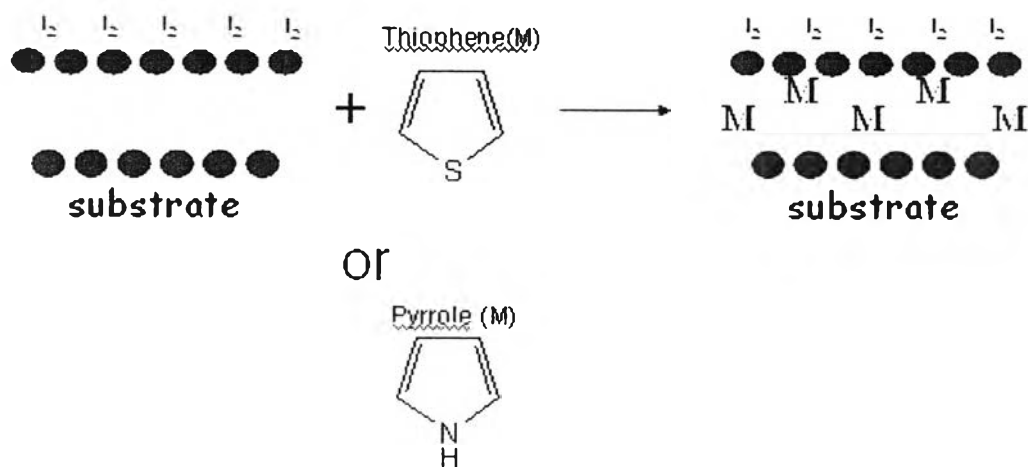
a. Step 1. Admicelle Formation and I_2-Doping

Reaction of cis-1,4 polyisoprene with iodine, followed by heat at 60°C to produce conjugated sequences.
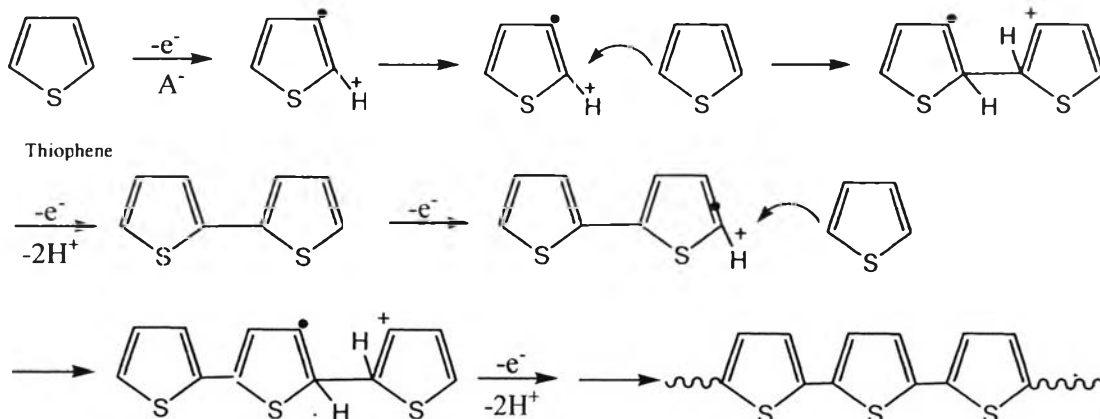
(I) Colorless

(1) +I$_2$

(II) Colorless

(2) -HI
△

(III) Pale-yellow, orange or dark brown

(3) +HI

(IV) Pale-yellow, orange or dark brown

R1, R2 refer to either H or CH$_3$ group.

b. Step 2. Monomer Adsolubilization

Thiophene(M)

substrate + Thiophene(M) → substrate

or

Pyrrole (M)

c. Step 3. Polymer formation

For *Thiophene when Applied voltage*

For *Pyrrole when Applied voltage*

(Polypyrrole)
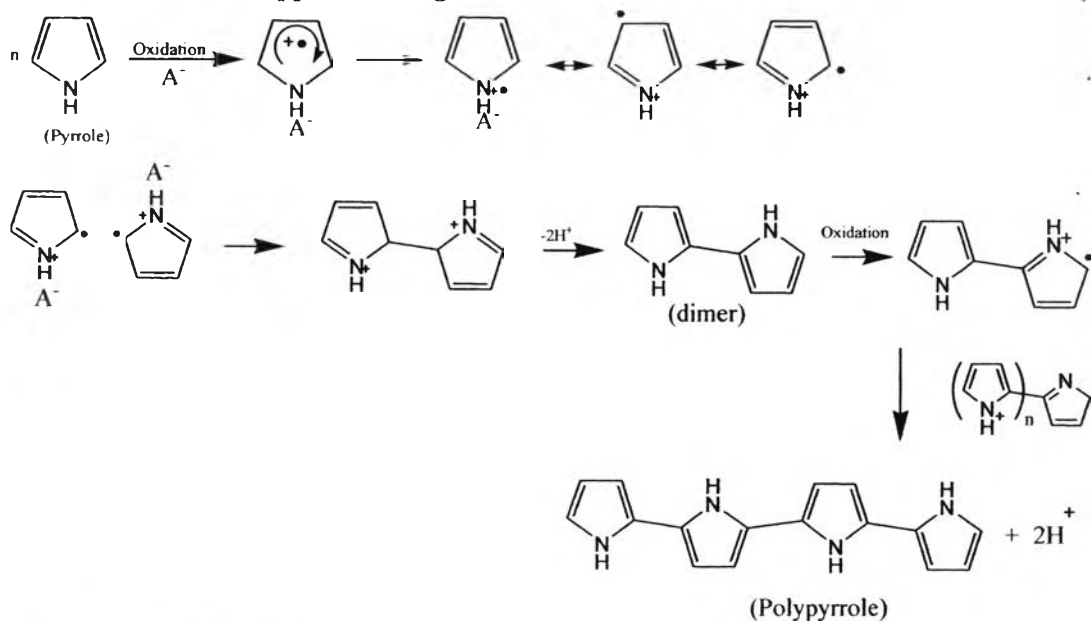
d. Step 4. Surfactant Removal
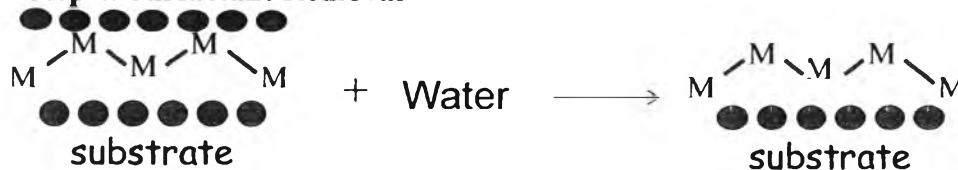
Figure 7.5 Phenomena of admicelled polymerization

7.3.5 Factors Measurement

In order to obtain the best conditions, factors such as applied potential (voltage), electrode size, time, and pH were studied. The thickness and mass can also be controlled by these factors. The voltage was applied by using an adaptor (0-30 Voltage, 3A, Kenji-model : K01). The average electrode sizes were about 3.5 x 7cm.

7.3.6 Morphology Study

The morphology of the samples after polymerization and drying was studied. The samples were pulled into small pieces and adhered to brass stubs by using adhesive tape. The samples on the stubs were painted with a thin layer of silver. The morphologies of the admicelled rubbers were observed by a scanning electron microscope (SEM, JOEL model JSM-5200). SEM digitized photographs were obtained with a magnification range between 1,000–5,000 times using an acceleration voltage of 15 kV.

7.3.7 Thermal Properties Measurement

Thermal stability, moisture content, and degradation process of the admicelled rubbers were studied by a thermogravimetric analyzer (DuPont, model Thermogravimetric-Differential Thermal Analyzer (Perkin Elmer, Pyris Diamond). The samples were weighed at 10-18 mg and put in a platinum pan. The instrument was set to operate at temperatures from 30 to $600^{\circ}C$ at a heating rate of $10^{\circ}C/min$ under nitrogen atmosphere, 100 ml/min.

7.3.8 FT-IR Observation

The adsorption of the admicelled rubber films with a thickness of 0.3–0.8 mm obtained by compression at $160^{\circ}C$ under a pressure of 25 tons for 15 min, were determined using the horizontal attenuated total reflection accessories for the FTIR (Nexus 670, HATR module) to measure the spectra of materials. The spectra were recorded in the absorbance mode in a wavenumber range of 400-4000 cm^{-1}. The sample spectra were recorded by using air as a background.

The KBr technique was used to prepare the powder sample of pure PPy/PTh for recording the spectrum. The specimen of pure PPy/PTh was prepared by grinding the powdered PPy/PTh with the KBr powder. The mixture was molded in special

dies under a pressure of 10 tons. The sample spectrum was recorded by using KBr as a background.

7.3.9 Mechanical Properties Measurement

The mechanical properties were determined for two specimen types with one type is a dimension 20x100 mm (thickness 0.3-0.8 mm) the test were prepared from compression molding. The test were following ASTM D822-91 with crosshead speed of 50 mm/min, guage length of 50 mm, and load cell 500 N under room temperature using Lloyd Universal Testing Machine, model :LRX. The test was repeated 5 times.

The Tensile Strength Test uses two clamps to hold the testing strip. When secured, the testing strip will be pulled, with a specified force, apart. The yield point and/or breaking point will be measured (Figure 7.6).
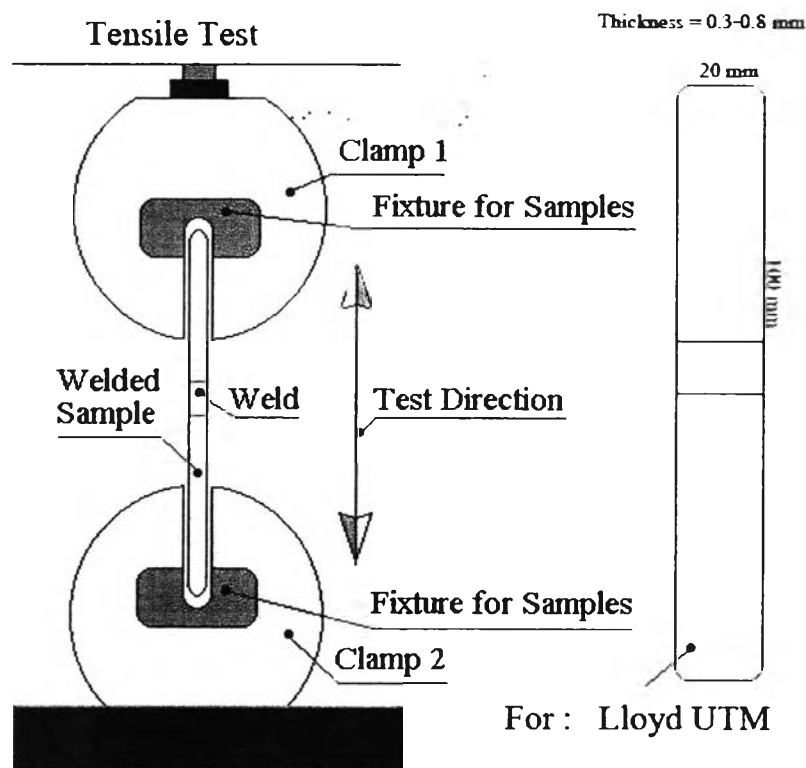
Figure 7.6 preparation specimens for tensile test.

7.3.10 Conductivity Measurement

The admicelled rubber films from compression (thickness 0.3-0.8 mm) were cut into a round shape with six inches in diameter and tested for their surface and volume resistivity by using a Keithley 8009 Resistivity Test Fixture and a Keithley 6517A Electrometer/High Resistance Meter. A dc voltage from 0.1 to 15 volts was applied to the specimen placed in the Keithley 8009 test fixture. Then, the current was read and the surface and volume resistivity were determined (ASTM D-257).

The resistance, R, of the films was calculated using Eq. 1, the volume resistivity, surface resistivity and the conductivity were found using Eqs. 2, 3 and 4, respectively:

$$R = \frac{V}{I} \tag{1}$$

$$\rho_v = \frac{22.9V}{tI} \tag{2}$$

$$\rho_s = \frac{53.4V}{I} \tag{3}$$

$$\sigma = \frac{1}{\rho_v} \tag{4}$$

where R is the resistance (watts), V is the voltage (volts), I is the current (amperes), ρ_v is the volume resistivity (ohm centimeters), ρ_s is the surface resistivity (ohm), t is the film thickness (centimeters), and σ is the conductivity (siemens per centimeter).

7.4 Results and Discussions

7.4.1 Effect of monomer content dope with Iodine on reaction time and %yield

The success of admicelled polymerization of PPy and PTh coated natural rubber latex was investigated in Chapter 4-6. However, the conductivity and other properties still need more improved. The polymerization reaction was carried out via admicellar polymerization of rubber with various Pyrrole and Thiophene concentrations (20 and 800 mM) by using the electrochemical method at 9V, 25°C. Then, samples were prepared by doped with iodine before polymerization. From Table 7.2 shows the dependence of %yield and reaction times on the monomer concentration. It is clearly shown in Figure7.7 and Table7.2 that % yield and reaction times of admicelled rubber were decreased along with the increased monomer concentration. The higher the concentration of monomer, the faster the reaction was (Tasakor, 1996)^2. Both Iodine doping and without Iodine doping show similar trends in results of % yield and reaction times along increased monomer. The surprisingly the %yield of doping with iodine was lower than that of the undoping (Figure 7.8). In the opposition, the reaction time of iodine doping was faster than another one (Figure 7.9). This observation might be enhanced for forming between the interaction of conjugate polymer and iodine (E.J.Loius,1977)[134,135]. This may result in faster polymerized to the molecule. At the end, the solution changed to a clear solution, indicating that the polymerization was completed. Then, other properties were also observed.

Table 7.2 Effect of PPy content on % yield and reaction times at 9 V

Types of Monomer		-	PPy	PPy	PTh	PTh
Code		E_{nr}	E_{A2}	E_{A80}	E_{B2}	E_{B80}
Amount (mM)		-	20	800	20	800
Amount (g)		-	0.67	26.72	0.841	33.656
I_2 (g)		0.6105	0.6105	0.6105	0.6105	0.6105
NR (g)		25	25	25	25	25
SDS (g)		2.307	2.307	2.307	2.307	2.307
Iodine dope	Mass at anode (g)	22.99	23.65	45.76	23.60	48.62
	%yield	89.79	89.98	87.44	89.24	82.03
	Time (hrs)	35	28	9	27	19
w/o iodine dope	Mass at anode (g)	n/a	23.224	45.31	23.677	48.91
	%yield	n/a	90,45	87,61	91,59	83,38
	Time (hrs)	n/a	35	10	30	23

When : $\%yield = M_{total} \times 100 \Big/ (M_{NR} + M_{monomer} + M_{I_2})$; M_{sds} is not calculated because it can be removed by water.
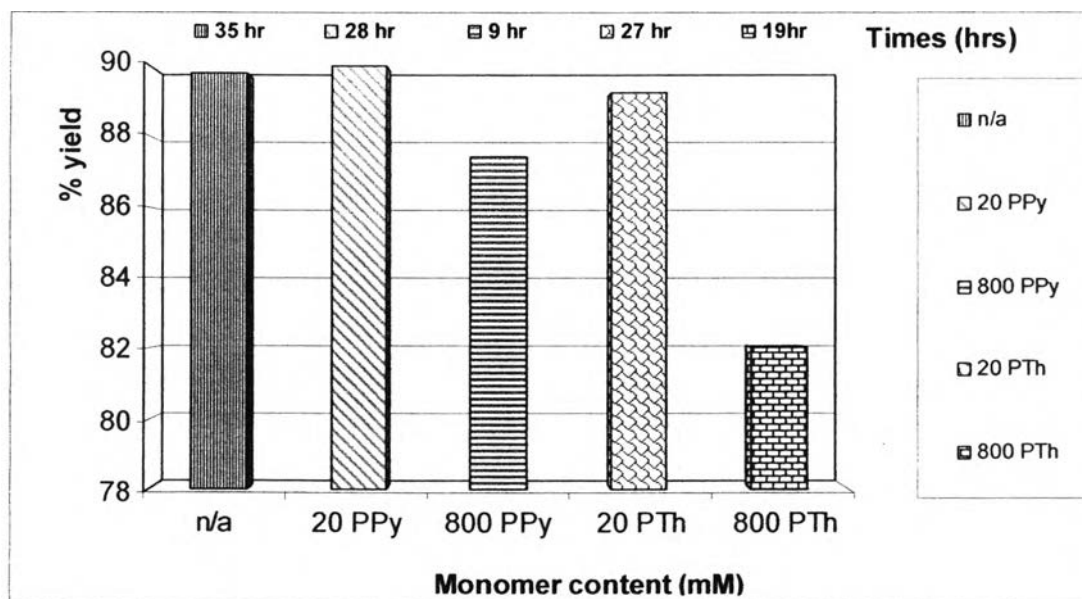
where $A = PPY$, $B = PTh$, $E = dope\ with\ iodine$

Figure 7.7 Effect of pyrrole concentration on reaction times and %yield
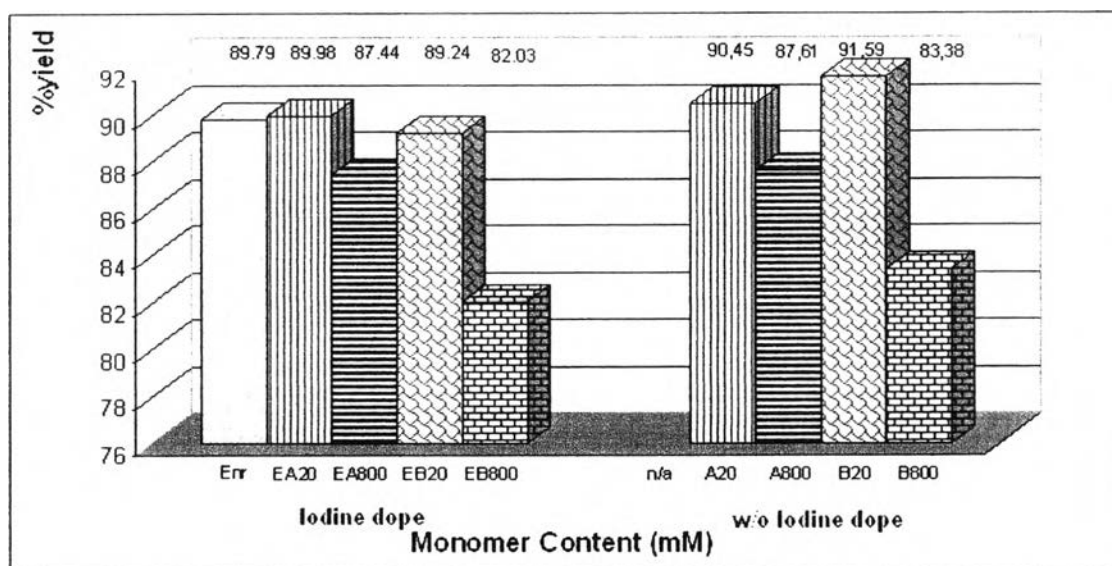
Figure 7.8 Compared the effect of pyrrole concentration on %yield between iodine doping and undoping.
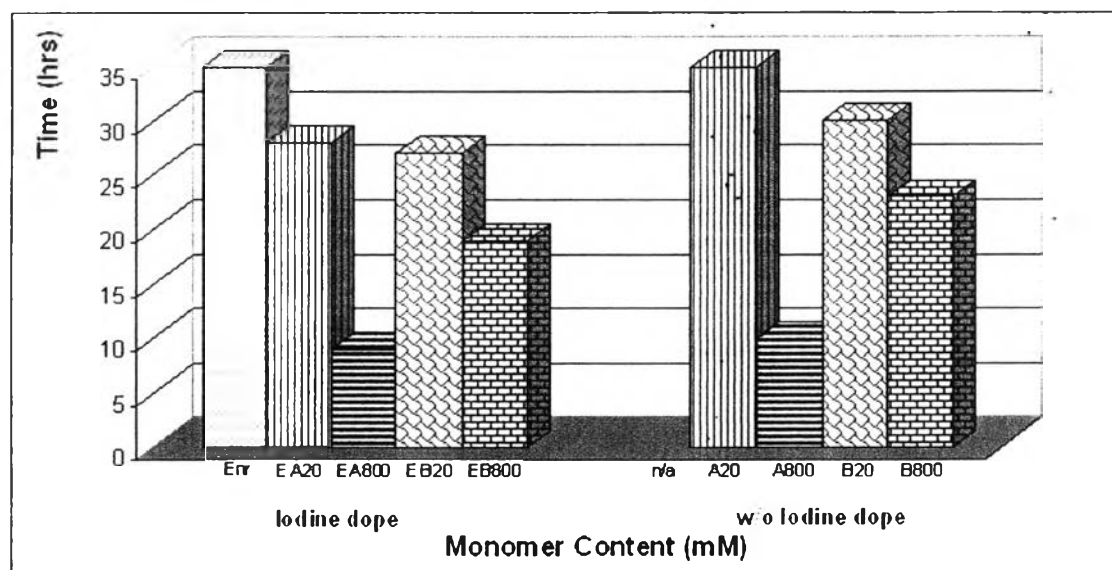

Figure 7.9 Compared the effect of pyrrole concentration on reaction times between iodine doping and undoping.

7.4.2 Scanning Electron Microscopy

The morphologies of the PPy/PTh-admicelled rubber were investigated in Chapter4-6. The effect of Iodine doping was carried out to study in this section.

SEM result can confirm the presence of polypyrrole in natural rubber. As observe in Figure 7.10 (a) a grained texture, coaser cauliflower are presented. Figure 7.10 (b) PTh demonstrated spong-like, rod, porous structure and globular structure.

The SEM micrographs (Figure 7.11-7.14) of admicelled rubber with different PPy/PTh concentrations reveal the round shape of rubber particle with even coating of monomer over the particles. However, effect of cracking can caused by Iodine-induced into the suface diffusion(A.K.Miller,1981)[145]. Iodine can post homogenously doped on molecule. While there are a lot of pinholes in the material after polymerization, this can caused by hydrogen gas occurred (S.Touihri,1997)[146]and (Shutaro.K.2006)[155]. Natural rubber sheet morphology (Figure 7.16) exhibited the smooth surface, without any coating whereas Iodine-dope on natural rubber was changed in their surface(Figure 7.15), it showed each molecule separate and overlap closely to different direction, but there was presented some smooth NR on the left side of figure. Comparisons of the SEM micrographs are corresponding to the various concentrations of PPy and PTh as shown in Figure 7.17. The SEM micrographs of admicelled rubber with different monomer concentration reveal round shape of rubber particles with evenly coating of monomer over the particles.
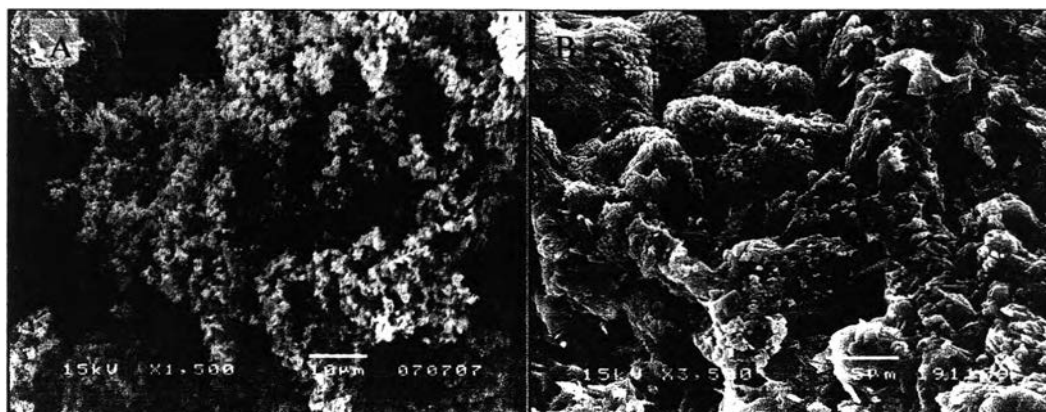

Figure 7.10 Scanning electron micrograph of the coating with

(a) polypyrrole (b) polythiophene

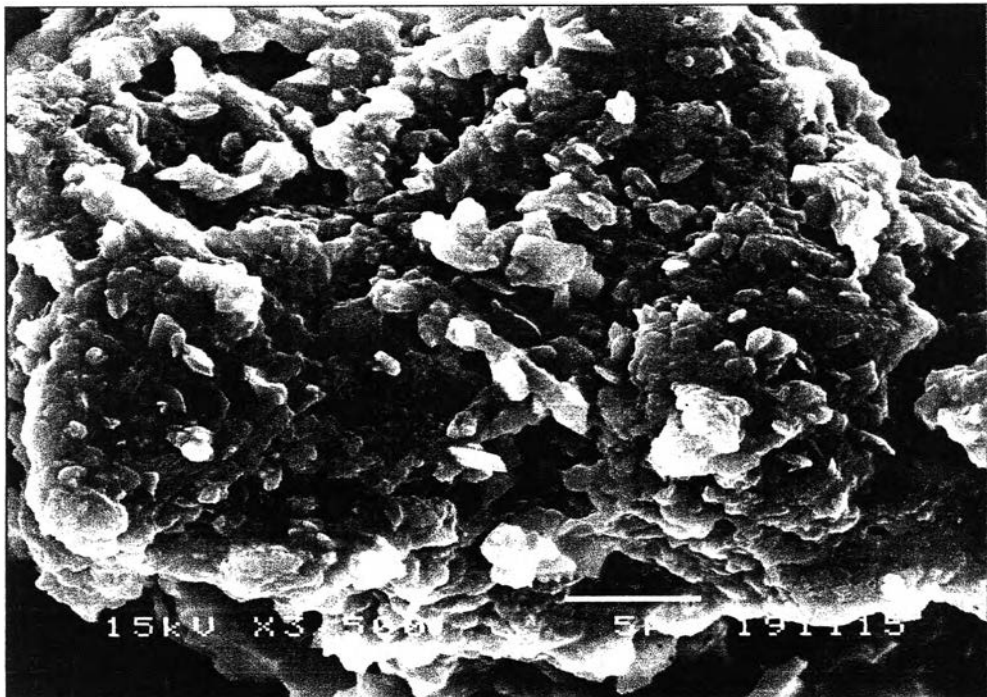by using electrochemical method magnification 1,500-3,500 /15 kV

Figure 7.11 Scanning electron micrograph of the coating admicelled rubber **(EA2)** by using electrochemical method magnification 3,500/15 kV.
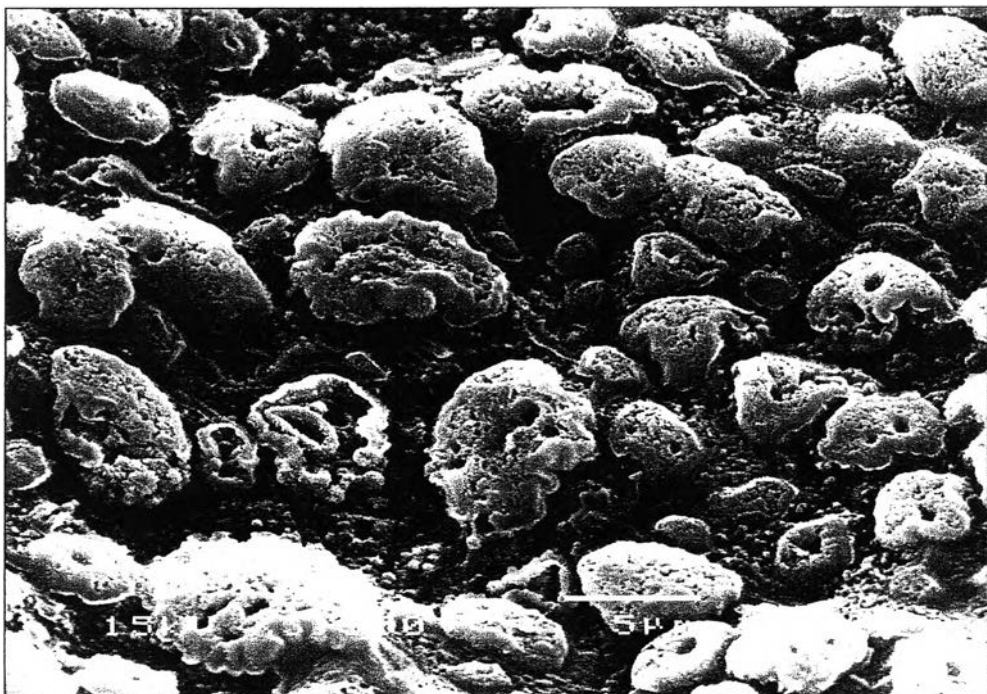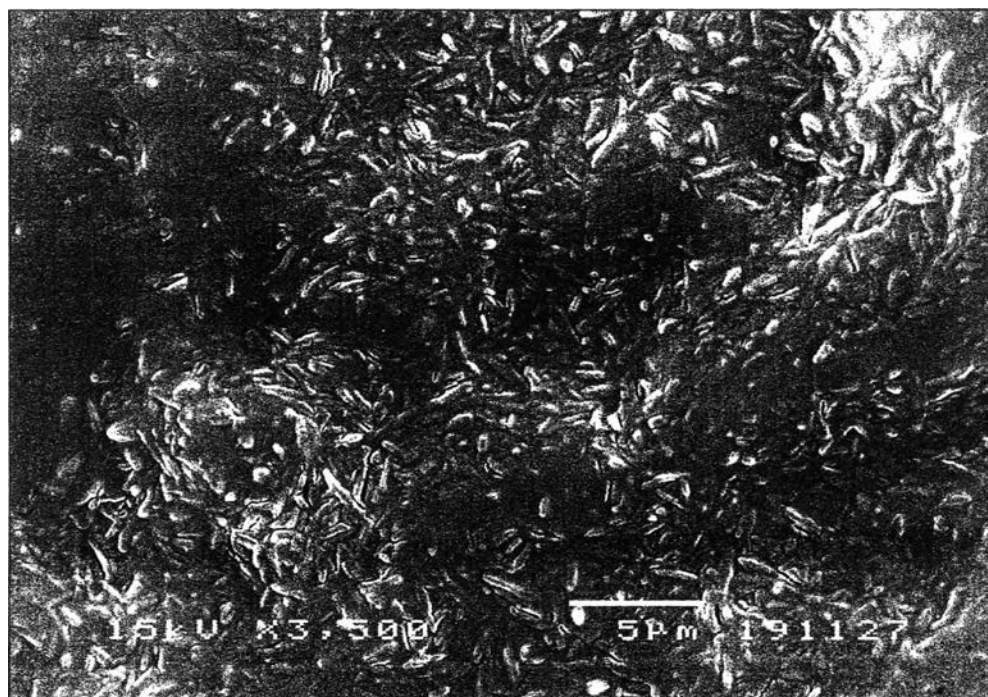

Figure 7.12 Scanning electron micrograph of the coating admicelled rubber **(EA80)** by using electrochemical method magnification 3,500/15 kV.

Figure 7.13 Scanning electron micrograph of the coating admicelled rubber **(EB2)** by using electrochemical method magnification 3,500/15 kV.
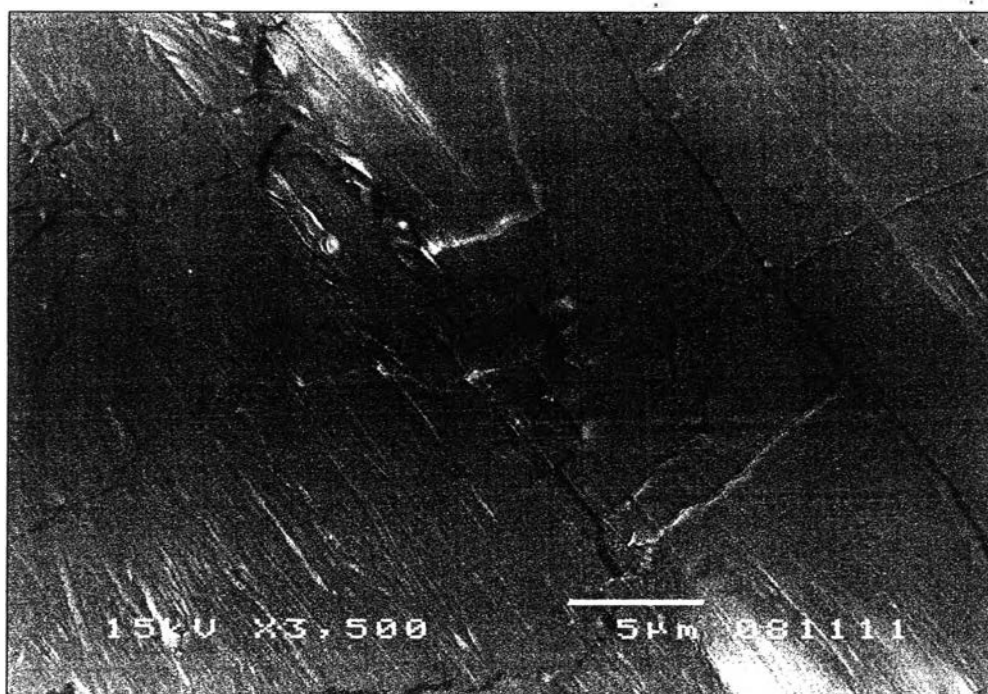

Figure 7.14 Scanning electron micrograph of the coating admicelled rubber **(EB80)** by using electrochemical method magnification 3,500/15 kV.

Figure 7.15 Scanning electron micrograph of the coating admicelled rubber **(Enr)** by using electrochemical method magnification 3,500/15 kV.

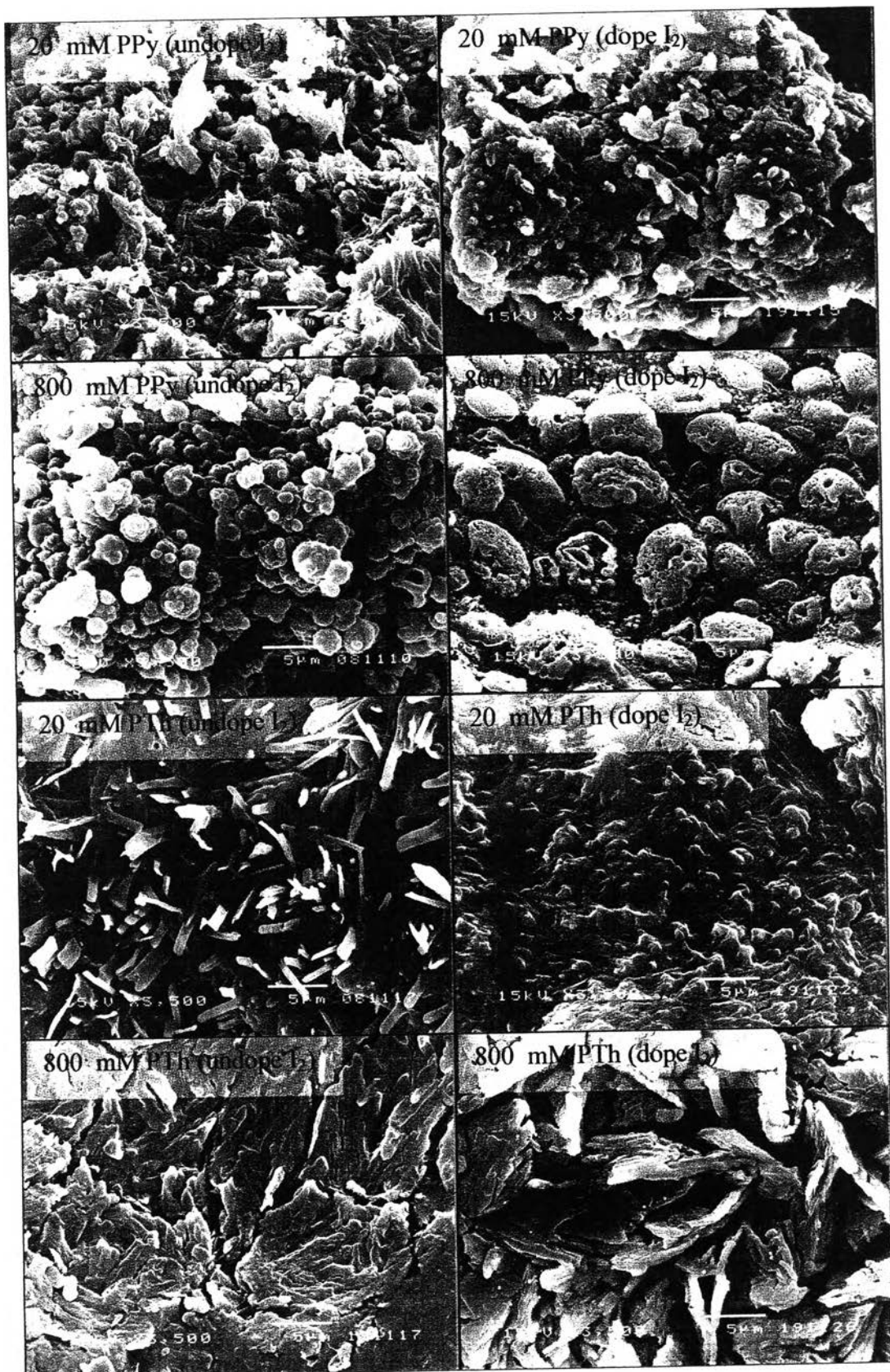**Figure 7.16** Scanning electron micrograph rubber **(NR)** magnification 3,500/15 kV

Figure 7.17 Compared scanning electron micrograph of the coating admicelled rubber with dope and undope of Iodine, at magnification 3,500/15 kV.

7.4.3 Fourier-Transform Infrared Spectroscopy of Admicelled NR Latex

The infrared spectra of pure rubber, pure PPy, PTh, and admicelled rubbers in the region from 4000 to 400 cm^{-1} are reported and shown in Chapter 4 and 5, respectively (Figure7.18-7.20) and the explanation of each band are also reported in Table 7.3-7.7, respectively.

FTIR spectra for Iodine doping and those polymer samples corresponding to Figure7.21. It is obviously found a new band attributable to the C-I stretching mode which shown in Table 7.3.

Table 7.3 Assignment for the FTIR spectrum of Iodine[140-143]

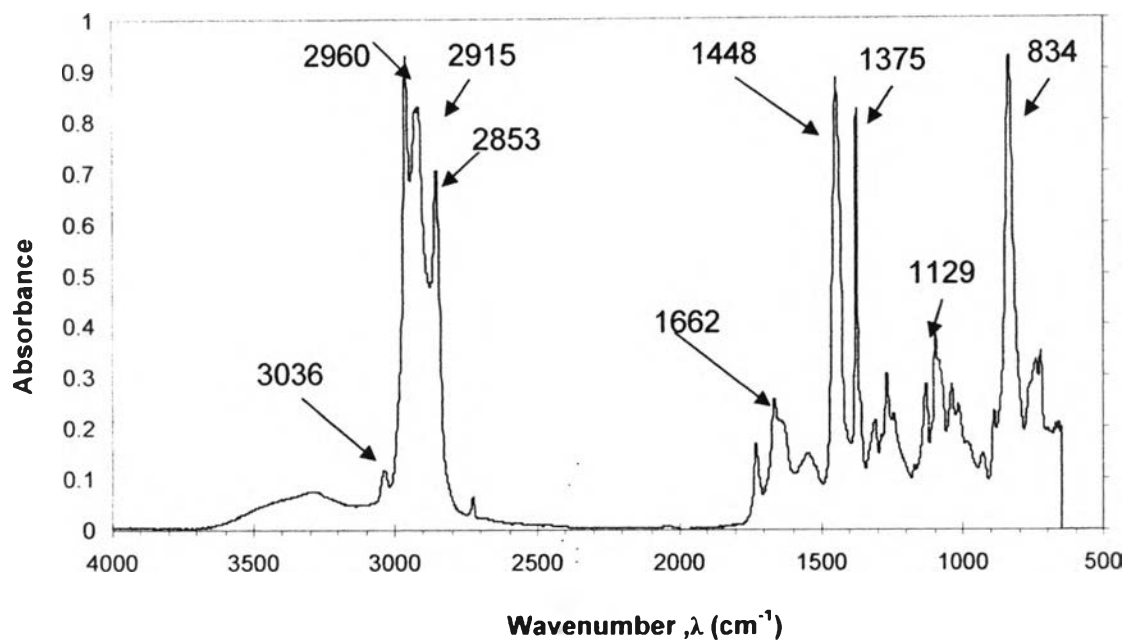| Wavenumber ,λ (cm^{-1})	Assignment	Ref
620-490	C-I stretching	140-143
495	C-I stretching	147
724,782,1530,1540	PPy doped with Iodine (C-C)-I	148-150
708,1450,1520,2300	PTh doped with Iodine (C-C)-I	148

Figure 7.18 FTIR spectrum of pure Natural rubber, Polyisoprene.

Table 7.4 Assignment for the FTIR spectrum of isoprene[106]

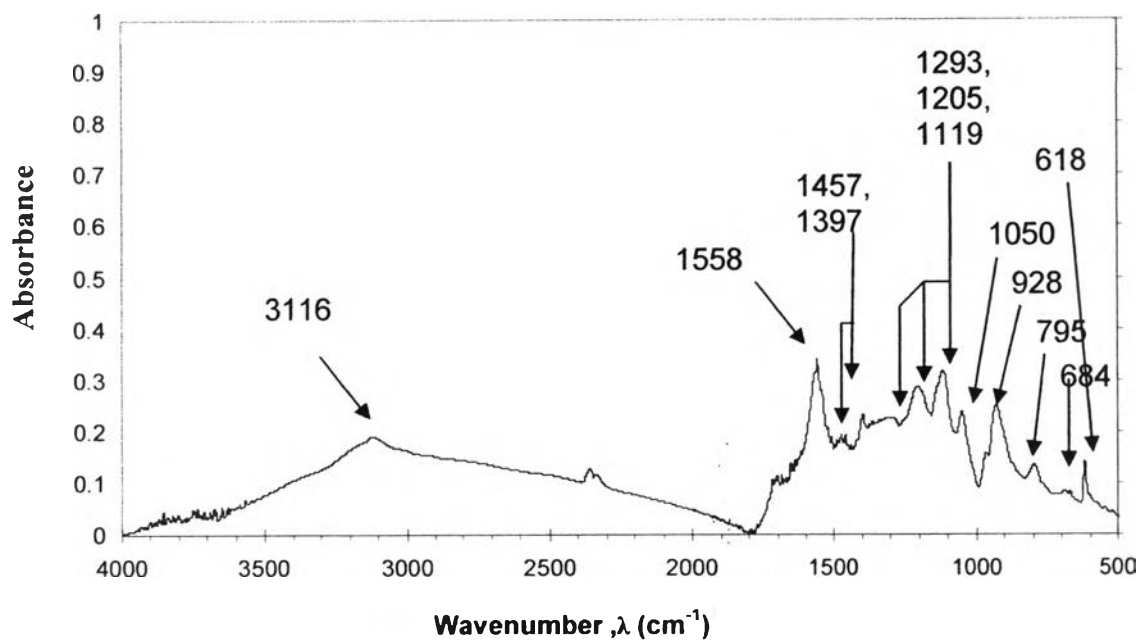| Wavenumber ,λ (cm⁻¹)	Assignment
3036	=CH stretching
2960	C-H stretching of CH_3
2915	C-H stretching of CH_2
2853	C-H stretching of CH_2 and CH_3
1662	C=C stretching
1448	C-H bending of CH_2
1375	C-H bending of CH_3
1129	C-H bending
834	C=CH wagging

Figure 7.19 FT-IR spectrum of Polypyrrole (PPy).

Table 7.5 Assignement for the FTIR spectrum of pyrrole[103,105]

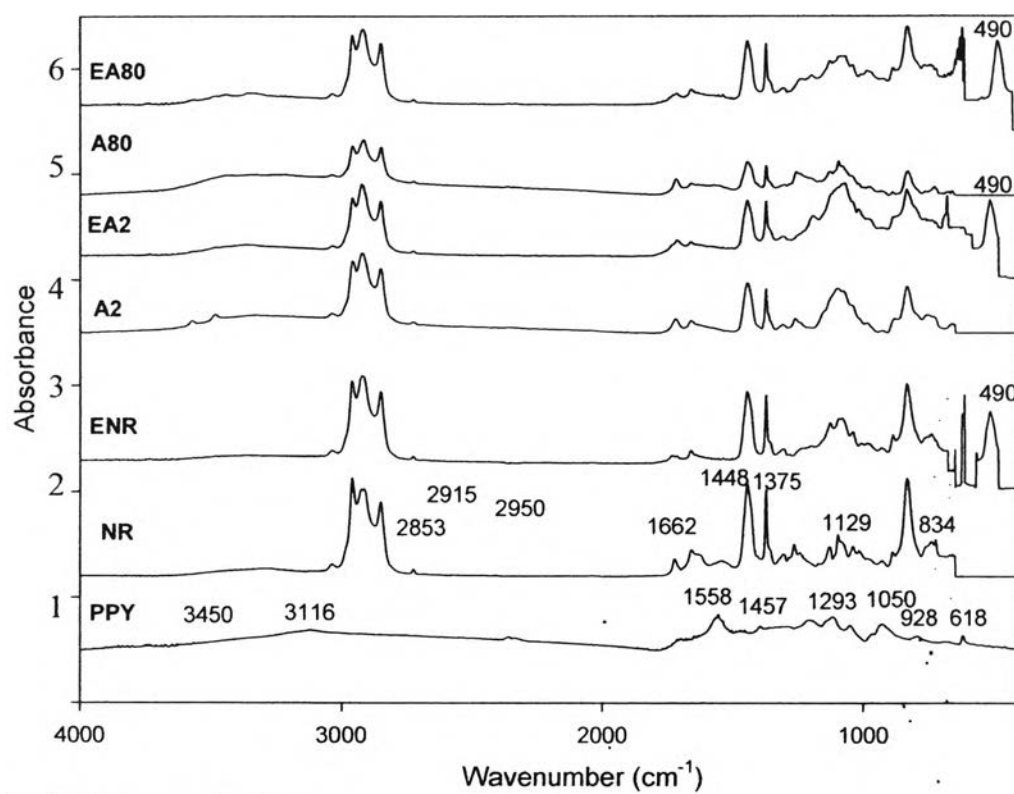| Wavenumber ,λ (cm⁻¹)	Assignment
3116	N-H stretching
1558	C=C stretching
1457,1397	C-C stretching
1293,1205,1119	=C-H in plane
1050	N-H in plane
928	C-H stretching
795	=C-H out of plane
684	C-C out of plane
618	N-H out of plane
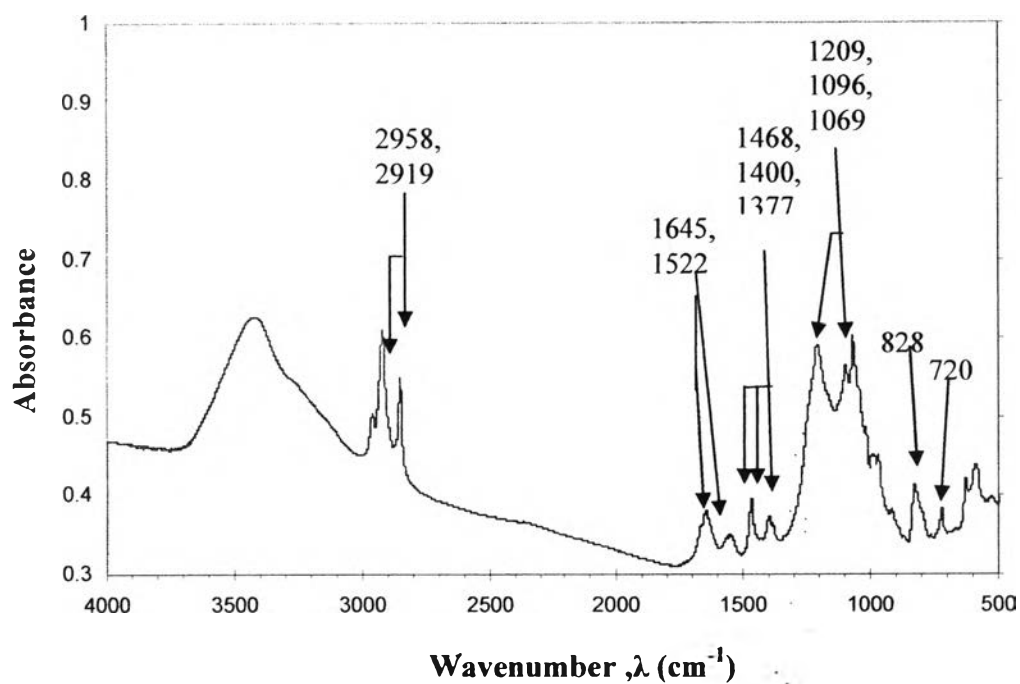
Figure 7.20 FT-IR spectrum of Polythiophene (PTh).

Table 7.6 The assignement for the FTIR spectrum of thiophene[94,106]

Wavenumber ,λ (cm⁻¹)	Assignment
2958,2919	C-H stretching
1645,1522	C=C and C-C stretching
1468, 1400, 1377	CH₂ deformation
1209,1096,1069	C-H in plane deformation
828	C-H out of plane deformation
720	C-S bending

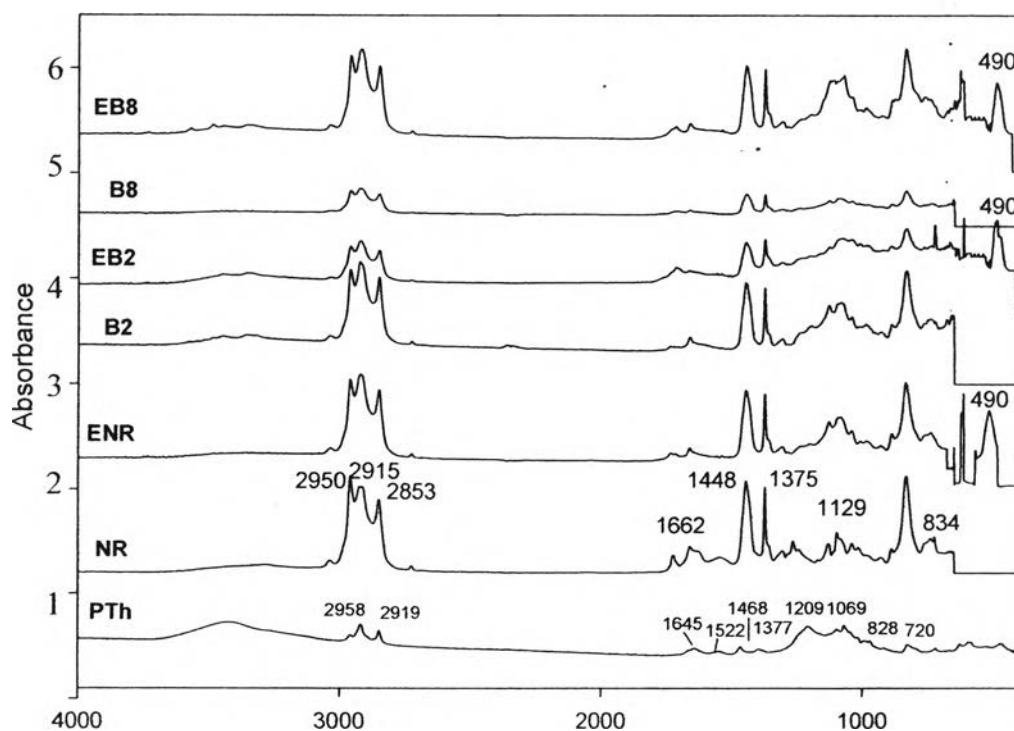**a) PPy dope with Iodine**

B) PTh dope with Iodine

Figure 7.21 FT-IR spectrum of admicelled rubber with Iodine doping and nondoping :
a) PPy dope with Iodine b)PTh dope with Iodine.

Table 7.7 Assignment for the FTIR spectrum of composite[94,106,140-150]

Wavenumber, λ(cm-1)	Assignment
3450,3116	NH stretching (PPy)
2958,2919	CH stretching (PTH)
2950,2915,2853	CH stretching(NR)
1662,1558	C=C stretching (NR+PPy)
1645, 1522	C=C stretching (PTh)
1662 ,1600	Ring stretching (PPy)
1468, 1400,1377	CH_2 deformation (PTh)
1448, 1375	CH in plane bending (NR)
1209,1096,1069	CH out plane deformation (PTh)
1293, 1205, 1119	CH in plane bending(PPy)
795, 684, 618, 600	Aromatic ring (PPy) and CH out of plane (NR+PPy)
620-490	C-I stretching
495	C-I stretching
724,782,1530,1540	PPy doped with Iodine (C-C)-I
708,1450,1520,2300	PTh doped with Iodine (C-C)-I

7.4.4 Thermogravimetric Analysis

TG-DTA patterns of PPy and PTh on natural rubber are described in Chapter4, 5,and 6. In this work, we discuss and studied undergo decomposition upon heating, leading to their total volatillation. It can be presented in Table 7.8. It can be seen from the TGA curve that 10% weight loss in the range of 100-250°C is due to the evaporation of physically absorbed water and some surfactant and some product surface. NR starts degrade at 351.6°C and it exhibit the major decomposition at 373.6°C. PPy start to degrade at 204.9, then the main loss is observed at 260.3°C whereas PTh is 194.8 and 211.4, respectively. The reason might be the rearrangement and degradation of the side chain (M.Han,2006)[95].The significant weight loss of iodine dope admicelled rubber stats at around 357 to 368.3°C whereas undope with iodine is higher at around 369.4 to 378.7°C. This can caused by Iodine molecule can give high oxidative potential (Pawel D.1990)[151]. Therefore, I_2 can enhance the decomposition temperature to the molecule. These also suggest that the admicelled rubber begin to lose weight at higher temperature compared to that of NR. The curves also demonstrate that char yield of admicelled rubbers increased from ~1% of pure rubber to 1.2 to 21.7% related to the content of monomer added such as PPy and PTh. The residual contents of sample with with PPy 20mM (2.553%wt) are about 8.7%; PPy 800mM(51.168%wt), 21.7%; PTh 20mM(3.181%wt), 1.2% ; and , PTh 800mM(56.788%wt), 4.4%. These indicate that an increase of I_2 content enhance the residue remaining. PPy and PTh also gives rising % residue remaining (The residual content of pure PPy is 66.58%, while PTh is 16.1%.).

In addition, the onset temperature of admicelled rubber (Dope I_2:337.5-349.4°C ; Undope I_2: 348.9 - 351.6°C), are nearly result of pure rubber (Dope I_2 348.8°C; Undope I_2 :351.6°C). The decomposition temperatures were also ended at higher temperature 521.1°C (PPy) ; 579.3°C (PTh) than that of pure rubber(471.9°C) as shown in the Table 7.10. The higher the monomer content (PPy,PTh) the slower the sample start to degrade. This fact also support above-mentioned results that coating PPy by admicellar polymerization improves the thermostability of natural rubber. Nevertheless samples doped with I_2 are more faster decompose than the other one due to Iodine can give high oxidative potential to the molecule.

Table 7.8 Degradation temperature of the admicelled rubbers

Sample		Onset Temperature	End point Temperature	Peak temperature	residual content (%)
Iodine dope	Enr	348.8	373.3	365.2	3.3
	EA2	337.5	470.7	357	8.7
	EA80	346.2	480.1	365.3	21.7
	EB2	336.3	464.9	356.4	1.2
	EB80	349.4	477.2	368.3	4.4
w/o dope	Rubber	351.6	471.9	373.6	1.1
	A2	348.9	481.5	369.4	4.9
	A80	352.2	521.9	374.5	22.3
	B2	351.6	471.9	373.6	1.1
	B80	350.8	480.9	378.7	3.9
	PPy	204.9	579.3	260.3	66.58
	PTH	194.8	597.4	211.4	16.1

where A= PPY, B= PTh , E= dope with iodine
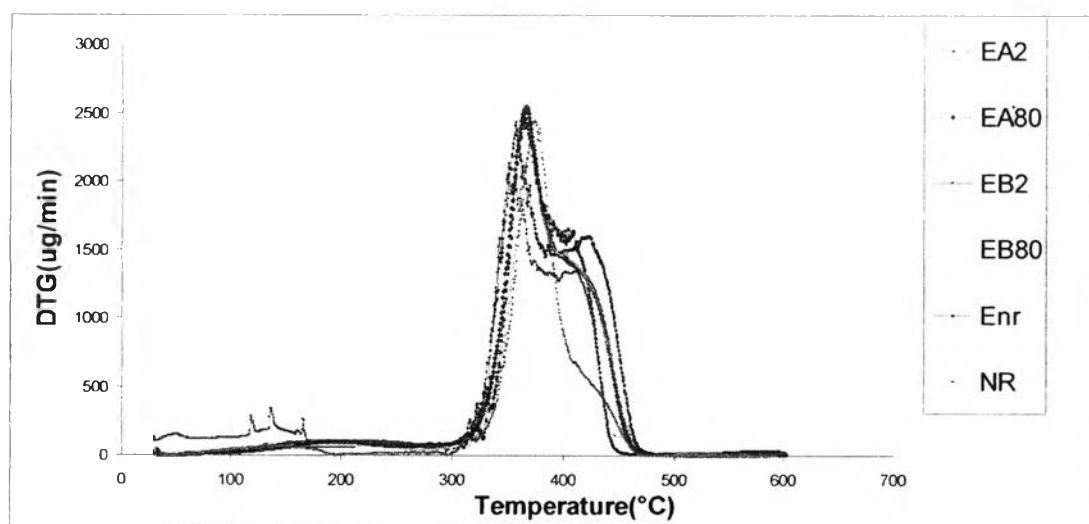
Figure 7.22 DTG thermograms at 10 °C/min of nitrogen atmosphere of admicellar rubbers with SDS by using electrochemical methods.
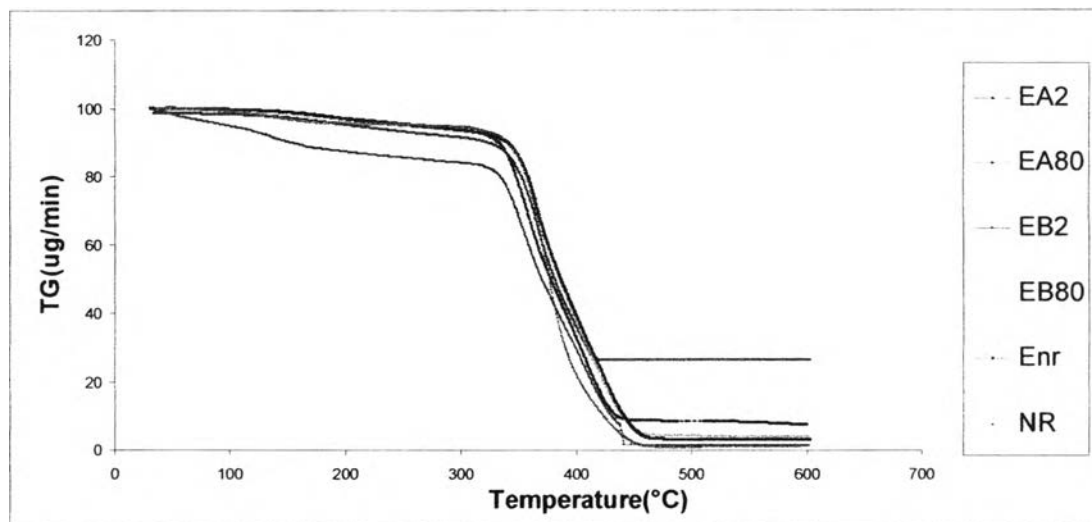
Figure 7.23 Thermogravimetric analysis thermograms at 10 °C/min of nitrogen atmosphere of admicellar rubbers with SDS by using electrochemical methods.
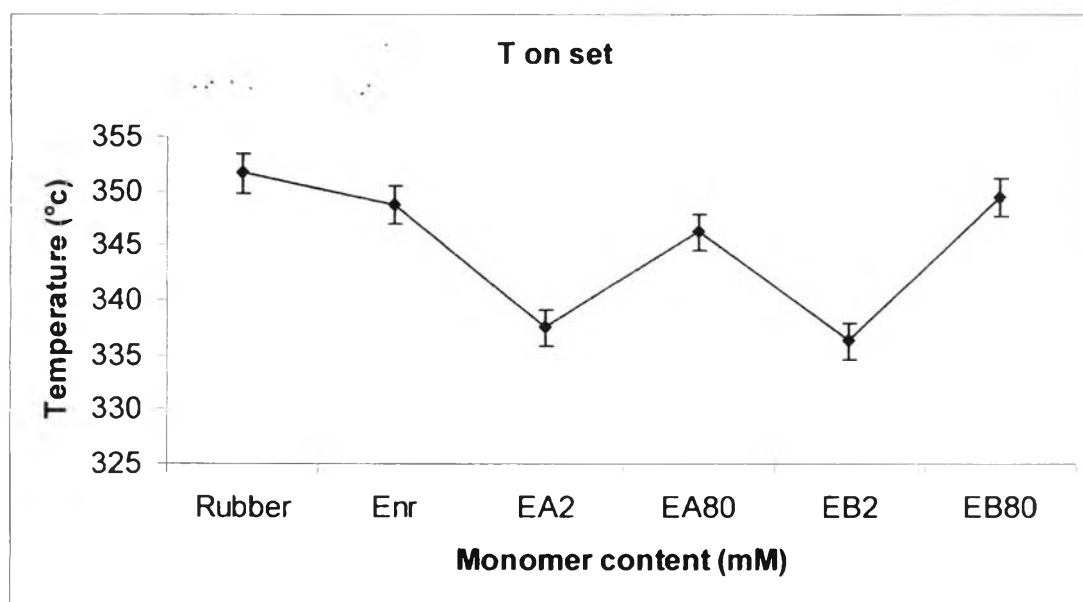

Figure 7.24 Thermogravimetric analysis thermograms of on set temperature at 10 °C/min nitrogen atmosphere of admicellar rubbers with SDS by using electrochemical methods.
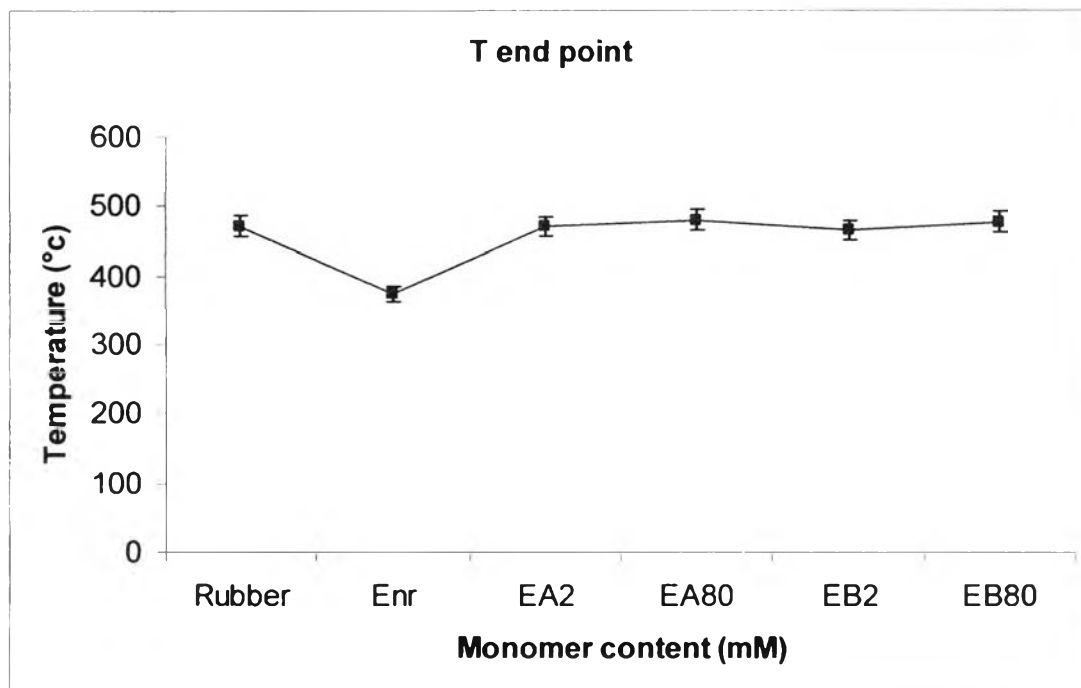
Figure 7.25 Thermogravimetric analysis thermograms of end point temperature at 10 °C/min nitrogen atmosphere of admicellar rubbers with SDS by using electrochemical methods.
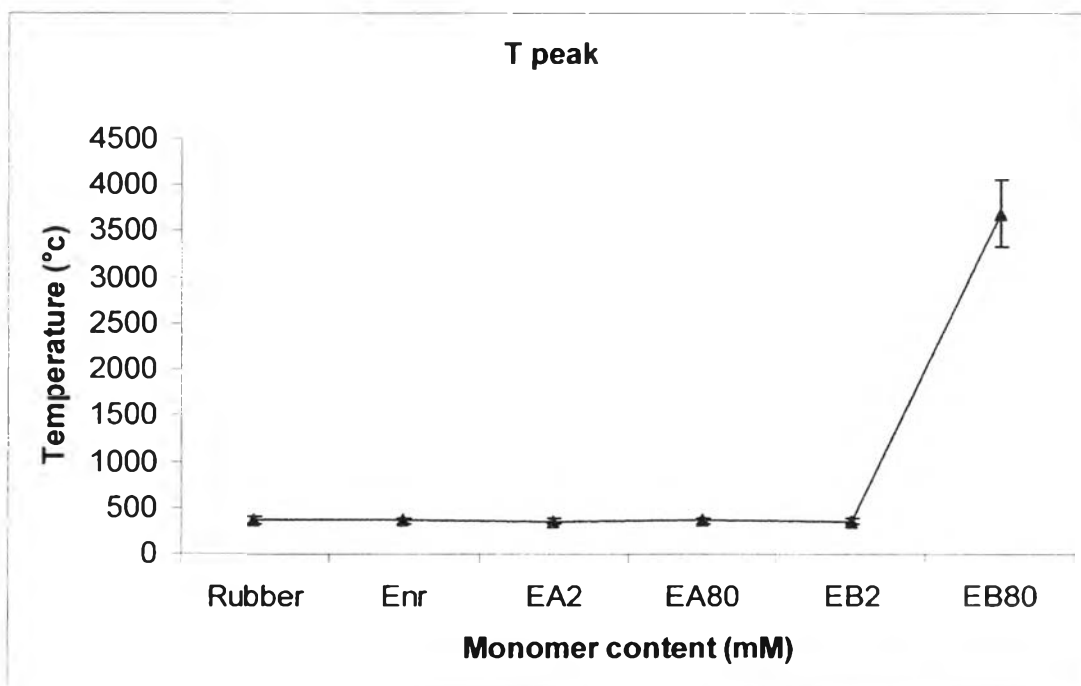

Figure 7.26 Thermogravimetric analysis thermograms of peak temperature at 10 °C/min nitrogen atmosphere of admicellar rubbers with SDS by using electrochemical methods.
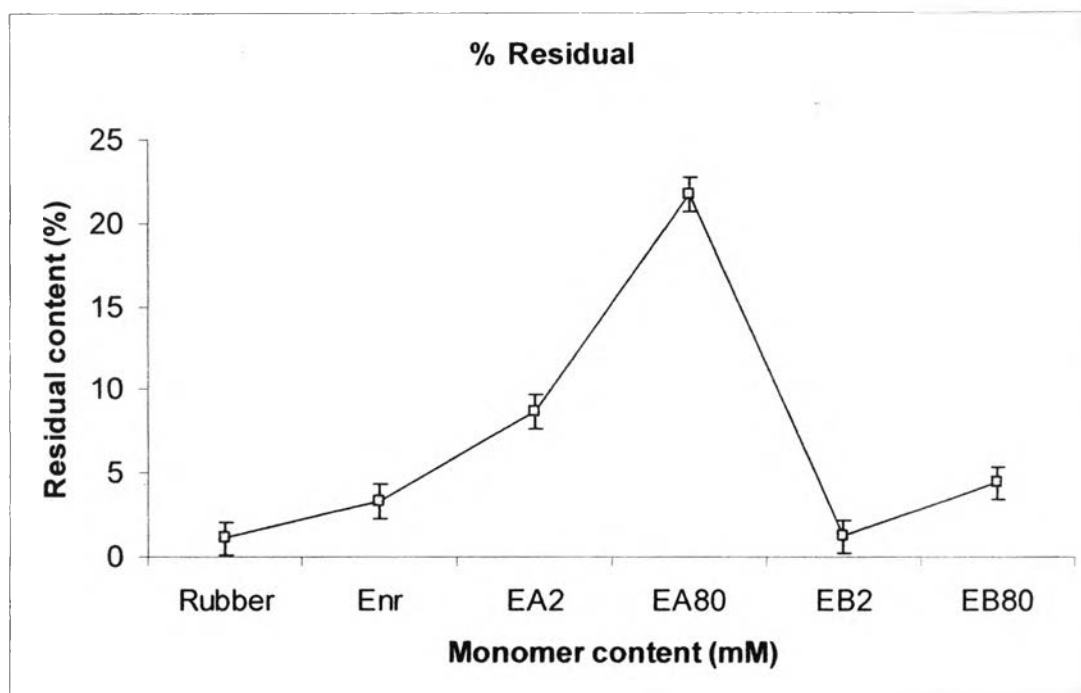
Figure 7.27 Thermogravimetric analysis thermograms of residual content at 10 °C/min nitrogen atmosphere of admicellar rubbers with SDS by using electrochemical methods.

7.4.5 Mechanical properties measurement

The admicelled rubber films were determine mechanical properties using a Lloyd Universal Testing Machine with a crosshead speed of 50 mm/min, and gauge length of 50 mm, under room temperature. The test followed ASTM D882-91. The effects of monomer concentration (PPy and PTh) on the mechanical properties of admicelled rubber are discovered in Chapter 4-6. and it shows the effect of iodine doping on the stress-strain curves of admicelled rubber in Figure7.28 and explain each factors in Figure 7.28-7.36.

Table 7.11 shows the effect of I_2 doping compared to undoping. It found that NR film was soft, tough and highly elastic, with higher elongation at break(311.75%), a high value for work to the break (0.672J), but low tensile strength at break (4.8657x 10^5 Pa) and yield modulus (0.167 MPa). Conversely, the mechanical properties of PPy and PTh change from soft and elastic to hard and brittle, depending on amount of them. The tensile strength at break can be improved from 0.486 MPa (0mM) to 1.87 MPa (800mM PPy) and 1.33 MPa (800mM PTh) However, the surprisingly, tensile strength at break of Iodine doping (1-3%wt) increased from 0.486 to 0.515 MPa (NR) and 1.33 to 1.486 (800mM PTh) whereas PPy (800) were decreased form 1.87 MPa to 1.78 MPa. This can be correlated them with SEM result. The SEM micrographs (Figure 7.11-7.14) of admicelled rubber with different PPy/PTh concentrations. The presented of the cracking and a lot of pinholes in the material after polymerization, this can caused by hydrogen gas occurred as explaination in Figure 7.5b-c (S.Touihri.1997)[146]. The higher amount monomer, PPy (Figure 7.12) can enhance higher number of pinholes the materials. This can results in the decreasing in their mechanical properties of PPy. However, PTh (Figure 7.14) was differ in the morphology, the molecule was arrange overlap, and separated closely for each chains. So the higher number PTh molecule was tightly contact and led to higher in their tensile strength. The other reason, Iodine can increase the more perfectly oriented to the molecule (Januasz.1991)[152]. It also confirms the similar trends by Jeff. M(1991)[153], doping with iodine vapor led to significant enhancement of the stiffness, strength and electrical conductivity of samples. The increase in stiffness, through the introduction I_2 vapor, was reversed

upon removal of the dopant. As previously found other conducting polymer systems, strong correlations were observed between mechanical properties and the electrical conductivity. The comparison tensile strength vary the monomer contents in Figure 7.34. It found that PPy has higher tensile strength than PTh. Although, Iodine doping can increased orientation to the molecule and conductivity, it gives lower elongation to the molecule. This study also shows the higher number of monomer (PPy/PTh) content in admicelled rubber, the lower elongation is. Figure 7.33 shows the elongation vary the concentration of monomer. At higher concentration of PPy has higher elongation than PTh whereas it was conversed at lower PPy concentration. A possible reason was caused by the induced cracking of iodine along the surface. Moreover, the effect of monomer concentration to the energy at break and young modulus are presented in Figure 7.35 and 7.36, respectively.

Table 7.9 Composition and properties of conductive rubber with effect of I_2 doping were tested by UTM (Lloyd universal machine)

| Sample (mM)		Elongation at break (%)	Tensile strength at break (Mpa)	Work to Break (J)	Young's modulus (Mpa)
Iodine dope	Enr	172.0 ±6.013	0.515 ± 0.415	0.694± 0.15	0.36± 0.018
	EA2	137.78 ± 5.012	1.064 ± 0.252	0.941± 0.024	0.78± 0.309
	EA80	108.77 ± 6.111	1.789 ± 0.622	0.411± 0.041	2.39± 0.119
	EB2	287.9 ± 6.545	0.912 ± 0.352	0.844± 0.114	0.40± 0.020
	EB80	107,23 ± 4.012	1.486 ± 0.536	0.390± 0.014	1.80± 0.090
w/o dope	Rubber	311.75 ± 6.23	0.4865 ± 0.002	0.6724 ± 0.013	0.1667± 0.013
	A2	180.95 ± 9.05	0.566 ± 0.006	0.557 ± 0.027	1.11 ± 0.022
	A80	88.87 ± 6.22	1.879 ±0.026	0.241 ± 0.016	2.85 ± 0.057
	B2	312.73 ± 15.378	0.203 ± 0.028	0.746 ± 0.040	0.285± 0.006
	B80	69.60 ± 5.143	1.338 ± 0.089	0.236 ± 0.0205	2.850± 0.057
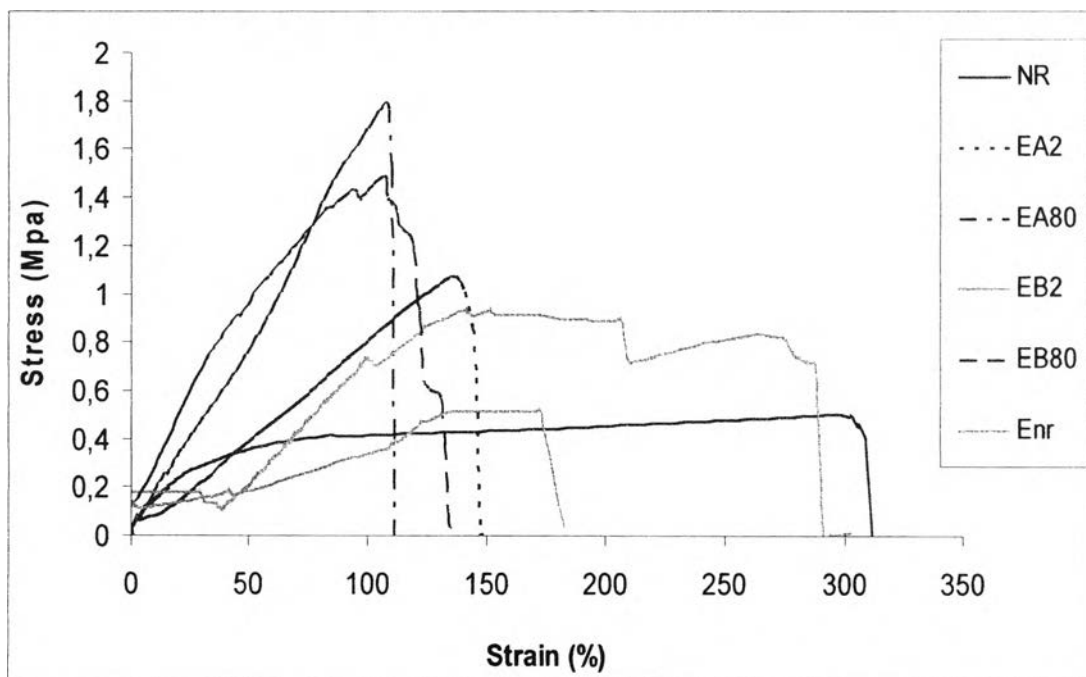
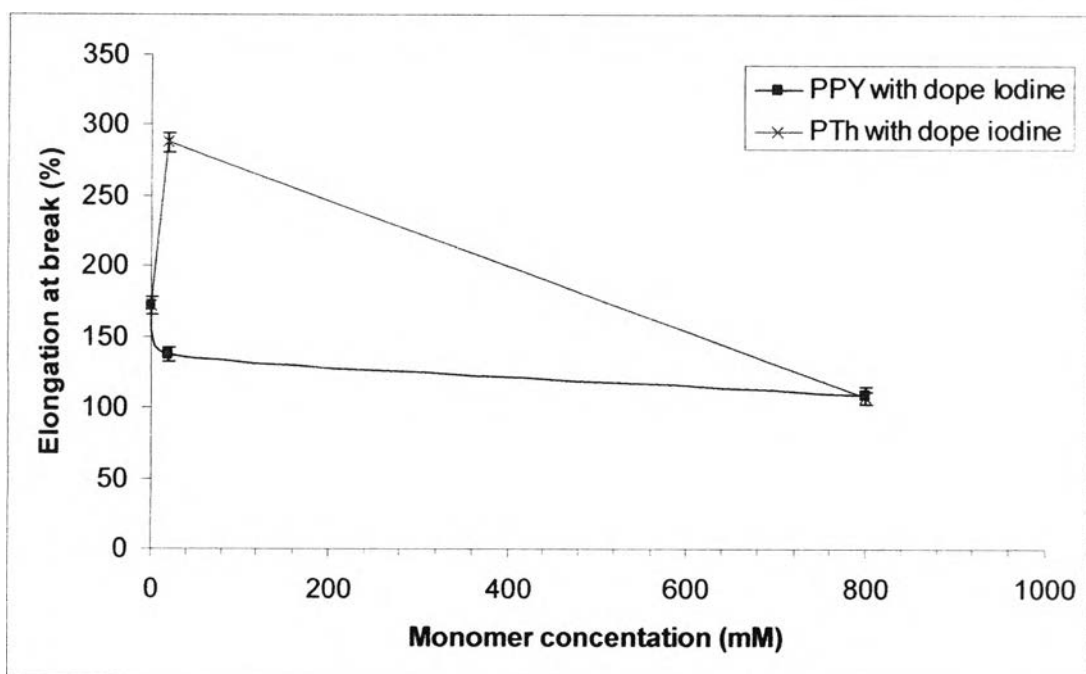**Figure 7.28** Effect of iodine doping on the stress-strain curves of admicelled rubber

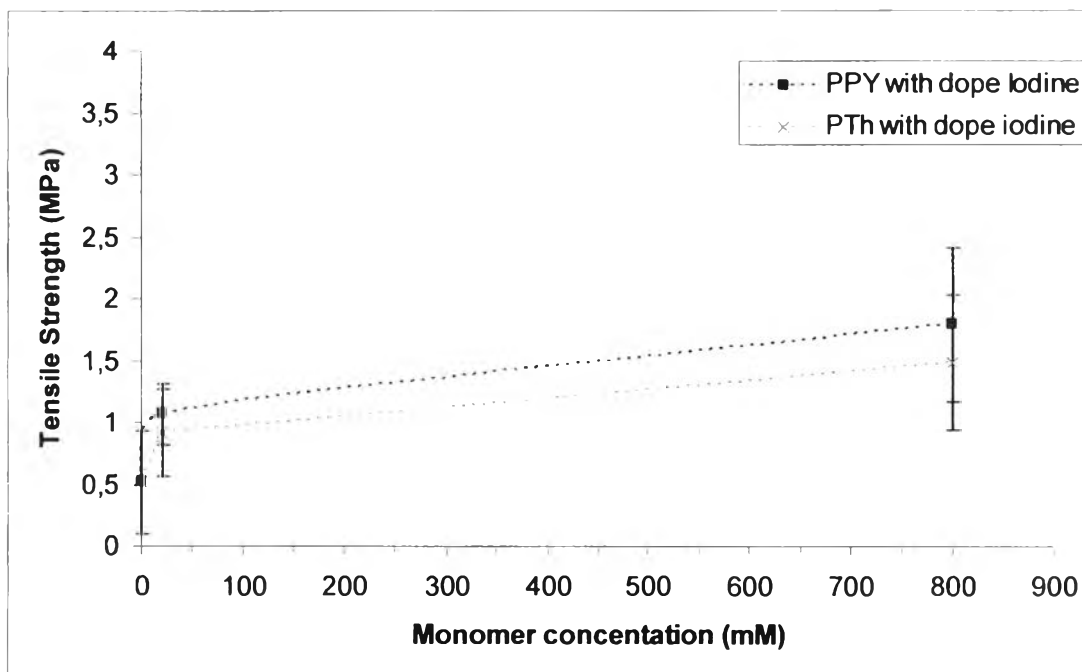**Figure 7.29** Elongation vary the concentration of monomer (Lloyd universal machine)

Figure7.30 Tensile strength vary the concentration of monomer (Lloyd universal machine)
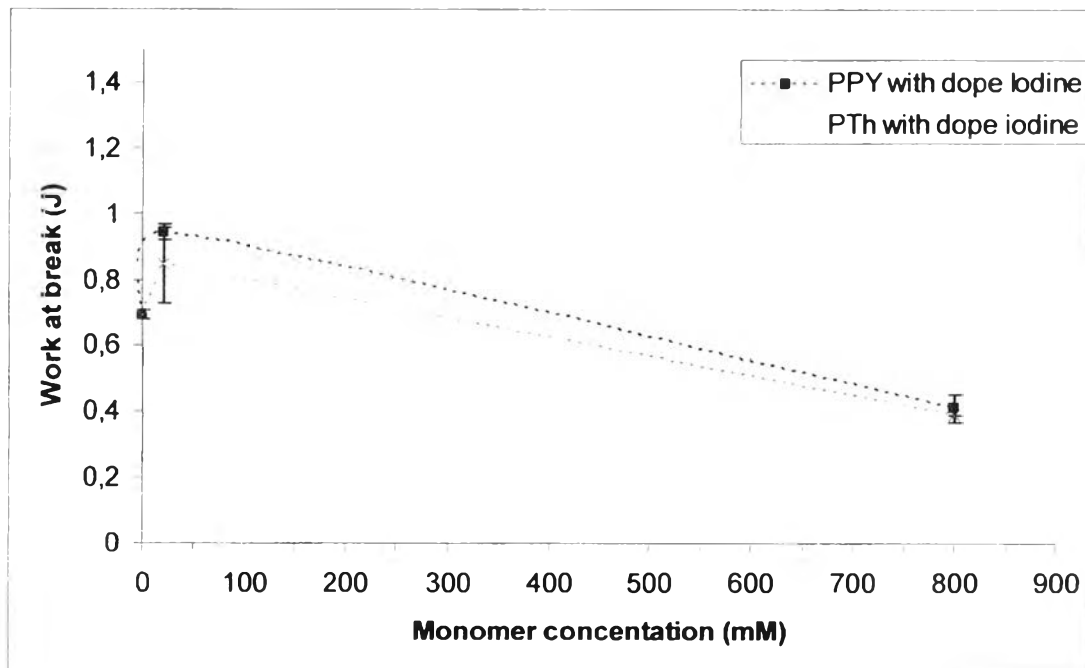

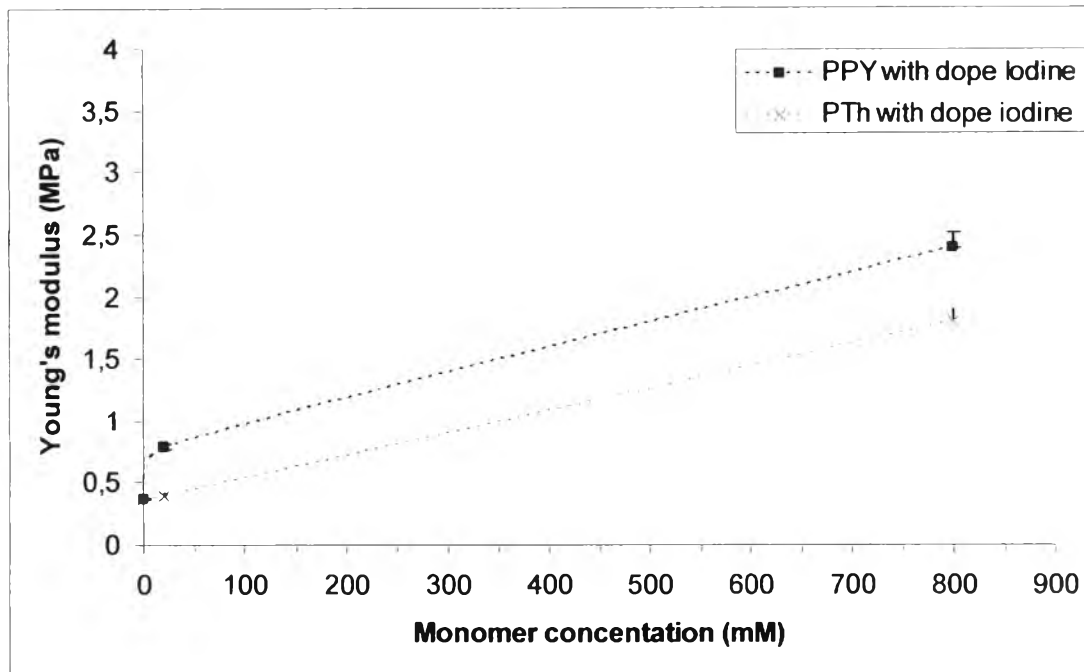**Figure 7.31** Effect of monomer concentration to the energy at break (Lloyd universal machine)

Figure7.32 Effect of monomer concentration to Young's modulus (Lloyd universal machine)

Figure 7.33 Elongation vary the concentration of monomer (Lloyd universal machine)

Figure 7.34 Tensile strength vary the concentration of monomer (Lloyd universal machine).

Figure 7.35 Effect of monomer concentration to the energy at break (Lloyd universal machine)

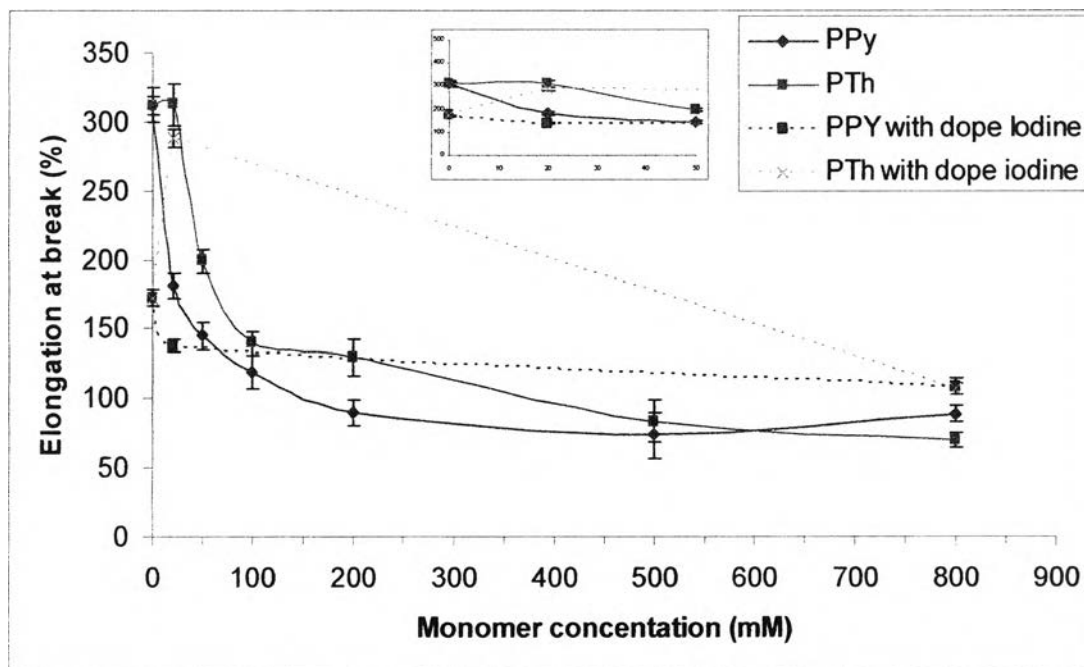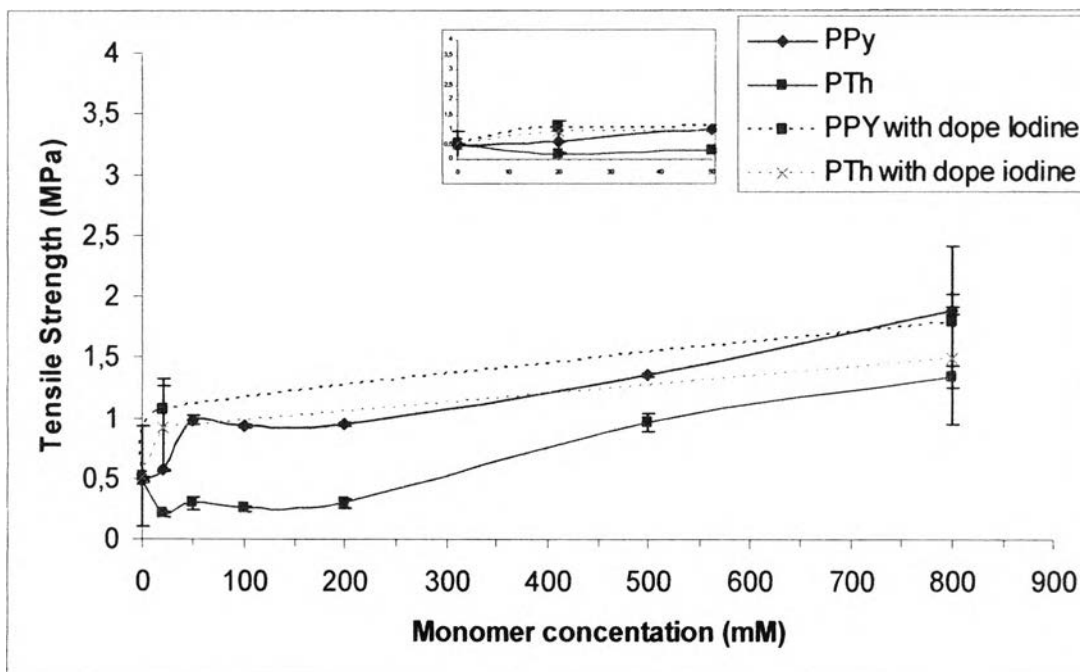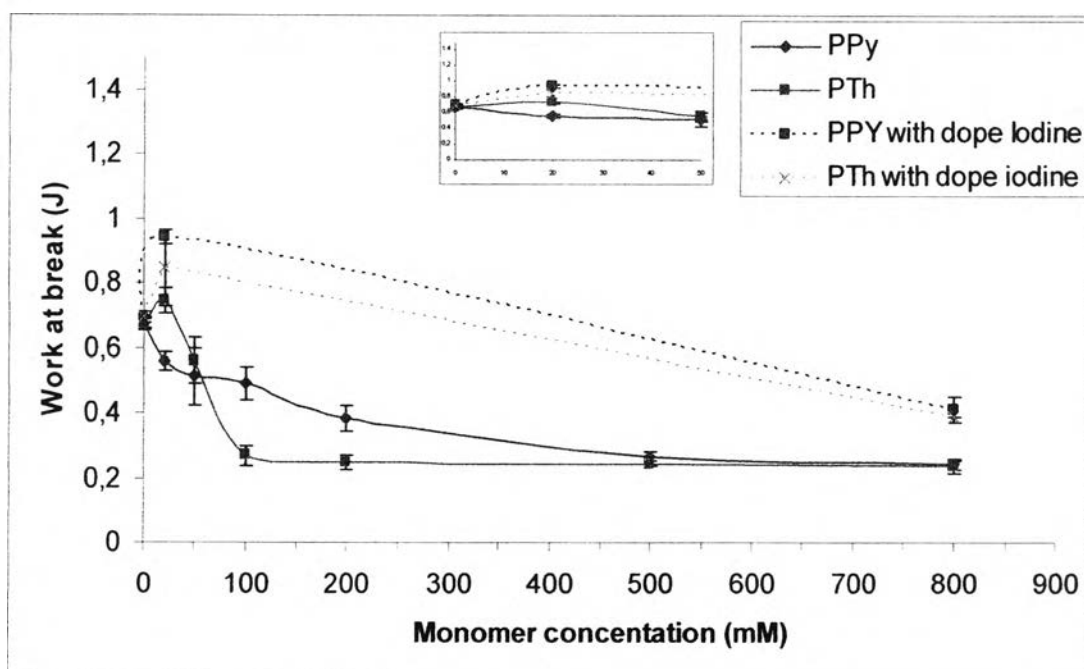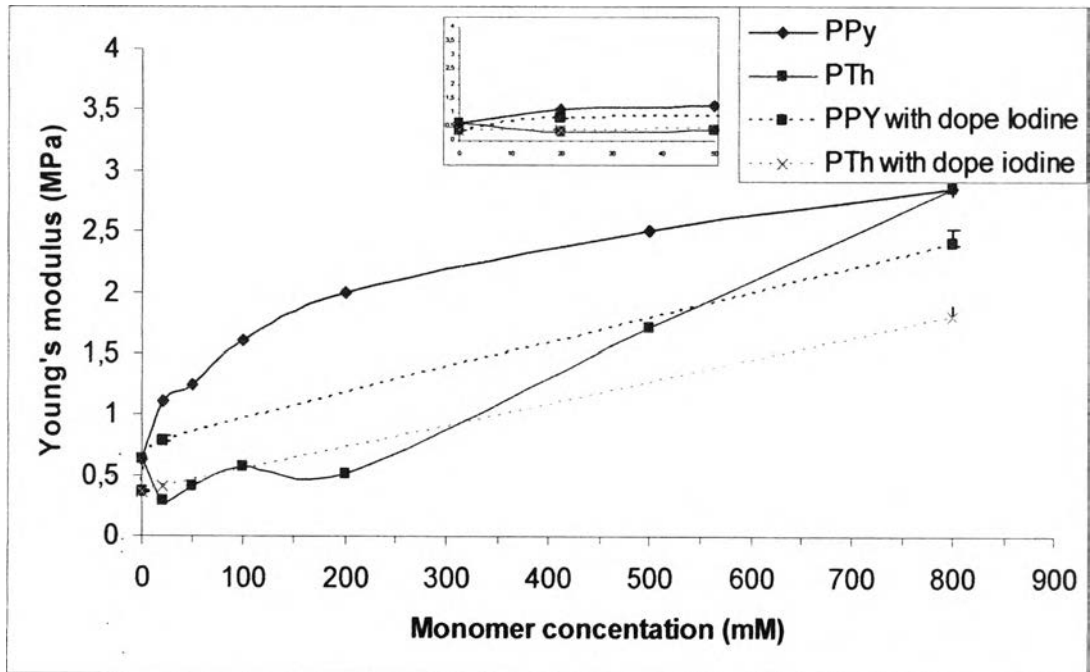**Figure 7.36** Effect of monomer concentration to Young's modulus (Lloyd universal machine)

7.4.6 Conductivity Properties Measurement

The conductivity of admicelled rubbers were tested by using Keithley 8009 Resistivity Test Fixture and a Keithley 6517A. Electrometer/High Resistance Meter. A dc voltage of 0.1 to 15 volt was applied to the specimen placed in the Keithley 8009 test fixture. Then, the current was read and the surface and volume resistivity were determined. The conductivity of PPy and PTh are reported in Chapter 4 – 6. Table7.12 summarized the effect of Iodine effect after doping to samples on the electrical conductivity.

From the discovered in chapter 4 and 5, pyrrole and thiophene can be promoted an increase of ninth to eleventh orders of magnitude on the conductivity, ranging from 10^{-15}S/cm (NR) to 10^{-4} S/cm (800mM PPy) and 10^{-6} S/cm (800mM PTH). The result is similar to that of natural rubber/polypyrrole composites, studied by Tasakorn P.,et at.(1996)[2], where adding 50% PPy can improve the conductivity as high as 7.604 x 10^{-3} S/cm. These results (Figure 7.39) also relate to polythiophene-synthesis rubber (PTh-SR) and polythiophene-natural rubber (PTh-NR) reported by Semih.Y et al.(1996)[81]. PTh-SR and PTh-NR composites were prepared by the electrochemical polymerization of thiophene onto rubbers. Then, the insulating rubber films were dip coated from the toluene solution. The conductivity which gives higher conductivity at higher compositions from 80%wt of PTh : 2.6-3.5 x 10^{-1} S/cm to 95%wt of PTh : 3.7-6 x10^{-1} S/cm. This results show the importance of doping agent, they are affected to conductivity of composites. Figure 7.38 demonstrates that the conductivity gradually increases at low amount of monomer. For above 100 mM PPy, the conductivity tends to increase slowly. It also presented significantly lower volume resistivity and higher surface resistivity coresponding physical properties, which relates to the NBR/ PAni.DBSA blends studied by Soares BG., el at.(2000)[121]. From the results, the electrical conductivity is still low around ~ 2x10^{-10} S/cm.

From the report of Dai.L et al.(1994)[136] suggest that for cis-1,4-polybutadiene the reaction with iodine stops after the addition step; the elimination of HI (reaction 2 in Figure 7.40) does not occur for the cis isomer whereas it does for the trans isomer. The absence of formation of the conjugated sequences of the double bonds, which are necessary structure elements for a polymer to be electrically

conductive, renders the cis isomer incapable of attaining conductivity upon I_2 doping on *cis-* and *trans-*1,4-polybutadienes, but do not indicate why the elimination of HI should be ineffective for the former isomer. At this point, there is no denying that the *trans* better than *cis* molecular structure because of their stability. Although this studied using natural rubber latex with compose of *cis* and *trans* polyisoprene, the conductivity can be improved by the properties of conductive polymer (PPy, PTh).

A significant improvement of the conductivity of the iodine-doped natural rubber latex was estimate one orders (from 7.18×10^{-15} to 7.25×10^{-14}) of magnitude higher than of nondoped (Figure 7.37). This is still low improved, but it correlated with iodine-doped polydiacetylene thin film was estimated to be $(3 \pm 0.3) \times 10^{-3}$ S/cm, which is three orders of magnitude (Kazuhiro T.,2005)[154].

After dope NR with Iodine, then monomer can be promoted from 3.19×10^{-4} to 5.71×10^{-4} S/cm (800mM PPy) and 8.26×10^{-6} to 3.39×10^{-5} S/cm (800mM PTh). Figures 7.38-7.39 exhibit the percolation threshold for adding the monomer with doped. Indeed, as monomer content increased, the conductivity also increased because the coating of monomer was more perfect at higher concentration, as supported by SEM micrographs and the result of TGA. The conductivity can be related to the formation of conjugation sequences of double bond, band gaps, positively charge, oxidation level, molecular structure, moister, and so on.

Table 7.10 Conductivity of natural rubber sheet at various monomer concentrations

| Sample (mM)		Resistivity V Ω.cm	σ_v S.cm^{-1}	Resistivity S Ω	σ_s	Thickness (cm)
Iodine dope	Enr	1,38E+13	7,25E-14	2,14E+12	4,67E-13	0.3310
	EA2	1.39E+09	7,17E-10	4,27E+09	2,34E-10	0.3287
	EA80	1.75E+03	5.71E-04	9,74E+03	1,03E-04	0.3095
	EB2	6.79E+09	1,47E-10	2,74E+07	3,65E-08	0.3375
	EB80	2.95E+04	3.39E-05	2,28E+04	4,39E-05	0.3305
w/o dope	Rubber	1,39E+14	7,18E-15	4,07E+14	2,46E-15	0.3336
	A2	1.80E+09	1.49E-10	4.35E+09	2.30E-10	0.3140
	A80	3.13E+03	3.19E-04	2.61E+03	3.83E-04	0.3095
	B2 ·	3.97E+11	2.52E-12	5.40E+11	1.85E-12	0.387
	B80	1.21E+05	8.26E-06	3.84E+05	2.61E-06	0.413

where A= PPY, B= PTh , E= dope with iodine
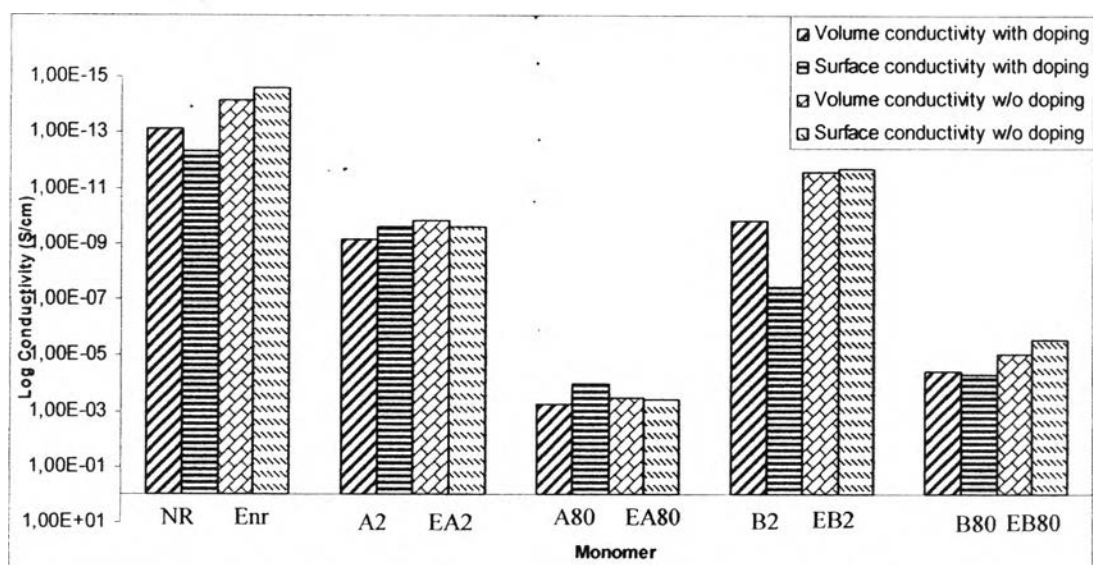
Figure 7.37 Electrical conductivity as a function of monomer content with iodine dope in composites with natural rubber latex (Apply dc 0.1-500 volt).
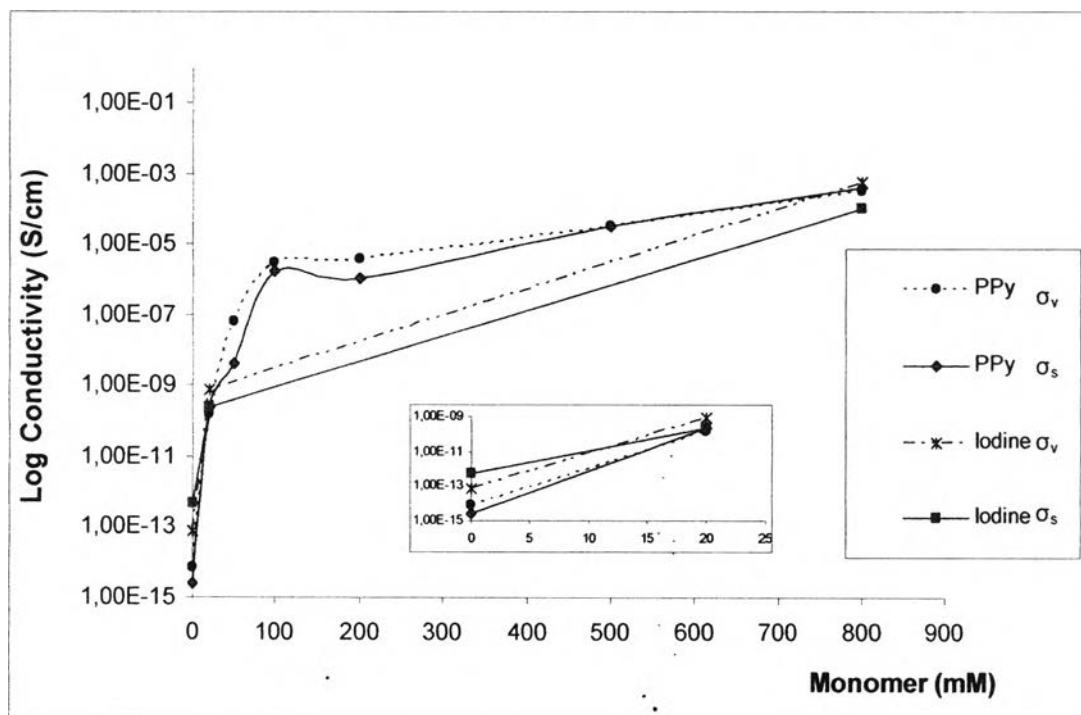
Figure 7.38 Electrical conductivity as a function of PPY content in composites with natural rubber latex and doping with iodine (Apply dc 0.1-20 volt).
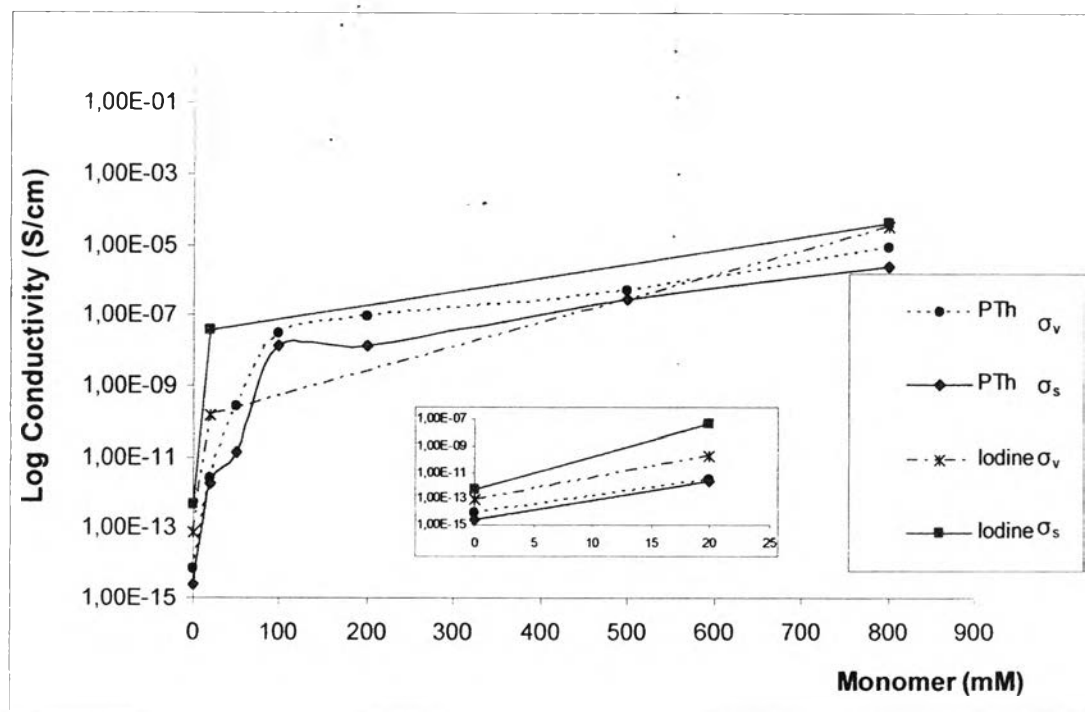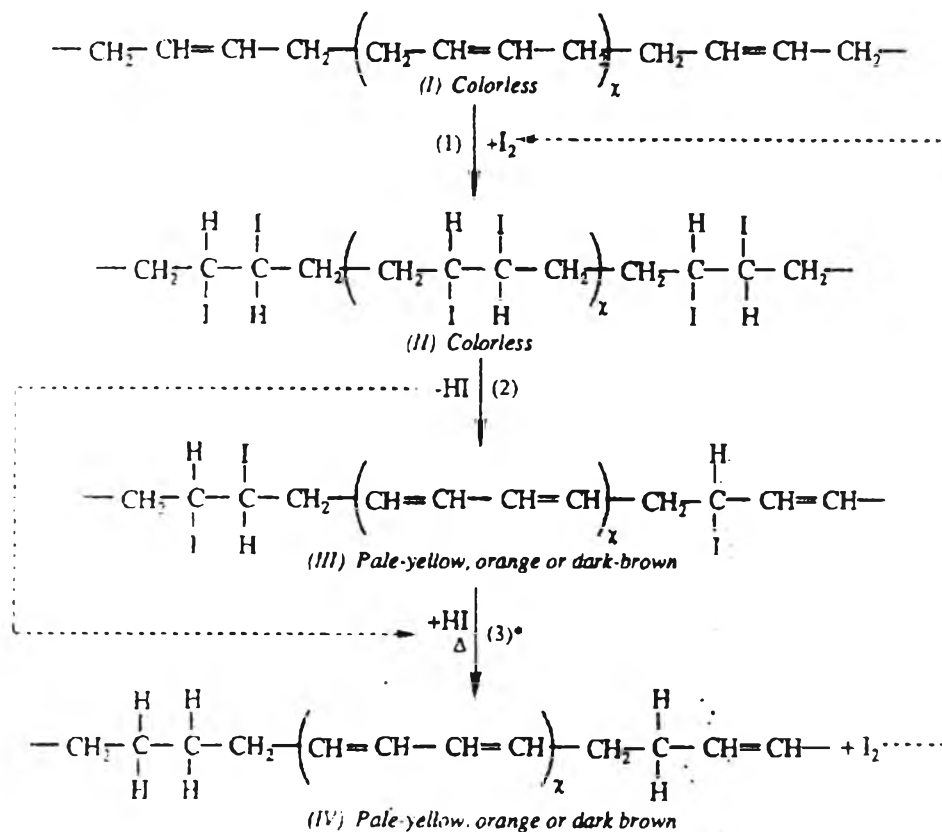

Figure 7.39 Electrical conductivity as a function of PTh content in composites with natural rubber latex and doping with iodine (Apply dc 0.1-20 volt).

In the reaction (3) most likely proceeds by the free radical mechanism[137] :

$$I_2 \rightleftharpoons 2I$$

$$I + RI \rightleftharpoons R + I_2$$

$$R + HI \rightleftharpoons RH + I$$

where, RI and RH represent polymer (III) and polymer (IV), respectively.

Figure 7.40 Reactions leading to the formation of conjugated sequences in polybutadienes following treatment with Iodine.

Table 7.11 doping levels and conductivites of a variety of CPs[90-92,133]

Polymer	Dopant (X⁻)	Structure	Conductivity(S/cm)
PPy	$CF_4SO_3^-$	$(C_4H_3N)X_{0.3}$	150 (Film)
			10 (PP)
	ClO_4^-	$(C_4H_3N)X_{0.3}$	100 (Flim)
PPy and NR	**I_3^-**		**$4.67 \times 10^{-13} - 1.03 \times 10^{-4}$**
PTh	$SO_3CF_3^-$	$(C_4H_2S)X_{0.3}$	10-20 (PP)
	None	$(C_4H_2S)X_{0.01}$	15×10^{-7} (PP)
	BF_4^- or PF_6^-	$(C_4H_2S)X_{0.06}$	0.02 (PP)
PTh and NR	**I_3^-**		**$4.67 \times 10^{-13} - 3.39 \times 10^{-5}$**
Poly(3-methylthiophene)	$SO_3CF_3^-$	$(C_5H_4S)X_{0.3}$	30-50 (PP)
	$SO_3CF_3^-$	$(C_5H_4S)X_{0.5}$	100 (PP)
	None	$(C_5H_4S)X_{0.005}$	10^{-7} (PP)
	PF_6^-	$(C_5H_4S)X_{0.12}$	1 (PP)
Poly(3,4-dimethylthiophene)	$SO_3CF_3^-$	$(C_6H_6S)X_{0.3}$	10-50(PP)

7.5 Conclusion

The success of the admicellar polymerization of iodine dope to latex particles, and using pyrrole and thiophene as monomer to polymerization, was investigated using FTIR, SEM, and TGA. From the FTIR study, the admicelled rubbers showed the characteristic peaks of polypyrrole, thiophene and iodine which confirmed the existence of PPy, PTh, and Iodine after the polymerization. This technique is efficient: % yield ~82-89%, but it lower than nondope. However, Iodine doped can enhance the faster reaction time to polymerization. As seen in the result of TGA, the admicelled rubbers began to lose weight at higher temperature, compared to that of NR, and they also showed the shift of major decomposition of pure PPy,PTh to lower temperature. This can caused by Iodine molecule can give high oxidative potential (Pawel D.1990)[151]. Therefore, I_2 can enhance the decomposition temperature to the molecule. The DTG curves also demonstrated an increase of char yields of the admicelled rubbers. As PPy,PTh content increased, the residual content also increased. Moreover, Iodine These indicate that an increase of I_2 content enhance the residue remaining. These indicated that the admicelled rubbers were less thermostable than natural rubber. This suggested that admicelled polymerization via the electrochemical method was not a unique method to prepare miscible core-shell structure of NR-monomer-I_2 due to there are presented of the pinholes from H_2. The mechanical properties from tensile testing showed the decrease of work to break of the admicelled rubbers. This indicated the higher stiffness of the admicelled rubbers compared to natural rubber. Since the monomer behaved like a hard and brittle material, the stiffness of the materials increased as monomer content increased. It found that PPy has higher tensile strength than PTh. Although, Iodine doping can increased orientation to the molecule and conductivity, it gives lower elongation to the molecule. At higher concentration of PPy has greater elongation than PTh whereas it was conversed at lower PPy concentration. As PPy or PTh content increased, the conductivity was also increased. A significant improvement of the conductivity of the iodine-doped natural rubber latex was estimate one orders (from 7.18×10^{-15} to 7.25×10^{-14}) of magnitude higher than of nondoped.

7.6 Acknowledgements