

PREPARATION AND ELECTRICAL CONDUCTIVITY OF  
NATURAL RUBBER/POLYPYRROLE/MONTMORILLONITE NANOCOMPOSITES

Miss Thiyapat Padprom

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By                                    Miss Thiyapat Padprom  
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Thesis Advisor                    Assistant Professor Korbratna Kriausakul, Ph.D.

---

Accepted by the Faculty of Science, Chulalongkorn University in Partial  
Fulfillment of the Requirements for the Master's Degree

.....Dean of the Faculty of Science  
(Professor Supot Hannongbua, Dr. rer. nat)

THESIS COMMITTEE

.....Chairman  
(Associate Professor Supawan Tantayanon, Ph.D.)

.....Thesis Advisor  
(Assistant Professor Korbratna Kriausakul, Ph.D.)

..... Thesis Examiner  
(Assistant Professor Warinthorn Chavasiri, Ph.D.)

.....External Examiner  
(Assistant Professor Toemsak Srikhirin, Ph.D.)

ติยาภัทร ปัดพรม : การเตรียมและการนำไฟฟ้าของนาโนคอมพอสิตของยางธรรมชาติ/พอลิไพโรล/มอนโมริลโลไนต์. (PREPARATION AND ELECTRICAL CONDUCTIVITY OF NATURAL RUBBER/POLYPYRROLE/MONTMORILLONITE NANOCOMPOSITES) อ.ที่ปรึกษาวิทยานิพนธ์หลัก : ผศ. ดร.กอบรัตน์ เกรียวสกุล, 72 หน้า.

ในงานวิจัยนี้ได้เตรียมคอมพอสิตของยางธรรมชาติ/พอลิไพโรล/ โดยการทำให้ปฏิกิริยาเคมีพอลิเมอไรเซชันแบบออกซิเดชันของพอลิไพโรลในน้ำยางธรรมชาติ ที่อุณหภูมิ 0 องศาเซลเซียสเป็นเวลา 1 ชั่วโมง โดยใช้สารละลายเพอริกคลอไรด์เป็นตัวออกซิเดนต์ ในอัตราส่วนต่อโมลระหว่างตัวออกซิเดนต์และไพโรลคงที่ 2.5 ปริมาณของพอลิไพโรลในคอมพอสิตหาจากน้ำหนักของสารอบแห้งที่ 60 องศาเซลเซียส ค่าการนำไฟฟ้าของคอมพอสิตที่เตรียมได้วัดด้วยชุดอุปกรณ์โพรพร้อยด์โพรบ ได้ทำการศึกษาปัจจัยต่างๆ ที่มีผลต่อค่าการนำไฟฟ้าของคอมพอสิต ได้แก่ ปริมาณของพอลิไพโรลในคอมพอสิต ชนิดของตัวทำละลาย การเติมเซอร์แฟคแตนต์ ปริมาณมอนโมริลโลไนต์ในคอมพอสิต และชนิดของสารอินทรีย์ที่ใช้ปรับปรุงมอนโมริลโลไนต์ พบว่าเมื่อเพิ่มปริมาณไพโรล ให้คอมพอสิตที่มีค่าการนำไฟฟ้าสูงขึ้น ซึ่งมีค่าสูงสุดเท่ากับ 4.44 ซีเมนต่อเซนติเมตร ที่ปริมาณ 15 เปอร์เซ็นต์โดยน้ำหนักของพอลิไพโรล เมื่อเติมโซเดียมโคดีซิลเบนซีน ชั้นโฟเนตในคอมพอสิตค่าการนำไฟฟ้ามีค่าสูงขึ้นเป็น 7.16 ซีเมนต่อเซนติเมตร เมื่อใช้มอนโมริลโลไนต์ในการเตรียมคอมพอสิตพบว่าค่าการนำไฟฟ้าของคอมพอสิตเพิ่มขึ้นกับปริมาณมอนโมริลโลไนต์ ค่าการนำไฟฟ้าของนาโนคอมพอสิตที่เตรียมโดยใช้โซเดียมโคดีซิลเบนซีน ชั้นโฟเนตในการปรับปรุงมอนโมริลโลไนต์ให้ค่าสูงสุดเท่ากับ 7.38 ซีเมนต่อเซนติเมตร จาก เอ็กซ์อาร์ดีพบว่าค่าระยะห่างระหว่างชั้นของมอนโมริลโลไนต์เพิ่มขึ้นจาก 1.26 นาโนเมตร เป็น 1.84 นาโนเมตร ของนาโนคอมพอสิตยางธรรมชาติ/พอลิไพโรล/มอนโมริลโลไนต์ ซึ่งยืนยันการแทรกตัวของพอลิไพโรลในชั้นของมอนโมริลโลไนต์ การใช้สารอินทรีย์เพื่อปรับปรุงจะเพิ่มระยะห่างชั้นของมอนโมริลโลไนต์เป็น 2.80 นาโนเมตร พบว่าคอมพอสิตของยางธรรมชาติ/พอลิไพโรล ยางธรรมชาติ/พอลิไพโรล/มอนโมริลโลไนต์ และยางธรรมชาติ/พอลิไพโรล/มอนโมริลโลไนต์ที่ปรับปรุงด้วยสารอินทรีย์มีเสถียรภาพทางความร้อนที่สูงกว่าพริสทินพอลิไพโรล

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The natural rubber (NR) /polypyrrole (PPy) composites were prepared by the chemical oxidative polymerization of pyrrole in aqueous solution of natural rubber latex. The reactions were carried out at 0 °C for 1 hour using FeCl<sub>3</sub> solution as an oxidant with constant FeCl<sub>3</sub>:pyrrole mole ratio of 2.5. The amount of PPy in the composite was weight determined from 60 °C oven-dried material. The electrical conductivities of the composites were measured with a home-made four-point probe set up. Parameters affecting the electrical conductivity of the composites were studied, i.e. the amount of pyrrole monomer, types of solvent, the addition of surfactant, the amount of montmorillonite (MMT), and types of organically modified montmorillonite (oMMT). It was found that loading of pyrrole gave the composites with increasing electrical conductivities, with the highest value of which was 4.44 Scm<sup>-1</sup> for 15 wt% of PPy. Higher electrical conductivity (7.16 Scm<sup>-1</sup>) was obtained with addition of sodium dodecylbenzene sulfonate(SDBS). In the presence of MMT, the nanocomposites exhibited higher electrical conductivity with increasing MMT content. The electrical conductivity of the nanocomposites prepared with sodium dodecylbenzene sulfonate montmorillonite modifier gave the highest value of 7.38 Scm<sup>-1</sup>. An XRD pattern showed an increase in d-spacing of MMT from 1.26 nm to 1.84 nm of NR/PPy/MMT nanocomposite, confirming the intercalation of conducting PPy into MMT layers. The use of organic modifier increased the d-spacing of MMT to 2.80 nm. The thermal stabilities of NR/PPy, NR/PPy/MMT, and NR/PPy/oMMT composites were found to be higher than pristine PPy.

Field of Study :Petrochemistry and Polymer science      Student's Signature .....

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## LIST OF ABBREVIATIONS

CB	:	Conduction Band
CPC	:	Conductive Polymer Composite
°C	:	Degree Celsius
DRC	:	Dry Rubber Content
Electron Volt	:	eV
mL	:	Millimeter
nm	:	Nanometer
MMT	:	Montmorillonite
μm	:	Micrometer
NR	:	Natural Rubber
PPy	:	Polypyrrole
SEM	:	Scanning Electron Microscopy
Scm <sup>-1</sup>	:	Siemens per centimeter
TGA	:	Thermal Gravimetric Analysis
VB	:	Valence Band

# CHAPTER I

## INTRODUCTION

### 1.1 Introduction

Electrically conducting polymers have been widely studied due to their excellent conductivity and electrical applications. Conducting polymers have been utilized in several fields, such as electronic devices and sensor [1]. Conductive polymer which is a conjugated polymer, for instance, polyaniline, polythiophene, polypyrrole etc, especially polypyrrole (PPy) is very interesting because of its simple synthesis, high electrical conductivity and good environmental stability. Normally, PPy can be prepared by either chemical oxidative polymerization and electrochemical polymerization. The chemical synthetic method produces a fine insoluble black powder, with a conductivity that varies from  $10^{-6} - 100 \text{ Scm}^{-1}$ [2], depending on the specific preparation condition. On the other hand, electrochemical method produces direct formation of conducting polymers with better control of polymer film thickness, morphology and better conductivity (as high as  $1000 \text{ Scm}^{-1}$ ) compared with chemical oxidative polymerization. The limitation of the electrochemical method is that it is difficult to prepare such films on a large scale. Pure PPy is brittle, insoluble, infusible and hence not processable [3]. To solve this problem, its conductivity and properties can be improved by creating a conducting polymer composite in which polypyrrole is mixed with conventional polymers.

Various approaches have been utilized to make PPy processable, including:

- (a) chemical and electrochemical modification of PPy backbone
- (b) co-polymerization with appropriate functional co-monomers
- (c) use of polymeric or surfactant-type dopant anions
- (d) preparation of stable colloidal dispersion of PPy particles in an aqueous or non-aqueous medium.

Conducting polypyrrole are potential fillers for the modification of the mechanical and conducting properties of polypropylene, polyethylene and other insulating polymer matrices. A combination of conducting polypyrrole with other insulating polymers such as natural rubber (*cis*-polyisoprene) which has good flexibility, low density, good mechanical resistance, and easily to process should created a new polymeric materials with specific electrical properties [4].

For the development of electrically conductive and mechanical properties of conducting polypyrrole composite, montmorillonite has been used to prepare the conducting polymer nanocomposites. Montmorillonite is the type of mineral clay which is widely used in preparation of nanocomposites because it has lamellar structure with a high aspect ratio (length-to-width ratio). Clay/polymer nanocomposites exhibit advanced gas barrier, thermal stability, mechanical strength, and fire retardant properties compared to individual polymers. Depending on the dispersion of the silicate layers in polymer matrix and the method of preparation, the type of nanocomposites can be classified into either intercalated or exfoliated structures. With an exfoliated structure, there are effective reinforcement in polymer nanocomposite. Exfoliated or delaminated structures are obtained when the silicate layers are completely and uniformly dispersed in polymer matrices.

## 1.2 Objective

- To prepare highly conductive natural rubber/polypyrrole/montmorillonite nanocomposites via the chemical oxidative polymerization.
- To characterize the nanocomposites using SEM, TGA, ATR FT-IR, and XRD techniques.



### **1.3 Scope of research**

1. Prepare the natural rubber/polypyrrole composites by oxidative polymerization for various weight ratios of pyrrole, 5 - 25 %wt.
2. Investigate the effect of solvent on the electrical conductivity of the nanocomposites, using water and 1:1 volume ratio of water/methanol.
3. Investigate the effect of surfactant on the preparation of nanocomposites using for 1:5 molar ratio of sodium dodecylbenzene sulfonate (SDBS) to pyrrole.
4. Prepare the natural rubber/polypyrrole/montmorillonite nanocomposite by varying amounts of montmorillonite content in nanocomposites from 5-25 %wt.
5. Study the effect of types of organically modified montmorillonite using octadecyl amine (ODA) and sodium dodecylbenzene sulfonate (SDBS) as organic agent modifiers.

## CHAPTER II

### THEORITICAL AND LITERATURE SURVEY

#### 2.1 Conducting polymer

Conducting polymers are the materials of increasing scientific and technical interest because of their high-tech applications on batteries, photovoltaic cells, chemical sensors, semiconductor devices, optical switches, electromagnetic shielding materials, and corrosion-protecting materials, etc. These conductive materials are usually classified in two large groups according to the modes of their electrical transport:

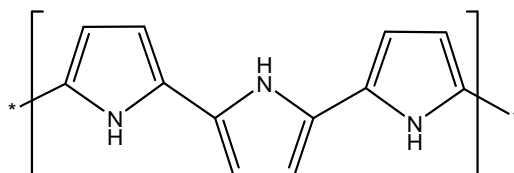
1. Ion-conducting polymer, being electrolyte polymers where the electric current is ensured by ions associated with polymer such as poly (ethylene oxide) (PEO).

2. Electronically conducting polymers, having conjugated bonds in the macromolecular network, conventionally classified into three main groups:

- a. Aromatic hydrocarbons e.g., polyaniline, (PANI)
- b. Heterocyclic hydrocarbons e.g., polythiophene, (PTh), polypyrrole, (PPy).
- c. Aliphatic hydrocarbons e.g., polyacetylene, (PA).

##### 2.1.1 Polypyrrole (PPy)

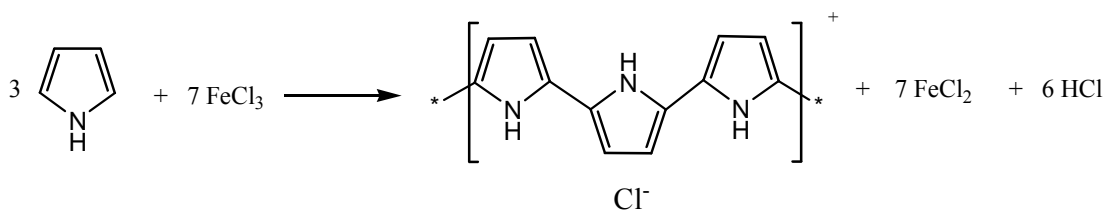
Polypyrrole is one of the representative conducting polymer. PPy was first synthesized in 1968[2]. The polymerization of PPy was succeeded through  $\alpha, \alpha'$ -coupling (2,5-position). The molecular structure of PPy are shown in Fig 2.1.



**Figure 2.1** The structure of polypyrrole molecular chain

Polypyrrole can be prepared either by electrochemical polymerization or chemical oxidative polymerization. The electrochemical polymerization of pyrrole produces free-standing conducting films with a conductivity, at room temperature, as high as  $1000 \text{ Scm}^{-1}$ . In contrast, the chemical oxidative polymerization method produces a fine insoluble black powder with a conductivity varies from  $10^{-6} \text{ Scm}^{-1}$  to  $100 \text{ Scm}^{-1}$ , depending on the specific preparation condition [2].

In chemical oxidative polymerization, ferric chloride is chosen as an initiator (oxidant) which also acts as a dopant. PPy prepared with initiator-dopant in the absence of any stabilizer contains about one  $\text{Cl}^-$  unit per three-pyrrole units[3]. The reaction stoichiometry is approximated as



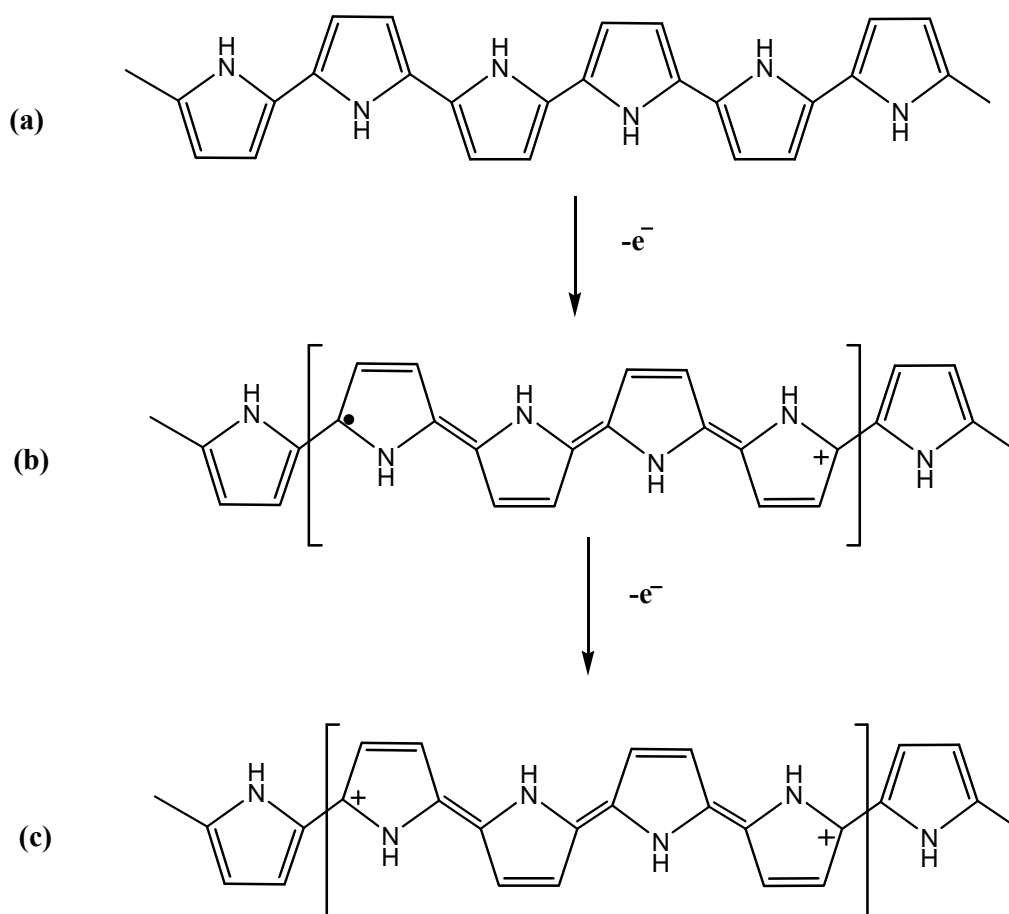
By this scheme, 2.33 moles of  $\text{FeCl}_3$  are required for the polymerization of one mole of pyrrole. Polymerization in non-aqueous medium requires the use of  $\text{FeCl}_3$  to pyrrole mole ratio of greater than 2:1 to achieve the highest conductivity [4]. However, in aqueous medium the latter may be obtained using a much lower ratio of  $\text{FeCl}_3$  to pyrrole, sacrificing the yield.

The black polypyrrole powder is insoluble, infusible, and hence difficult to process. The electrophysical properties of polypyrrole are determined by a variety of factors such as the degree of polymerization, the nature of dopant and the heteroatoms on the molecule. The band gap of PPy changes from 2.0eV to 3.2 eV [4]. Because PPy has two inequivalent structures, the coupling of electronic excitation to chain distortions can lead to polaron and bipolaron as the dominant charged species[5].

### 2.1.2 Electrical transport of polypyrrole

The hetero aromatic and extended p-conjugated backbone structures provide PPy with a chemical stability and an electrical conductivity, respectively. The p-conjugated backbone structure, however, is not sufficient to produce appreciable conductivity on its own. Partial charge extraction from PPy chain is also required, which is achieved by a chemical or an electrochemical process referred to as doping. The conductivity of the neutral PPy remarkably changes from an insulating regime to a metallic one by doping. This is a very worthwhile feature for applications in which the electrical conductivity of a material must be controlled.

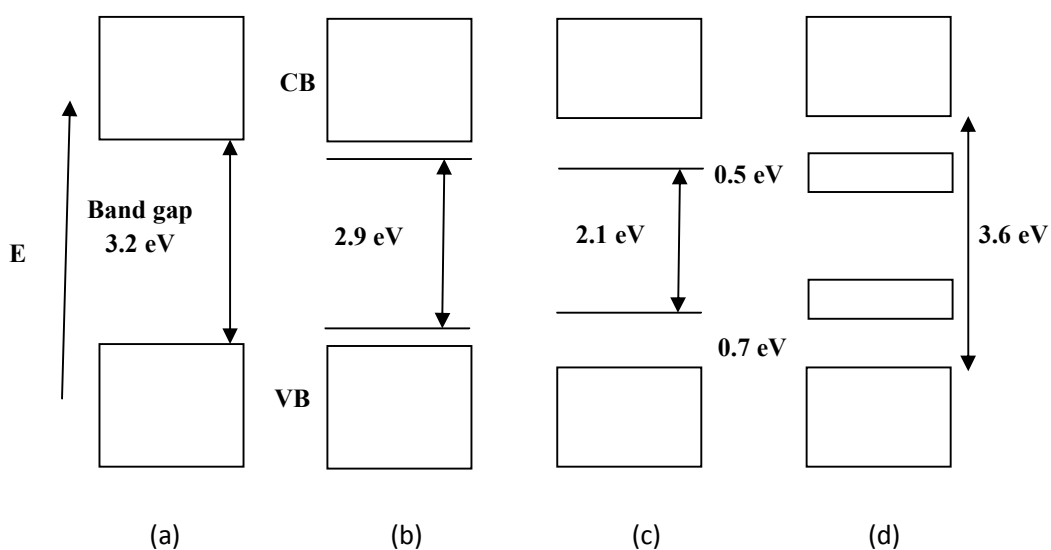
It was reported that the electronic and band structure of PPy were changed with the doping level of the PPy chain. Neutral PPy, with the benzenoid structure shown in Fig. 2.3a, is categorized as an insulator and its proposed electronic energy diagram is shown in Fig. 2.4a. The band gap of neutral PPy is reported to be 3.16 eV, which is not too wide for electrons to transfer from the valence band to the conducting band at room temperature. The PPy chain is, however, simultaneously doped during polymerization. Counteranions in the reaction medium are incorporated into the growing PPy chain to maintain electrical neutrality of the polymer system. Upon extraction of a negative charge from a neutral segment of a PPy chain by the doping process, a local deformation to the energetically favored quinoid structure occurs (Fig 2.3b). In combination with the quinoid structure, the positive charge and the unpaired spin are referred to as a polaron, the formation of a polaron (Fig. 2.4b) induces two new intermediate states (bonding and antibonding) within the band gap while the unpaired electron occupies the bonding (low energy) state, thus giving the polaron spin of 1/2 [7].



**Figure 2.2** Electronic structures of (a) neutral PPy, (b) polaron in partially doped PPy and (c) bipolaron in fully doped PPy [8].

As oxidation continues further, another electron has to be removed from a PPy chain that already contains a polaron, resulting in the formation of a bipolaron which is energetically preferred to the formation of two polarons. A bipolaron is known to extend over about four pyrrole rings (Fig. 2.3c). The bipolaron states lie further from the band edges (Fig 2.3c). The lower energy state of the bipolaron is empty, thereby leading to a species with zero spin. As the degree of oxidation increases, the bipolaron energy states overlap, resulting in the formation of a narrow intermediate band structure (Fig. 2.4d). The energy diagram shown in Fig 2.4d corresponds to a doped state of about 33 mol%, which is close to the maximum value found in electrochemically oxidized PPy.

The typical doping level of PPy is in the range of 20 to 40 mol%. At this doping level, bipolarons are predominant in PPy with few polarons, and thus the charge carriers in the conducting PPy have zero-spin number.



**Figure 2.3** Electronic energy diagrams for (a) neutral PPy, (b) polaron (c) bipolaron and (d) fully doped PPy [9].

The main disadvantages of PPy are poor thermal stability and poor processability in states of both melt and solution due to the nature of rigidity of its backbone. The rigidity of its chain originates from the presence of strong interchain interactions, which greatly limits the application of PPy in many commercial fields.

The most important research in conducting polymers concerns with the methods for making them processable. The main approaches can be divided into three groups:

- (a) Preparation of composites with other polymers
- (b) Synthesis of soluble derivatives
- (c) Synthesis of dispersions of insoluble conducting polymers

### 2.1.3 Preparation of polypyrrole composites with polymers

In modern conducting composites, the use of only two or more type polymers have been developed. Most of the methods have one insulating polymer acting as a core or smooth plate, and the other as a conductive polymer (such as polypyrrole, polyaniline, etc.), covering the core or insulating plate. The polymer composites, are considered as highly promising new materials for electronic devices, electrical applications, electrochromic displays, polymer batteries, and polymer modified electrodes. The different properties of these composite are necessary.. Changing the polymer composition can improve the disadvantage of each composite. With appropriate composite design, blending one type of conducting polymer with another insulating polymer provide a wide range of the composite applications.

The methods of preparation of polymer-conductive filler systems depend primarily on the type of polymer, its initial form and the properties of the conductive filler. Generally, preparation of polypyrrole and insulating polymer can be chemically prepared by different methods. The most reported routes include :

(1) *Melt mixing*: This is a popular method of composite preparation. This process involves the mixing of different components with a polymer at a temperature beyond the melting point of the polymer. This process is used mainly for thermoplastics, especially in the preparation of conductive or anti-static composites. The disadvantage of the method is the low mechanical strength and high viscosity of the prepared compounds that contain high levels of additives.

(2) *Solution/dispersion mixing*: This method involves the dissolution /dispersion of PPy and a matrix polymer either in the same solvent or in a different solvent, stirring of the mixture and finally drying out of the solvent [10].

(3) *Composite preparation through in situ polymerization*: This method involves either:

(a) Preparation of both PPy and the counterpart of the composite simultaneously in the same medium.

(b) dissolution/dispersion of the counterpart of the composite in a suitable solvent/water and polymerization of pyrrole in that medium [11]

(c) dissolution/dispersion of pyrrole in a suitable solvent/water and preparation of the counterpart of the composite in that medium .

(4) *Composite preparation through electrochemical polymerization:* This method involves the dispersion of the counterpart of the composite either in water or in a solvent containing pyrrole, acid or dopant and potential cycling is then repeated at the working electrode

(5) *Covering of polymeric film or textiles by polypyrrole.* The insulating matrix is immersed in a mixture of oxidizing agent and pyrrole [12].

(6) *Interfacial polymerization.* An insulating polymer separates a monomer solution and a solution of an oxidizing agent. The monomer and the oxidant diffuse across the matrix and the polymerization occurs [13].

(7) *Preparation of blend by swelling of insulating matrices in a solution of an oxidizing agent,* followed by exposure to pyrrole vapors [14-17].

(8) *Preparation of blend by mixing the insulating polymer and oxidizing agent solution,* followed by film casting by solvent evaporation. The matrices containing oxidant are subsequently exposed to monomer vapor [18].

Polypyrrole is the conducting polymer that is most chosen for composite research because of its high electrical conductivity, environmental stability and unique properties, such as biocompatibility, redox-tunable conductivity and easy to synthesis. Combining of polypyrrole with insulating polymer is well known. Different synthetic procedures have been reported. The use of insulating polymer such as polystyrene, poly(vinyl chloride), polypropylene, polyethylene, and poly (methylmethacrylate) to prepare electrical conducting composites was investigated thoroughly. High electrical conductivity of polymer composites, however, has not yet been exhibited and the processability is still difficult. Most of the prepared polymer composites are not good enough for commercial applications. For the above reasons, the improvement of the composite properties is very important. In this study, the introduction of polypyrrole onto



natural rubber has been investigated. Natural rubber abundantly available in Thailand can be prepared as a host polymer.

## 2.2 Natural rubber

Natural rubber is an elastomer (an elastic hydrocarbon polymer) that was originally derived from a milky colloidal suspension, or *latex*, found in the sap of some plants. The purified form of natural rubber is the chemical polyisoprene, which can also be produced synthetically. Natural rubber is used extensively in many applications and products as is synthetic rubber.

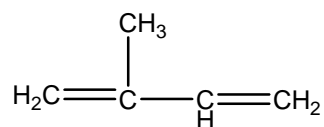
Charles Marie de La Condamine is credited with introducing samples of rubber to the Academie Royale des Sciences of France in 1736. In 1751, he presented a paper by Francois Fresneau to the Academie (eventually published in 1755) which described many of the properties of rubber. This has been referred to as the first scientific paper on rubber.

The para rubber tree initially grew in South America, and the first European to return to Portugal from Brazil with samples of water-repellent rubberized cloth so shocked people that he was brought to court on the charge of witchcraft. When samples of rubber first arrived in England, it was observed by Joseph Priestley, in 1770, that a piece of the material was extremely good for rubbing out pencil marks on paper, hence the name rubber.

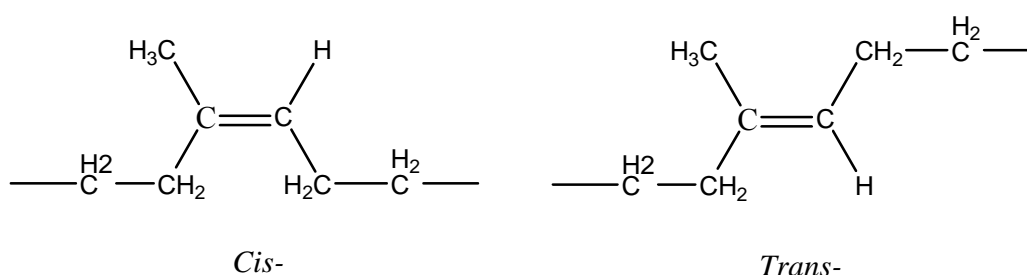
### 2.2.1 The chemical formula of natural rubber

The empirical formula for the natural rubber molecule was first determined by Faraday, reporting his finding in 1826. He concluded that carbon and hydrogen were only elements present and his results corresponding to the formula  $C_5H_8$ . While his result was obtained, using a product which contained associated non-rubbery materials, subsequent studies with highly purified materials have confirmed Faraday's conclusion.

The first isoprene was found to have the formula  $C_5H_8$ , for which Tilden proposed the structure.



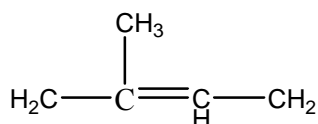
The linear structures proposed by Pickles which provided the possibility of structure isomerism with both *cis*- and *trans*- repeating units.



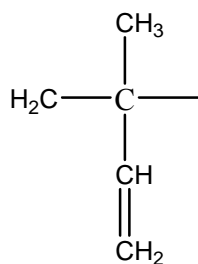
It was known [19] that the major hydrocarbon component of both gutta percha and bakata (at the time important in belting, submarine cable, golf ball and container applications) was a polyisoprene, which when reacted with bromine and ozone gave similar results to those obtained with natural rubber. It was therefore tempting to suggest that one isomer was that of gutta percha and balata and the other was of natural rubber. The earlier work of Staudinger suggested that the *trans*-isomer was nature rubber and gutta percha the *cis*-. However, lasestt studies of X-ray fiber diagrams of stretched rubber led Meyer and Mark to the view that natural rubber was the *cis*-polymer, a view reinforced by Bunn (1942) who ecucidated the structure and unit cell of stretchrd rubber molecule.

The possibility that the natural rubber molecule might contain a mixture of *cis*- and *trans*- groups was considered to be unlikely because such a mixed polymer would have an irregular structure and to be unable to crystallize in the manner of natural rubber. Infrared studies have subsequently confirmed that natural rubber was the *cis*-polymer. Infrared studies have indeed shown that natural rubber was at least 97% *cis*-1,4-iosprene. The absence of measurable amounts of 1,2-structure, but an infrared

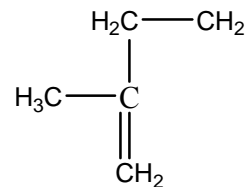
band at  $890\text{ cm}^{-1}$ , was at one time thought to be due possibly to the product of a 3,4-structure[20].



1,4



1,2



3,4

Time-averaging techniques using high resolution NMR which are capable of detecting 3,4-group at concentration of less than 0.3% have however failed to establish the existence of any such moiety and have also failed to show up any trace of trans-material. The conclusion must therefore be that the molecules are more than 99 % cis-1,4-polyisoprene, since all the evidences point out that the natural rubber molecule is not obtained in nature by the polymerization of isoprene. The absence of detectable pendant groups as would be produced by 1,2 and 3,4 addition is hardly surprising[21].

### 2.2.2 Properties of raw natural rubber [22]

Rubber exhibits unique physical and chemical properties. Rubber's stress-strain behavior exhibits the Mullins effect, the Payne effect and is often modeled as hyperelastic. Rubber strain crystallizes. Owing to the presence of a double bond in each and every repeat unit, natural rubber is sensitive to ozone cracking. Natural rubber consists of particles of rubber hydrocarbon and non rubber constituents suspended in an aqueous serum phase. The average dry rubber content of latex may range between 30% and 45%. A typical composition of fresh latex is shown in table 2.1.

**Table 2.1** Typical composition of fresh latex and dry rubber.

<b>Composition</b>	<b>Latex (%)</b>	<b>Dry rubber (%)</b>
Rubber hydrocarbon	36.0	93.7
Protein	1.40	2.20
Carbonhydrates	1.60	0.40
Neutral lipid	0.60	2.40
Glycolipids & Phospholipids	0.50	1.00
Inorganic constituents	0.40	0.20
Other	0.40	0.10
water	58.5	-

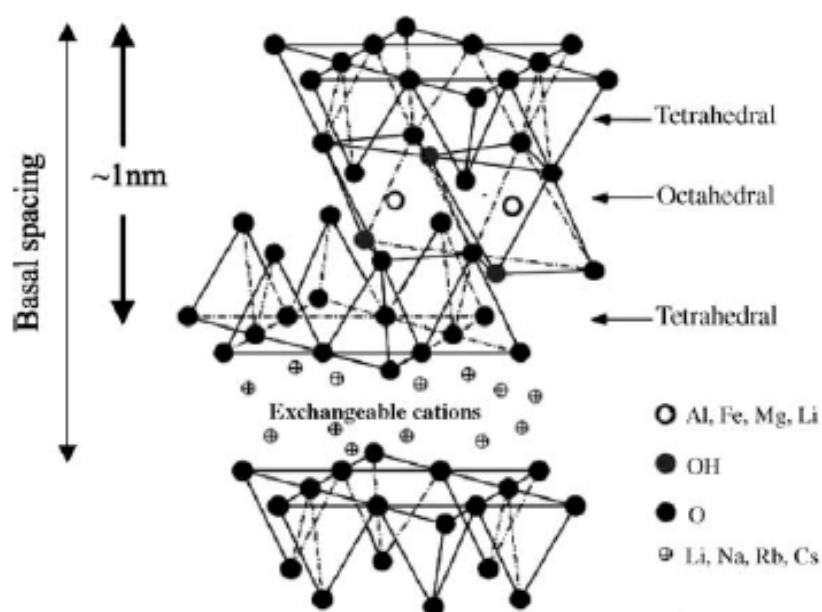
### 2.3 Clay and clay mineral

The polymer/layered silicate nanocomposites (PLSN) have received attention as new ionic conductive materials. The ionic conductivity of nanocomposites has been found to be several orders of magnitude higher than that of the parent silica. As compared with a polymer electrolyte, nanocomposites display enhanced conductivity, mechanical stability and improved interfacial stability towards electrode materials [23]. Due to their high specific area, resulting from their nanometric dispersion. Clay or layer silicate is a nature, earthy, fine-grained material composed largely of a limited group of crystalline minerals, known as the clay minerals. Generally, it can be classified into many types according to differences in its structure and composition. The clay minerals are hydrous silicates, which obtain tetrahedral silicate sheet and octahedral aluminium or magnesium sheet. The clay minerals are classified by used layer type 1:1 or 2:1. Among several types of clays, the smectite is usually used as additive in polymer composite. The layered silicates are the most attractive because it can intercalate the organic molecules.

Smectite is a group of clay minerals which process expandability, taking up water or organic molecules between their structural layers, and also marked cation

exchange properties. The structure can be either dioctahedral or trioctahedral depending on a type of substituted center cationic atom. Dioctahedral means two of octahedrons are filled with trivalent cations such as  $\text{Al}^{3+}$  or  $\text{Fe}^{3+}$ . Trioctahedral means all their octahedrons are filled with divalent  $\text{Mg}^{2+}$  or  $\text{Fe}^{2+}$ .

The smectite clay consists of many layers of octahedral aluminate sheets sandwiched between tetrahedral silicate layers. Illustrated Oxygen atoms reveal the layer edges of tetrahedral sites. in Fig. 2.5.



**Figure 2.4** Structure of 2:1 phyllosilicates

The 2:1 type layers of smectites have various cation substitutions in both the tetrahedral and octahedral positions. Substitutions of ions of the same valence, notably Mg-Fe(II) and Al-Fe(III) substitutions, are common in octahedral position. Coupled substitutions also occur such as  $\text{Fe}^{3+} + \text{O}^{2-}$  replacing  $\text{Fe}^{2+} + (\text{OH})^-$  which is equivalent to a combined oxidation-dehydration process. Anion substitutions, particularly  $\text{F}^-$  for  $(\text{OH})^-$ , are not common in natural smectites but are utilized in synthetic materials.

The isomorphous substitutions within metal oxide with the lower valency species give the silicate layer slightly negative charge, and it is counterbalanced by interlayer cations namely  $\text{Na}^+$  and  $\text{K}^+$ . As the forces that hold the stacks together are relatively weak, the intercalation of small molecules between the layers is easy.

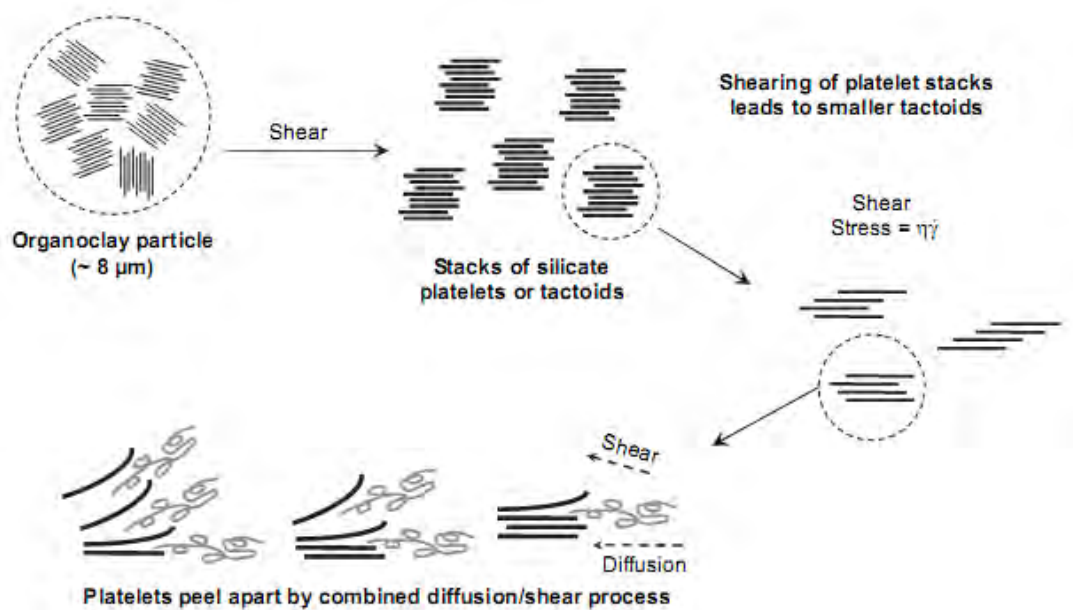
Smectites, belonging to a group of clay minerals (layered aluminosilicates, including two-dimensional phyllosilicates), such as montmorillonite (MMT), hectorite, saponite [24], and mica-type layered silicates, find a wide spectrum of practical applications, primarily by virtue of their well-pronounced intercalation properties.

### 2.3.1 Montmorillonite

Montmorillonite has low thermal expansion coefficient and high gas barrier property. Stacking of this structure leads to regular weak dipolar or Van Der Waals interaction between the layers. Isomorphous substitution in each layer generates negative charges counterbalanced by hydrate sodium or potassium ions residing in the interlayer spacing. In aqueous suspension, cations in interlayer may exchange with ions in the bulk solution, known as exchangeable cations. The total amounts of cation adsorbed into the clay interlayer, expressed in milliequivalents per hundred grams of dry clay, is called the cation exchange capacity (CEC). It is an important characteristic of clay mineral. The cation exchange capacity is high for sodium montmorillonite, comparing it to the other clay minerals.

On a large scale of MMT, each layer can be seen as a high aspect ratio lamella about 100-200 nm in diameter and 1 nm in thickness, (Fig 2.6).

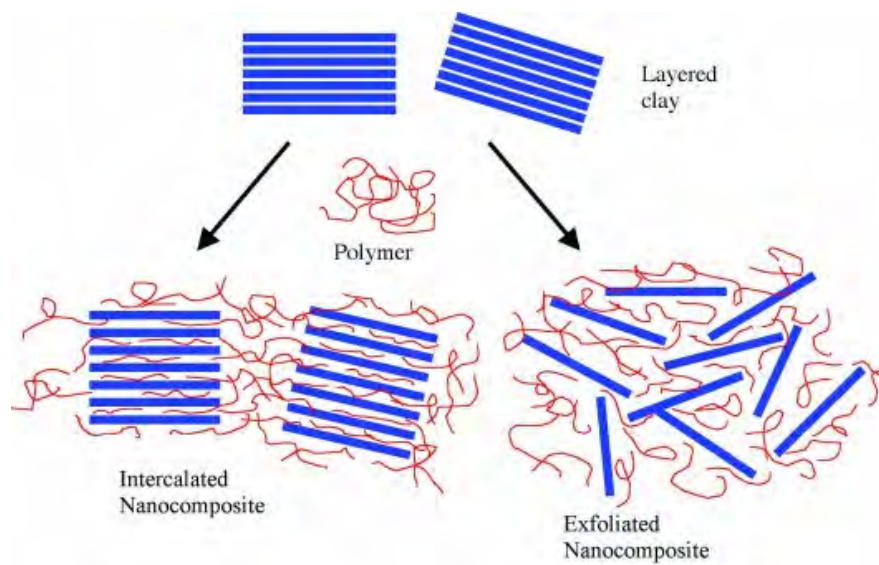
Five to ten lamellar are associated by interlayer ion primary particles (8-10 nm) in the “transverse” direction which, in turn, form larger irregular aggregates (0.1-10  $\mu\text{m}$  in diameter) leading to turbostratic structure of the clay. Due to this special characteristic, MMT can be easily dispersed in water resulting in a stable colloid.



**Figure 2.5** Microstructure of montmorillonite[25]

### 2.3.2 Montmorillonite nanocomposite

Depending on the nature of the components used (layered silicate, organic cation, and polymer matrix) and the method of preparation, two main types of nanocomposites may be obtained when layered clay is associated with a polymer (Fig. 2.7).



**Figure 2.6** The different types of nanocomposite arising from the interaction of layer silicates and polymer[25]:

**(a) Intercalated nanocomposite**

Intercalated structure in which a single (and sometimes more than one) extended polymer chain is intercalated between the silicate layers resulting in a well dormered multilayer morphology built up with alternation of polymeric and inorganic layers.

**(b) Exfoliated nanocomposite**

Exfoliated or delaminated structure is obtained when the silicate layers are completely and uniformly dispersed in a continuous polymer matrix.

## 2.4 Van der pauw method

In order to determine both the relaxation time (mean free path) and the carrier density (Fermi parameters), a combination of a resistivity measurement and a Hall measurement is needed. The van der Pauw technique which, due to its convenience, is widely used in research and industry to determine the resistivity of uniform samples. As originally devised by van der Pauw, one uses an arbitrarily shaped (but simply connected,



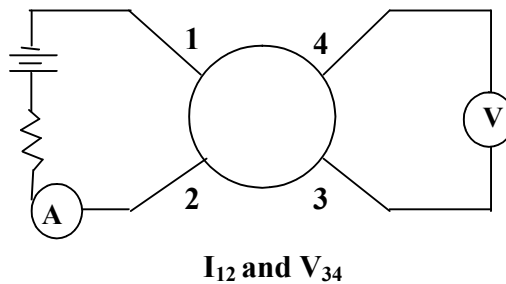
i.e., no holes or nonconducting islands or inclusions), thin-plate sample containing four very small contacts placed on the periphery (preferably in the corners) of the plate.

The objective of the resistivity measurement is to determine the sheet resistance  $R_A$ . Van der Pauw demonstrated that there are actually two characteristic resistances  $R_A$  and  $R_B$ .  $R_A$  and  $R_B$  are related to the sheet resistance  $R_S$  through the van der Pauw equation

$$\text{Exp}(-\pi R_A/R_S) + \text{Exp}(-\pi R_B/R_S) = 1$$

which can be solved numerically for  $R_S$ . The bulk electrical resistivity can be calculated using.  $\rho = R_S d$

To obtain the two characteristic resistances, one applies a dc current  $I$  into contact 1 and out of contact 2 and measures the voltage  $V_{34}$  from contact 4 to contact 3. Next, one applies the current  $I$  into contact 2 and out of contact 3 while measuring the voltage  $V_{12}$  from contact 1 to contact 4.  $R_A$  and  $R_B$  are in Fig 2.8



**Fig 2.8** Conductivity measurement by van der pauw method

$$R_A = V_{43}/I_{12} ; R_B = V_{14}/I_{23}$$

The objective of the Hall measurement in the van der Pauw technique is to determine the sheet carrier density  $n_S$  by measuring the Hall voltage  $V_H$ . The Hall voltage measurement consists of a series of voltage measurements with a constant current  $I$  and a constant magnetic field  $B$  applied perpendicular to the plane of the sample.

## 2.4 Literature survey

The use of polypyrrole in composite form was studied to improve the disadvantageous properties. Difficulty in preparing thick film, and various limited shape led to an increasing the interest of polypyrrole composite. The any methods have been proposed to prepare composites that have sufficiently high conductivity, good mechanical strength and easy processability.

Omastova *et al.* [28] studied the polypyrrole composite of polyethylene (PP). Like other particle composites, PPy was coated on the PP particle.  $FeCl_3$  was used as the dopant of the water-methanol mixture. All compounds were stirred for a few hours. The characterization by elemental analysis, infrared spectroscopy, scanning electrical microscopy (SEM) and thermogravimetric analysis (TGA) were carried out. The conductivity of PP/PPy composites was measured with the values range from  $10^{-10}$  to  $10^{-20} \text{ Scm}^{-1}$ . These values are small compared with that of pure PPy. The suggested were applications in antistatic packaging and electromagnetic radiation shielding.

Meng and Chi [29] prepared PPy composites by synthesis of PPy on the surface of poly(vinyl chloride) (PVC) particles, which have the average size of 0.10  $\mu\text{m}$ . By their method, PVC particles were covered by PPy, The oxidation solution was  $FeCl_3$  in distilled water. The PVC/PPy products were compressed in both hot and cool pressing to give the samples of which the conductivities were measured. The PVC/PPy composite samples had the continuous surface after compression. This raised the conductivity along the surface materials. The optimum electrical conductivity was  $\sim 10^{-1} \text{ Scm}^{-1}$ .

Xie *et al.* [30] synthesized chlorinated polyethylene (CPE)/PPy and natural rubber composites by in-situ oxidative polymerization, using  $FeCl_3$  as an oxidant. The

optimum molar ratio of oxidant/monomer is 2.25 or 2.50 in the temperature range of 0-40 C° for 4-6 hr. They prepared the natural rubber composites with suitable amount of non ionic surfactant as stabilizer before the in-situ polymerization of pyrrole at pH less than 3. The best electrical conductivity of the composites was about 2 Scm<sup>-1</sup>.

Lee *et al.* [31] prepared electrical conducting composite by chemical oxidative polymerization using PPy and polycarbonate (PC) or sulfonated polycarbonate (SPC) in chloroform. The oxidant solution was FeCl<sub>3</sub> in methanol. All compounds were stirred for 1 day at room temperature. The product was compressed in a hot pressing to give the samples the conductivities of which were measured by a standard four-probe method. The electrical conductivity of PPy/SPC composite was higher than that of PPy/PC composite, increased up to 0.82 Scm<sup>-1</sup> with the amount of PPy. The PPy/SPC composites were very stable in the atmosphere.

Bunsomsit and Magaraphan [32] studied polypyrrole composite by preparing PPy-coated natural rubber latex by admicellar polymerization. In this method, pyrrole monomer was adsolubilized on to the surface of latex particles with surfactant. Concentration of the monomer at the interface by partitioning it into an adsorbed surfactant bilayer changes the reaction conditions to be more favorable to the formation of ultrathin film. After the polymerization had finished, excess surfactant was washed away with water to obtain a thin PPy coating over the latex surfaces. The present of a small amount of salt, sodium chloride, substantially improves the surfactant adsorption and PPy adsolubilization. A PPy-coated natural rubber latex prepared in the absence of surfactant exhibited slightly higher conductivity than a PPy-coated natural rubber latex prepared with surfactant with or without salt.

Conductive PPy/polymer composites may be prepared by impregnating the host polymer with a suitable oxidant, followed by the in situ solution or vapor-phase polymerization of pyrrole. Many different oxidizing agents, e.g. nitrous acid, lead dioxide, potassium persulfate, ferric chloride, ferric perchlorate, ferric nitrate, and quinine have been used to promote the oxidative polymerization [33].

Shenoy *et al.* [33] prepared conductive polyurethane (PU) foams by first impregnating a PU foams with ferric trifluoromethane sulfonate (ferric triflate) using supercritical carbon dioxide (scCO<sub>2</sub>) containing 0.2-1.4 vol% ethanol as a cosolvent, and exposing the foam to pyrrole vapor. PPy was formed in situ by chemical oxidative polymerization. The conductivity of the composite foams ranged from 10<sup>-7</sup> to 10<sup>-2</sup> Scm<sup>-1</sup>, depending on the amount of ethanol and impregnation time used.

Sreeja *et al.* [34] studied the composites of PPy and pre-vulcanized NR by dispersion polymerization of PPy precursor within the prevulcanize NR latex. The composite was synthesized in an aqueous solution of the anionic surfactant dodecylbenzene sulfonic acid (DBSA) and used ammonium peroxydisulfate (APS) as oxidant. The uv/vis and fourier transfer infrared (FT-IR) spectra indicate the formation of PPy conjugated segment with in the matrix polymer. The electrical conductivity increased with an increased in PPy content in the matrix polymer. And studied the swelling of NR and mechanical properties such as young's modulus, elongation at break, and modulus which found to be increased of those with increased the PPy content.

The improvement of the electrical conductivity and the processibility of PPy composites have been studied in many reports. An attempt to combine high conductivity or processibility properties with the others is interesting. In this research, with an appropriate condition, it was believed that the improvement of the conductivity of PPy coating composite could be achieved.

# CHAPTER III

## EXPERIMENTAL

### 3.1 Chemicals

1. Pyrrole	FLUKA
2. Anhydrous ferric chloride, FeCl <sub>3</sub>	CARLO ERBA
3. Methanol, CH <sub>3</sub> OH	MERCK
4. Natural rubber latex( 60% DRC)	THAI RUBBER LATEX
5. Montmorillonite	VOLCLAY SIAM
6. Hydrochloric acid, HCl	MERCK
7. Octadecyl amine	FLUKA
8. Dodecyl benzene sulfonate	ALDRICH
9. Nitrogen gas, N <sub>2</sub>	TIG

### 3.2 Instrumentation

#### 3.2.1 Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy

The absorption spectra of nanocomposites were obtained by Attenuated Total Reflectance Fourier Transform Infrared (ATR FT-IR) technique. The frequency range of measurement was 4000 – 400 cm<sup>-1</sup> at a resolution of 4.0 cm<sup>-1</sup> and 128 scans using Nicolet Magnatelluride (MCT) detector. Sample powders were prepared as a KBr

pellet, by grinding a small amount of sample with dried KBr and pressing to 6000 psi in pellet press. The measurement was controlled by the Omnic software.

### **3.2.2 Scanning Electron Microscopy**

Morphology of polymer particles was investigated by scanning electron microscopy. Polypyrrole nanocomposite samples were prepared by first coating with gold in order to discharge electron from the electron beam in the electron microscope. The photographs of polymer samples were then taken.

### **3.2.2 Thermal Gravimetric Analysis**

The combustion stage and the melting point of nanocomposites were investigated by a Mettler Toledo thermogravimetric analyzer. Following the weight loss of 10 mg sample between 50 – 600 °C while the system was purged with nitrogen gas. The heating rate was 10 °C/min.

### **3.2.4 X-ray powder diffraction**

The X-ray diffractometer used in this study is Rigaku D/MAX 2000 ultima<sup>+</sup> with CuK $\alpha$  radiation ( 1.5406 Å). The voltage and the current of the X-ray tube were 40 kV and 30 mA, respectively. The scanning was done by step scanning with step size of 0.02 degree 2 theta.

## **3.3. Electrical conductivity measurement**

The nanocomposites were transformed into a thin disc by pressing under 2000 psi of hydraulic force in evacuable die for 3 minutes. Three samples of each nanocomposite were prepared for electrical conductivity measurement. The thickness of samples were measured by a micrometer. In general a disc sample was measured around 10 points. Then all data were averaged.

The electrical conductivity of each sample was measured by van der pauw method, described in Appendix A. Three samples were measured with the same contact points and the average value of measurements were taken.

Van der Pauw method is the technique for measuring conductivity ( $\sigma$ ) of sample, which has constant thickness but arbitrary shape. First, four ohms contacts are made at the edge of the sample (Figure 3.1). Then applied suitable current ( $I_{12}$ ) through contacts 1 and 2 and measured potential difference ( $V_{34}$ ) between contacts 3 and 4. In this case, the suitable current ( $I_{12}$ ) is assigned to the three values using the resistance 100 K $\Omega$ , 200 K $\Omega$ , and 300 K $\Omega$ , respectively. The obtained data is shown in Table 3.1.

**Table 3.1** Current and potential data measuring as  $I_{12}$  and  $V_{34}$ , respectively

Resistance (K $\Omega$ )	Current (Ampere)	Potential (Volt)
100	$I_{12(1)}$	$V_{34(1)}$
200	$I_{12(2)}$	$V_{34(2)}$
300	$I_{12(3)}$	$V_{34(3)}$

The resistance is obtained by plotting the graph of current and voltage value from Table 3.1. The slope, which is the resistance, is assigned to  $R_1$ . In the other way,  $I_{23}$  is applied through contacts 2 and 3 and potential difference,  $V_{41}$  is measured to obtain the group of the same method, and  $R_2$  is obtained.

$R_1$  and  $R_2$  are taken into the Equation 1 to obtain the electrical conductivity. Equation 1 was used to obtain the electrical conductivity, where  $d$  is the thickness of the sample and  $\sigma$  is the electrical conductivity.

$$\exp(-\Pi d\sigma (V_{32}/I_{14})) + \exp(-\Pi d\sigma (V_{34}/I_{12})) = 1 \quad (1)$$

### 3.4 Purification and preparation of materials

#### 3.4.1 Pyrrole monomer

The pyrrole monomer was distilled at atmospheric pressure as colorless liquid. The distillate was collected in the glass bottle and sealed instantly. The sealed pyrrole bottle was stored at 4 °C and used before 1 week.

#### 3.4.2 Oxidant solution

To obtain 0.35 M oxidant solution of FeCl<sub>3</sub>, Anhydrous ferric chloride 5.3 g was dissolved in 100 ml of deionized water at 0 °C. The precipitates and impurities were filtered of and the clear orange solution was obtained. The oxidant solution was kept at 4 °C and used within 24 hours.

#### 3.4.3 Organically modified montmorillonite

##### (1) Octadecylamine modified montmorillonite

Octadecylamine (3.57 g 14 mmol) and conc. hydrochloric acid (1.45 ml) were mixed into 250 ml of hot water (80 °C). This solution was then poured into the hot clay, made up of 10 g montmorillonite dispersed in 500 ml of hot water (80 °C) with continuous stirring for 50 min to flocculate the clay. The precipitate, thus obtained, was collected on a filter, washed three times with 250 ml of hot water (80 °C), and dried to yield the organoclay.

##### (2) Sodium dodecylbenzene sulfonate modified montmorillonite

10 g of MMT were introduced into 200 ml ( $1 \times 10^{-2}$  M) of NaCl in a flask and stirred for 1h. then, 1 g of sodium dodecylbenzene sulfonate (SDBS) in 50 ml distilled water was added to the flask and continuously stirred for 2 hr. The solid and the aqueous phases were separated by centrifugation (4000 rpm) for 30 min and the solid was dried to yield .



### **3.5 Preparation of natural rubber/polypyrrole composites**

The host polymer (natural rubber latex) was dispersed in 100 ml of water or water/methanol mixture (volume ratio = 1/1) in 500 ml three-neck round bottom flask, equipped with drying tube and gas inlet for bubbling nitrogen gas. Then, SDBS the molar ratio SDBS to pyrrole of 1:5 in water was added to the latex solution. The mixture was continuously stirred for 30 min while the temperature was kept at 0 °C using ice and salt bath. Pyrrole monomer was then added into the mixture and stirred for 15 min before adding 100 ml 0.35 M FeCl<sub>3</sub>. The oxidative polymerization of pyrrole proceeds for 1 hour under stirring then quenched by adding 100 ml of 1:1 methanol/distilled water. The composite was filtered and washed with 1:1 methanol/distilled water until the filtrate was colorless. Then dried at 60 °C in a vacuum oven for 6 hr and kept in a desiccator.

### **3.6 Determination of the parameters affecting the electrical conductivity of the composites**

#### **3.6.1 Amount of pyrrole in the composites**

The natural rubber/polypyrrole composites with the pyrrole content of 5-30 wt% were prepared by chemical oxidative polymerization of pyrrole in the two different solvents, water and water/methanol, to study the effect of the amount of pyrrole on the electrical conductivity of the composites.

#### **3.6.2 Types of solvent**

To study the effect of the solvent on the preparation of polymer composite, 100 ml of water and water/methanol (volume ratio = 1/1) were used in the polymerization of pyrrole.

### **3.6.3 Surfactant**

To study the effect of surfactant on composite, the molar ratio SDBS to pyrrole of 1:5 was added in the preparation of the composite to compared with the composite without surfactant.

## **3.7 Preparation of natural rubber/polypyrrole/montmorillonite nanocomposites**

NR/PPy/MMT nanocomposites with 15 wt% pyrrole were prepared in situ by oxidative polymerization of pyrrole in the presence of water and SDBS. The amount of montmorillonite containing in nanocomposite was varied from 5 to 20 wt %. The NR and MMT were first dispersed in 100 ml of water and then the procedure in section 3.4 was followed for the preparation of NR/PPy composites.

### **3.7.1 Amount of montmorillonite content in nanocomposites**

To study the effect of the MMT content in nanocomposites on the electrical conductivity of the nanocomposite 5 to 20 wt% of MMT were used for the preparation of the NR/PPy /MMT nanocomposites.

### **3.7.2 Organically modified montmorillonite**

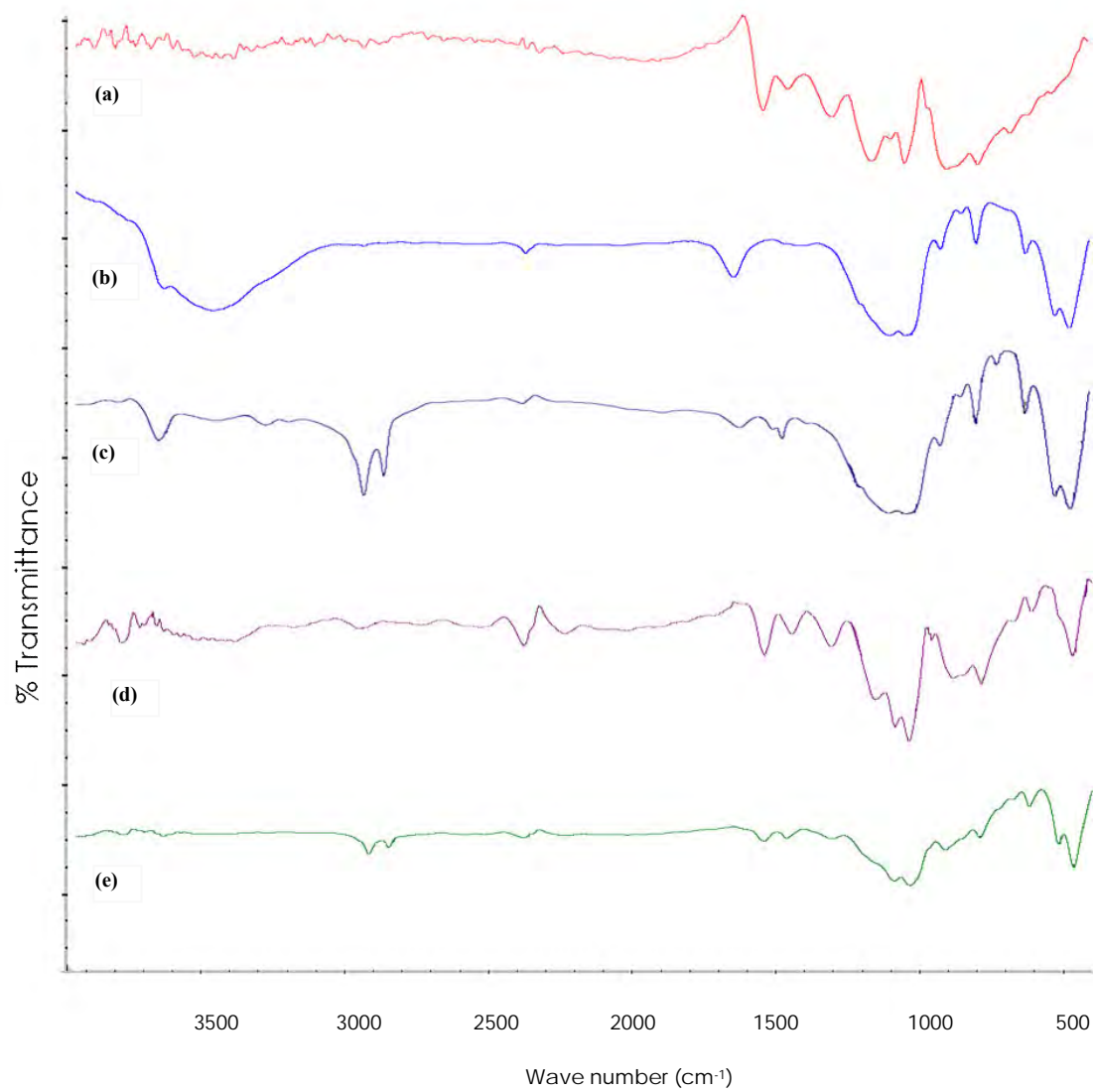
The effect of the types of MMT modifier in the nanocomposites was studied using octadecyl amine (ODA) and sodium dodecylbenzene sulfonate (SDBS), varying the amount of the MMT modifier was varied from 5 to 20 wt %.

## CHAPTER IV

### RESULTS AND DISCUSSION

#### 4.1 Preliminary study on the preparation of natural rubber/polypyrrole/montmorillonite nanocomposites

The natural rubber/polypyrrole/montmorillonite nanocomposites were prepared via chemical oxidative polymerization using  $\text{FeCl}_3$  as the oxidant at  $0\text{ }^\circ\text{C}$ . The resulting black powder materials of NR/PPy/MMT nanocomposite were identified by infrared spectscopy technique. The characteristic FTIR spectra of PPy, MMT, oMMT, NR/PPy/MMT and NR/PPy/oMMT were illustrated in Fig.4.1 The representative vibration bands of PPy (Fig.4.1(a)) were at  $1525\text{ cm}^{-1}$  (2,5 substituted pyrrole),  $1446\text{ cm}^{-1}$  (C-N stretching),  $1050, 1301$  and  $1167\text{ cm}^{-1}$  (C-H stretching of 2,5 substituted pyrrole), The N-H stretching vibration of the pyrrole ring at about  $3400\text{ cm}^{-1}$  was not found. It was reported that its absence was attributed to the masking effect of the charge absorption band, which was also active in this range. The infrared spectrum of the MMT (Fig.4.1(b)) shows three peaks corresponding to Si-O stretchings ( $1037$  and  $1094\text{ cm}^{-1}$ ) and the interlayer water deformation vibrations ( $1644\text{ cm}^{-1}$ ). For oMMT (Fig.4.1(c)), two new peaks at  $2917$  and  $2855\text{ cm}^{-1}$  are due to C-H symmetric and asymmetric stretching vibrations of octadecylamine, respectively. The third band at  $1467\text{ cm}^{-1}$  is assigned to that of the ammonium salt. The spectra of nanocomposites of NR/PPy/MMT shown in Fig.1(d) and NR/PPy/oMMT) in Fig.1 (e) were the combinations of (a) and (b) spectra and (a) and (c) spectra, respectively, These results confirmed that nanocomposites were composed of polypyrrole and montmorillonite.



**Figure. 4.1** The FTIR spectra (a) PPy, (b) MMT, (c) oMMT, (d) NR/PPy/MMT and (e) NR/PPy/oMMT

## 4.2 Parameters affecting the electrical conductivity of the natural rubber/polypyrrole composites

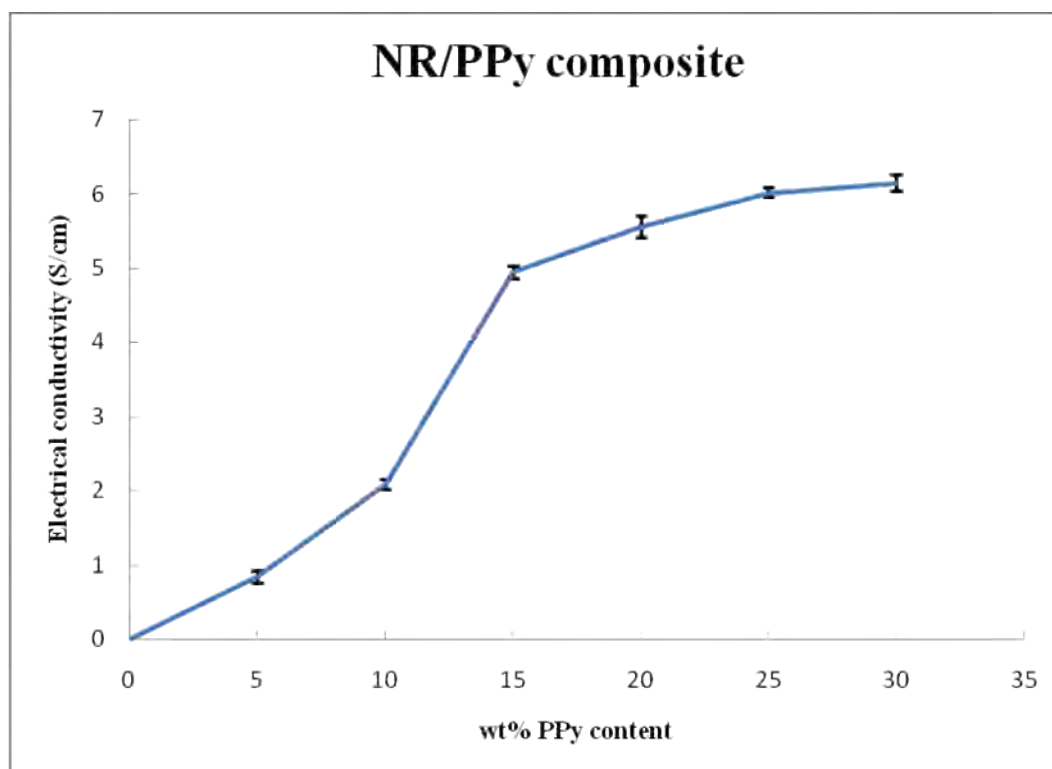
In order to determine the optimal condition for preparing natural rubber/polypyrrole/montmorillonite nanocomposite with high electrical conductivity, various polymerization conditions were studied. The molar ratio of  $\text{FeCl}_3$ /pyrrole was kept constant at 2.5.

### 4.2.1 The effect of the amount of pyrrole in the composites

The composites can be prepared following the method in section 3.5 by varying the amount of pyrrole monomer in the composite. Table 4.1 shows the electrical conductivity of NR/PPy composites and pure PPy. It was found that the electrical conductivity of the composite increased from 0.84 to 6.15  $\text{Scm}^{-1}$  when the amount of PPy in the composite increased from 5 to 30 wt %. Fig. 4.2 is a plot of electrical conductivity vs 5 to 30 wt% of pyrrole in the composite. With PPy loading range of 5-15 wt%, the electrical conductivity of composites increased linearly with PPy content. The reason is that the more pyrrole in the reaction, the more core-shell like material can be the formation of interpenetrating networks when the amount of PPy increased. Charge transport can then occur through the material interference from the underlying electrically insulating natural rubber component. However, in the range of 20-30 wt%, the increasing slope of electrical conductivity with PPy content was found to be much lower, because the NR surface was almost saturated with PPy in that range. The similar results were obtained for polystyrene/polypyrrole and polypropylene/polypyrrole composites studied by Lascelles [34] and Omastova [27]. The NR/PPy composite showed less electrical conductivity than pure polypyrrole due to NR, an insulating material having an electrical conductivity of  $7.18 \times 10^{-15} \text{Scm}^{-1}$ , which could interrupt polypyrrole network. [33].

**Table 4.1** Effect of the amount of polypyrrole on electrical conductivity of natural rubber/polypyrrole composites

% PPy in composite	Electrical conductivity ( $\text{Scm}^{-1}$ )
5	$0.84 \pm 0.08$
10	$2.09 \pm 0.07$
15	$4.95 \pm 0.08$
20	$5.56 \pm 0.14$
25	$6.02 \pm 0.07$
30	$6.15 \pm 0.11$
100	$7.88 \pm 0.12$



**Figure 4.2** The electrical conductivity of natural rubber/polypyrrole composites at different ratio of natural rubber and pyrrole

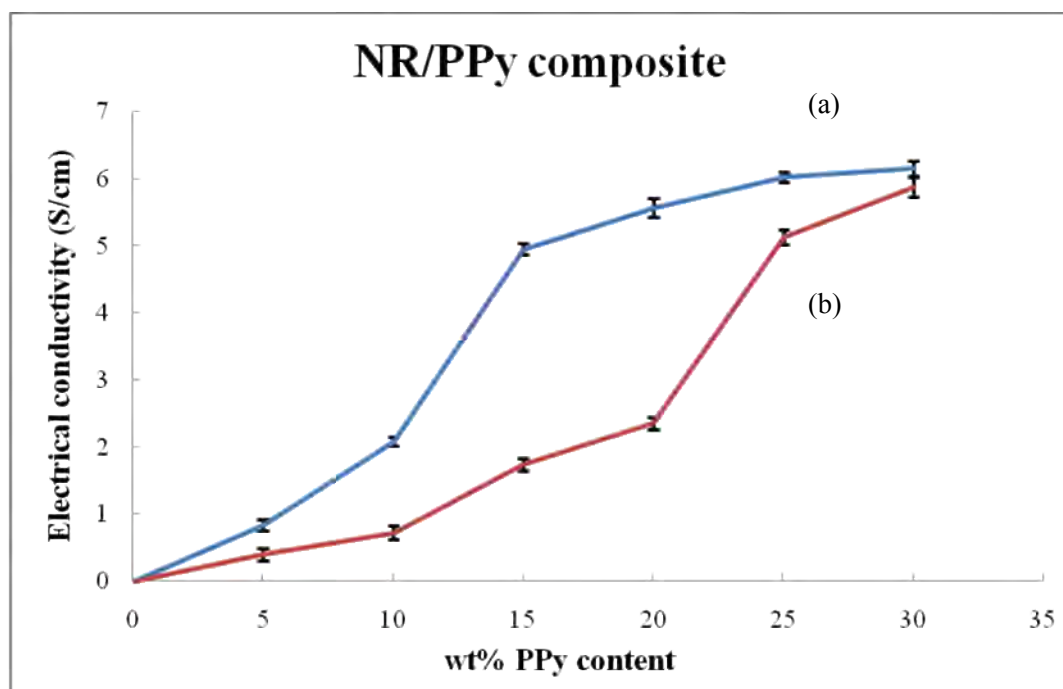
#### 4.2.2 The effect of solvent

For the preparation of NR/PPy composites, 1:1 water/methanol was used as a solvent in stead of water to study the effect on the electrical conductivity of the product. Table 4.2 showed that the electrical conductivity of NR/PPy composites increased with loading amount of PPy in both cases. Using water in the preparation of the composite, the electrical conductivity was higher than that using 1:1 water/methanol. It was observed that, within the same period of time (1 hr.), when water was used as a solvent, the formation of a black thin film was faster than when 1:1 methanol/water was used. In the case of 1:1 water/methanol, the color of solution changed slowly from orange  $\text{FeCl}_3$  color to black PPy color. The orange color of the filterate due to the unreacted  $\text{FeCl}_3$  indicated incomplete polymerization, resulting in less PPy chain in the composite. Fig. 4.3 showed the plot of electrical conductivity of NR/PPy composite vs wt% of PPy in the composite, prepared by using water and 1:1 water/methanol as solvents.

**Table 4.2** Effect of the solvent on electrical conductivity of NR/PPy composites

% PPy in composite	Electrical conductivity ( $\text{Scm}^{-1}$ )	
	Water	Water/methanol
5	$0.84 \pm 0.08$	$0.41 \pm 0.09$
10	$2.09 \pm 0.07$	$0.73 \pm 0.10$
15	$4.95 \pm 0.08$	$1.74 \pm 0.09$
20	$5.56 \pm 0.14$	$2.36 \pm 0.09$
25	$6.02 \pm 0.07$	$5.13 \pm 0.11$
30	$6.15 \pm 0.11$	$5.88 \pm 0.15$





**Figure 4.3** The electrical conductivity of NR/PPy composite using (a) water and (b) 1:1 water/methanol

### 4.2.3 The effect of surfactant

Recent study showed that the addition of the water-soluble polymer during the preparation of PPy could influence the electrical conductivity of the PPy [1 cited in 35]. Kang and coworkers [35] reported that the electrical conductivity of PPy prepared by chemical oxidative polymerization in the presence of SDBS was higher than without. For the preparation of the composite, SDBS was used as a surfactant and a dopant.

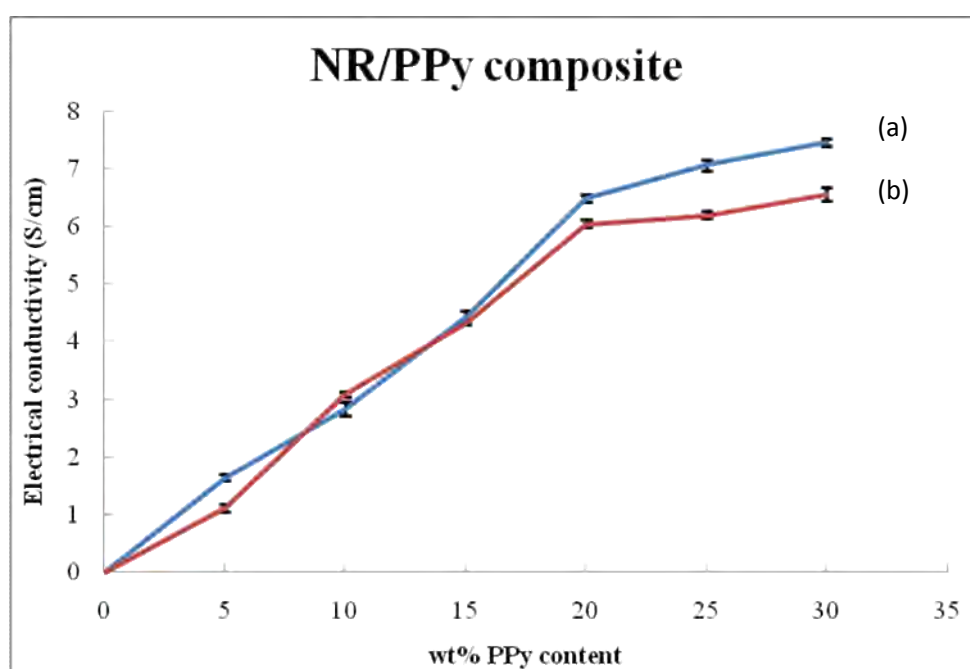
To study the effect of SDBS on electrical conductivity of NR/PPy composite, mole ratio of SDBS:PPy was kept constant at 1:5. Water and 1:1 water/methanol were used as the reaction media for comparison.

According to Table 4.3, the electrical conductivity of NR/PPy composite prepared in the presence of SDBS was found to be higher than without. The SDBS that acting as a surfactant and a dopant for PPy initialized the polymerization process before adding  $\text{FeCl}_3$ . It was expected that SDBS may cause more dissolution of pyrrole in the organic phase and therefore more PPy particles formed in the organic phase, resulting in uniform distribution of PPy in the composite, leading to high electrical conductivity.

**Table 4.3** Effect of the surfactant on electrical conductivity of NR/PPy composites

% PPy in composite	Electrical conductivity ( $\text{Scm}^{-1}$ )	
	water/SDBS	1:1 water/methanol /SDBS
5	$1.65 \pm 0.06$	$1.12 \pm 0.05$
10	$2.84 \pm 0.11$	$3.09 \pm 0.09$
15	$4.44 \pm 0.10$	$4.34 \pm 0.07$
20	$6.49 \pm 0.07$	$6.05 \pm 0.05$
25	$7.06 \pm 0.10$	$6.2 \pm 0.05$
30	$7.16 \pm 0.07$	$6.56 \pm 0.08$

Comparing the results when using 1:1 water/methanol and water for the preparation the of composite in presence of SDBS, it was found that with water as a solvent, the electrical conductivity was higher than when 1:1 water/methanol was used as showed in Fig.4.4. The electrical conductivity of the composite prepared with SDBS a as surfactant and a dopant was higher than without in every case shown in table 4.2.



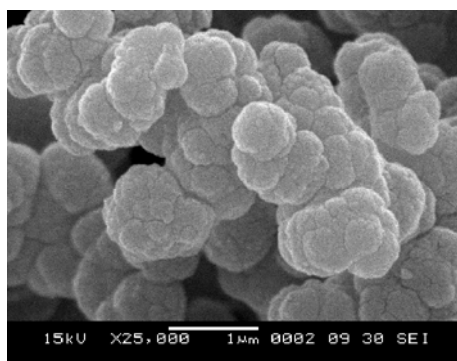
**Figure 4.4** The effect of surfactant on the electrical conductivity of NR/PPy composite  
(a) water/SDBS and (b) 1:1 water/methanol/SDBS

### **4.3 The morphology of natural rubber/polypyrrole composites**

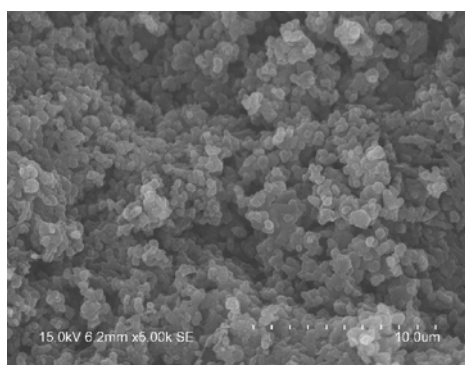
The scanning electron microscopy was employed to investigate the morphology of NR/PPy composites, shown in Figure 4.5.

SEM of PPy (Fig. 4.5(a)) exhibited submicron-sized, bright globular particles. From Fig.4.5 (a), (b), (c), (d), (e), (f), (g), (h), and (i), it was found that for 15 wt% PPy, the dispersion of PPy, resulting in the interchain electron hopping, leading to an increased in the electrical conductivity. The results indicated that more PPy chain on NR confirming that electrical conductivity increased as PPy increased.

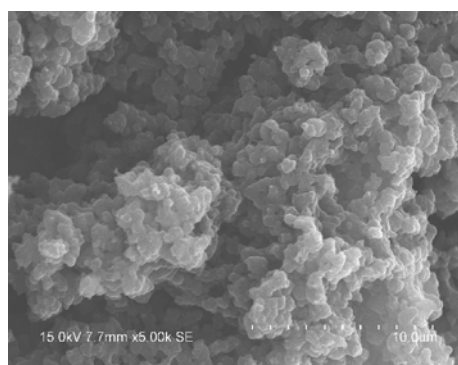
SEM of NR/PPy composite in the presence of SDBS are shown in Fig. 4.5(f), (g), (h), and (i). In the presence of SDBS were found that more PPy diffused on the surface of NR compared to Fig.4.5 (b), (c), (d), and (e) that without SDBS resulting in higher electrical conductivity in composite with using SDBS. It was explained that the SDBS played role as a surfactant to dissolved pyrrole in NR phase and act as a dopant to doped PPy, resulting in more polymerization of PPy in NR/SDBS phase and formation of PPy chain on the surface of NR than without.



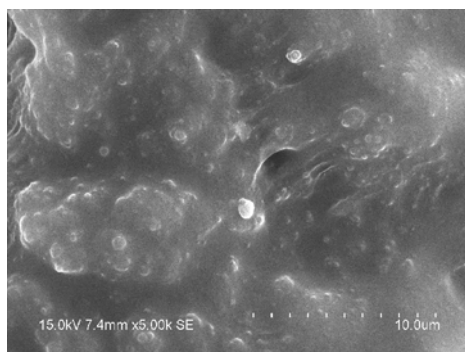
(a) PPy



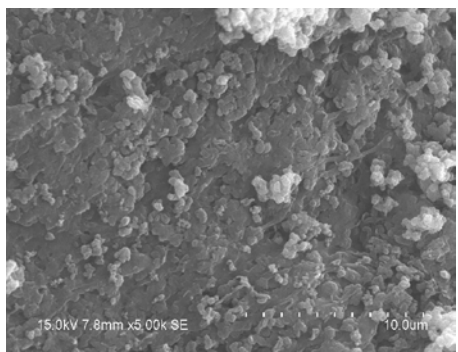
(b) NR/PPy 5wt% in water



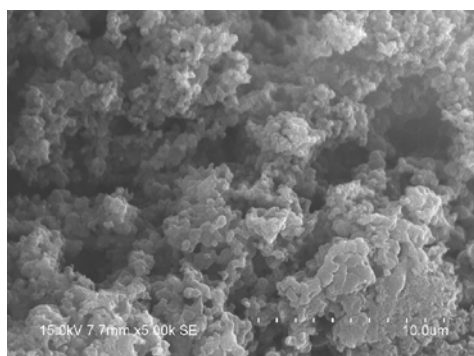
(c) NR/PPy 15wt% in water



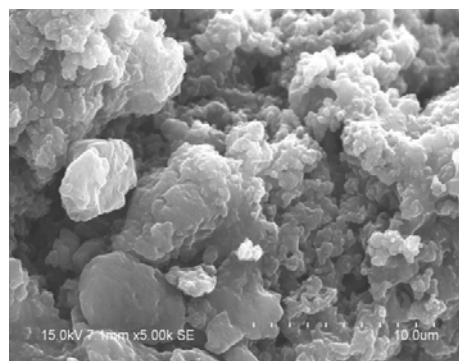
(d) NR/PPy 5wt% in 1:1 water/methanol



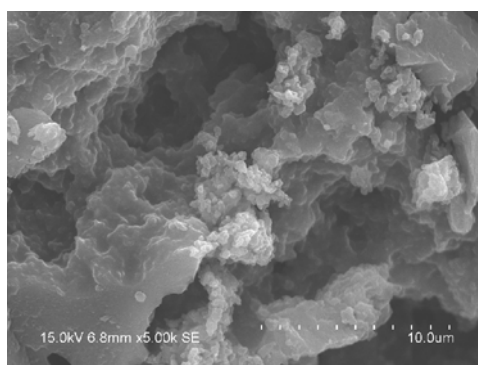
(e) NR/PPy 15wt% in 1:1 water/methanol



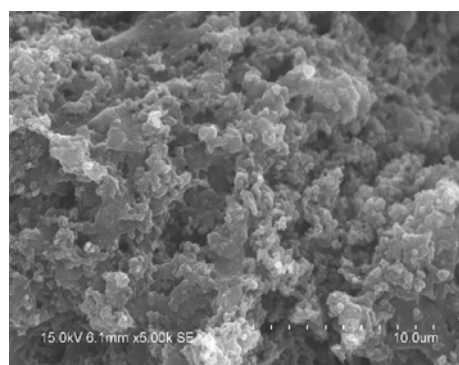
(f) NR/PPy 5wt% in water and SDBS



(g) NR/PPy 15wt% in water and SDBS



(h) NR/PPy 5 wt% in water/methanol and SDBS



(i) NR/PPy 15 wt% in water/methanol and SDBS

**Figure.4.5** SEM micrographs of PPy (a), NR/PPy 5 and 15wt% in 1:1 water/methanol (b) and (c), NR/PPy 5 and 15wt% in water (e) and (f), NR/PPy 5 and 15wt% in water and SDBS (g) and (f), and NR/PPy 5 and 15 wt% in water/methanol and SDBS (h) and (i)

## **4.4 Parameters affecting the electrical conductivity of the natural rubber/polypyrrole/montmorillonite nanocomposites**

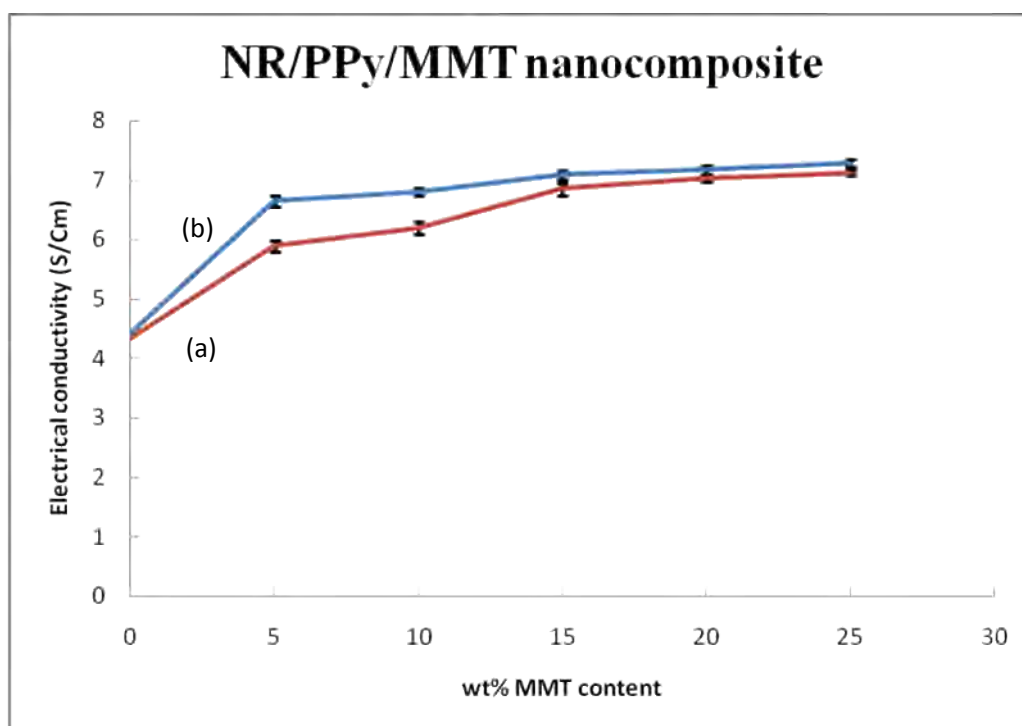
### **4.4.1. The effect of amount of montmorillonite in nanocomposites**

The NR/PPy/MMT nanocomposites exhibit higher electrical conductivity than the composite without MMT. Furthermore, the electrical conductivity of NR/PPy/MMT nanocomposites increased with increasing MMT content. These results conformed with the increasing weight of PPy in the composites. The weight of PPy in the NR/PPy/MMT nanocomposites was found to be significantly higher than the composite without MMT. From Fig. 4.6, it indicated that the electrical conductivity of NR/PPy/MMT nanocomposites depended on the PPy loading. It was also implied that the structure of MMT influenced the electrical conductivity of the composites. The PPy chain was formed in the layers and on the surface of MMT giving the intercalated and exfoliated MMT. It was found that more PPy chain length of increased the electrical conductivity of the composite [34].

From table 4.4, it was found that the electrical conductivity of nanocomposite prepared using SDBS was higher than without. When the amount of MMT increased, the weight of PPy in the composite was higher, indicating that nearly all pyrrole was polymerized to form NR/PPy/MMT nanocomposites.

**Table 4.4** Electrical conductivity of NR/PPy/MMT nanocomposite .

% MMT in nanocomposite	Electrical conductivity ( $\text{Scm}^{-1}$ )	
	water	water/SDBS
5	$6.65 \pm 0.10$	$5.89 \pm 0.10$
10	$6.81 \pm 0.11$	$6.19 \pm 0.06$
15	$7.09 \pm 0.10$	$6.85 \pm 0.07$
20	$7.17 \pm 0.05$	$7.03 \pm 0.08$
25	$7.28 \pm 0.04$	$7.11 \pm 0.06$

**Figure 4.6** The electrical conductivity of NR/PPy/MMT nanocomposite using (a) water and (b) water/SDBS



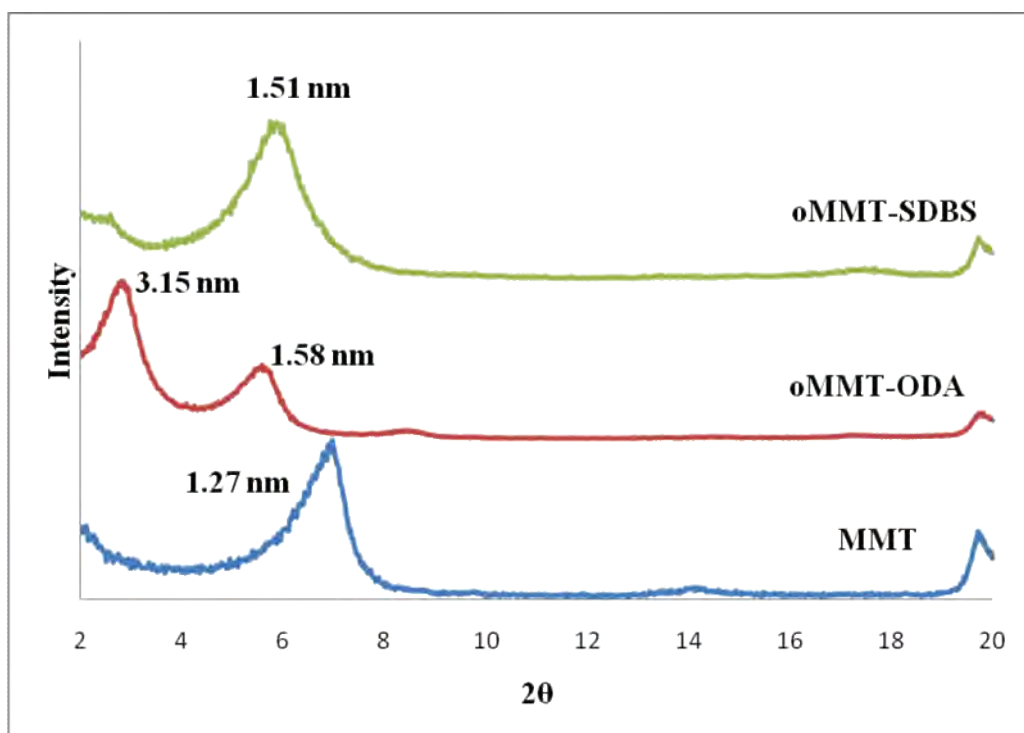
#### 4.4.2 The effect of the types of organically modified montmorillonite

In this study, montmorillonite (MMT) was modified with organic agent to obtain the d-spacing higher than pristine MMT. Using ODA and SDBS as an organically modified agent, the layer and the surface gave the significant increase in electrical conductivity of the nanocomposite as shown in Table 4.5. The electrical conductivity of nanocomposites prepared using ODA was lower than that using SDBS. From Table 4.4 and 4.5 the preparation of the nanocomposites using oMMT gave higher electrical conductivity than that using MMT. Because of the organic modifier, the surface of MMT became more organophilic, resulting in the coverage of long chain PPy on the surface of the nanocomposite. More PPy chains were able to intercalate within the MMT galleries and exfoliate the layers of MMT.

**Table 4.5** Effect of the amount of oMMT on electrical conductivity of NR/PPy/MMT nanocomposites

% MMT in nanocomposite	Electrical conductivity ( $\text{Scm}^{-1}$ )	
	Octadecyl amine	Dodecylbenzene sulfonate
5	$6.70 \pm 0.08$	$6.68 \pm 0.05$
10	$7.05 \pm 0.09$	$7.02 \pm 0.10$
15	$7.13 \pm 0.07$	$7.15 \pm 0.07$
20	$7.24 \pm 0.06$	$7.25 \pm 0.12$
25	$7.32 \pm 0.09$	$7.38 \pm 0.08$

Insertion of the NR and PPy into the layers of MMT was also examined by an XRD, which confirmed that NR and PPy chain was intercalated into the layers of MMT. Fig. 4.7 represents XRD patterns of the MMT, oMMT-ODA, and oMMT-SDBS samples. Shifts in the oMMT spectra to lower angles were found, corresponding to the increase of the interlayer d(001) spacing from 1.27 nm for original MMT to 3.15 and 1.51 nm for oMMT-ODA and oMMT-SDBS, respectively. The variation in d-spacing was estimated by Bragg formula,  $n\lambda=2d\sin\theta$ .



**Figure 4.7** XRD patterns of MMT, oMMT-ODA and oMMT-SDBS samples.

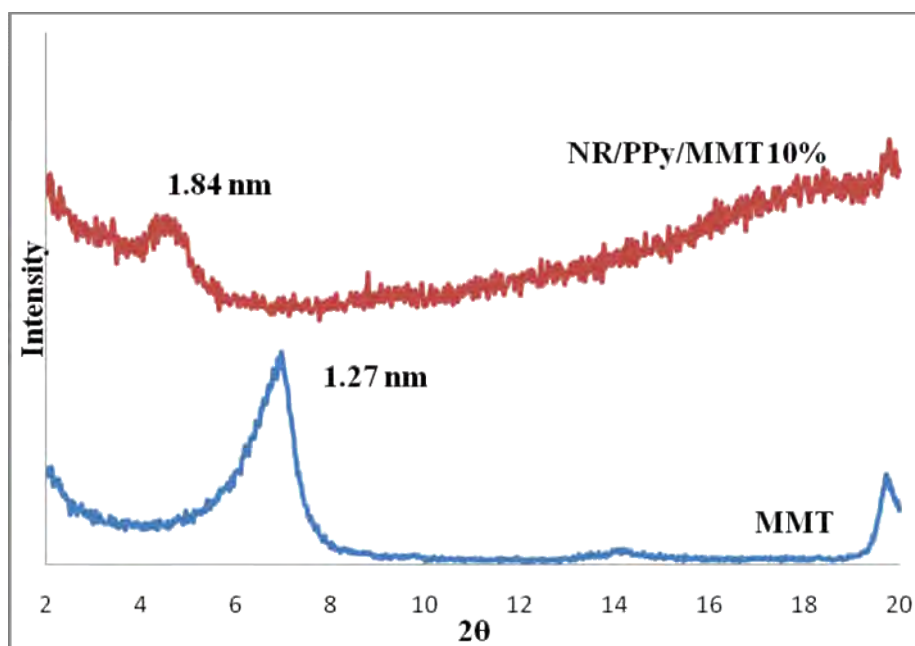
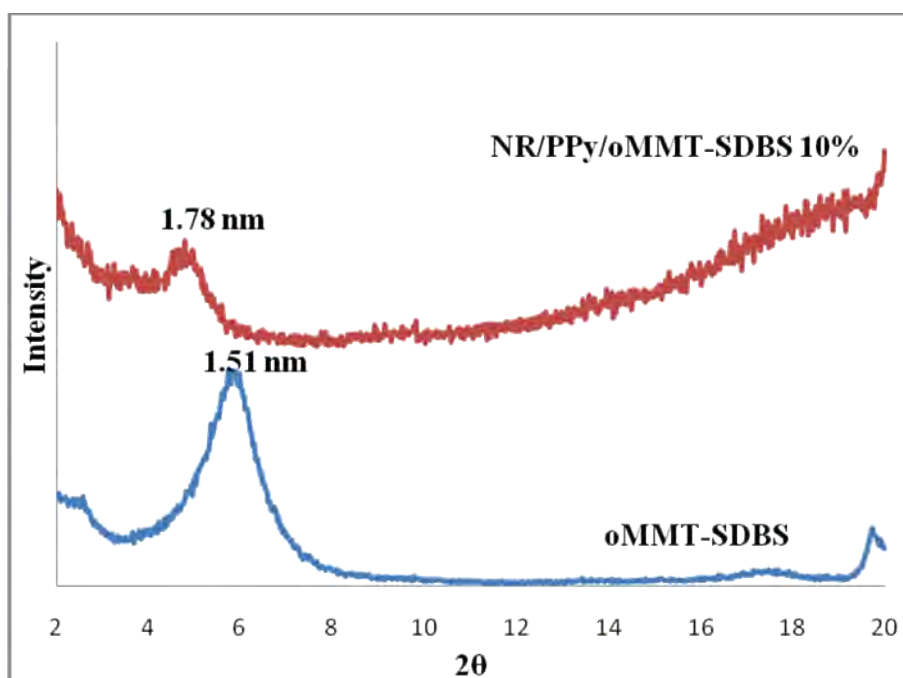


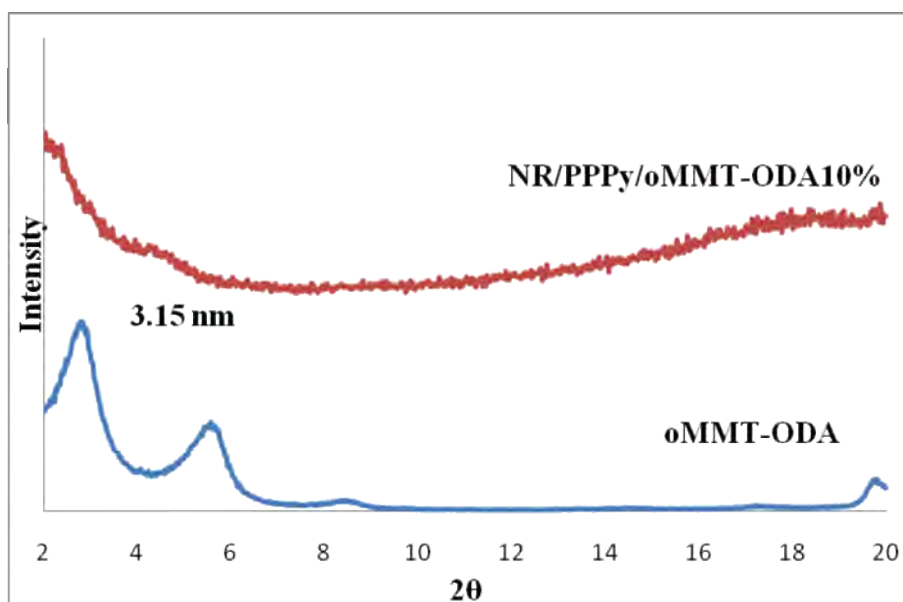
Figure 4.8 XRD patterns of MMT and NR/PPy/MMT nanocomposite .



**Figure 4.9** XRD patterns of oMMT-SDBS and NR/PPy/oMMT-SDBS nanocomposite .

From Fig. 4.8 and 4.9, the d-spacings of MMT and oMMT-SDBS were found to increase when they were in nanocomposites, confirming that PPy intercalates in the silicate layers of MMT and oMMT-SDBS.

With NR/PPy/oMMT-ODA (Fig.4.10), d(001) peak was absent, indicating the intercalation/exfoliation of the silicate layers by PPy.

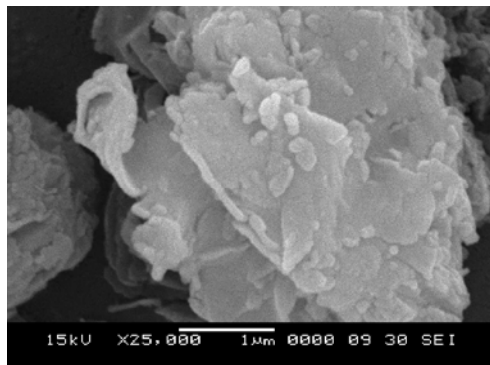


**Figure 4.10** XRD patterns of oMMT-ODA and NR/PPy/oMMT-ODA nanocomposite .

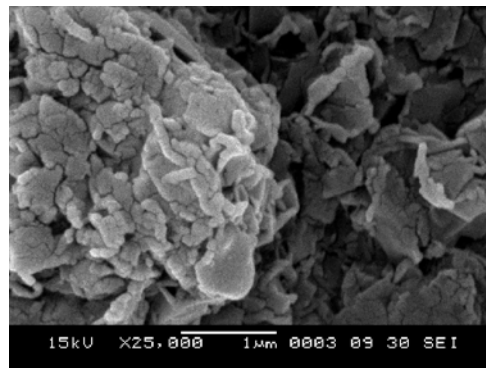
#### **4.5 The morphology of natural rubber/polypyrrole/montmorillonite nanocomposite**

SEM micrographs of original MMT, oMMT-ODA, and oMMT-SDBS are shown in Fig.4.11 (a), (b), and (c), respectively. MMT consists of spherical particles with diameters up to 15  $\mu\text{m}$ . The oMMT-ODA and oMMT-SDBS particles are mixtures of spherical and flat particles with lengths and widths of a few microns. oMMT particles are smaller than MMT particles. The morphology of MMT and NR/PPy/MMT nanocomposite were shown in Figure 4.11 (a) and (d). It could be seen that the surface exhibits bright inclusions that could be assigned to PPy. PPy exhibited submicrometer-sized, bright globular particles on the surface of NR and MMT (Fig.4.11 (d)) and slightly differs from that of the original MMT (Figure 4.11 (a)) because the particles have some rearrangement of the original MMT flakes.

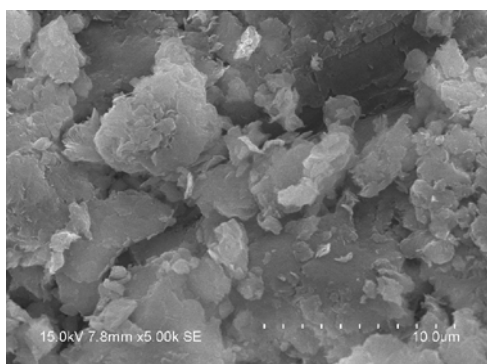
The morphology of NR/PPy/MMT and NR/PPy/oMMT nanocomposites were slightly different from that of the original montmorillonite, which was altered by modification with PPy (Fig. 4.11 (d), (e), and (f)) due to the covering of MMT layers by conducting polymers. The presence of NR and PPy particles caused the rearrangement of the organically modified montmorillonite flakes. Because oMMT is organophilic and more compatible with PPy, the NR/PPy/oMMT nanocomposites appeared to have more bright globular particles of PPy covered on the surface than that obtained from the NR/PPy/MMT nanocomposite.



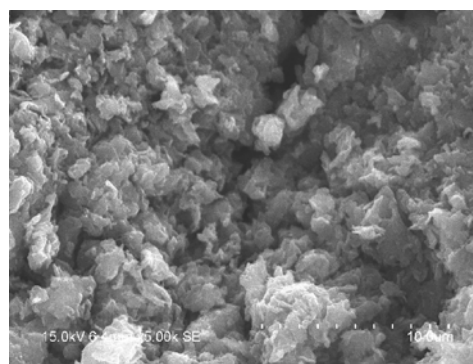
(a) MMT



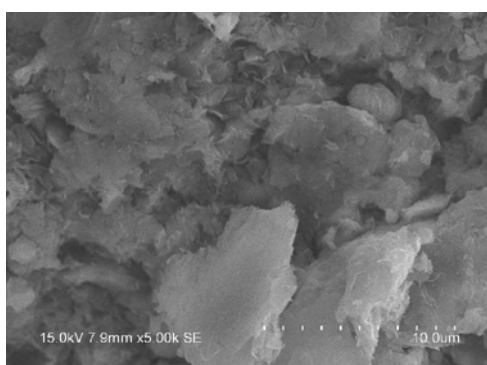
(d) NR/PPy/MMT 15%wt



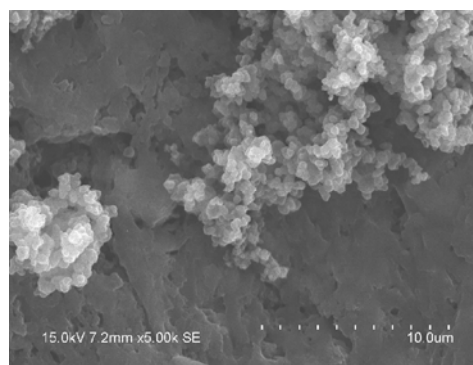
(b) oMMT-ODA



(e) NR/PPy/oMMT-ODA 15%wt



(c) oMMT-SDBS

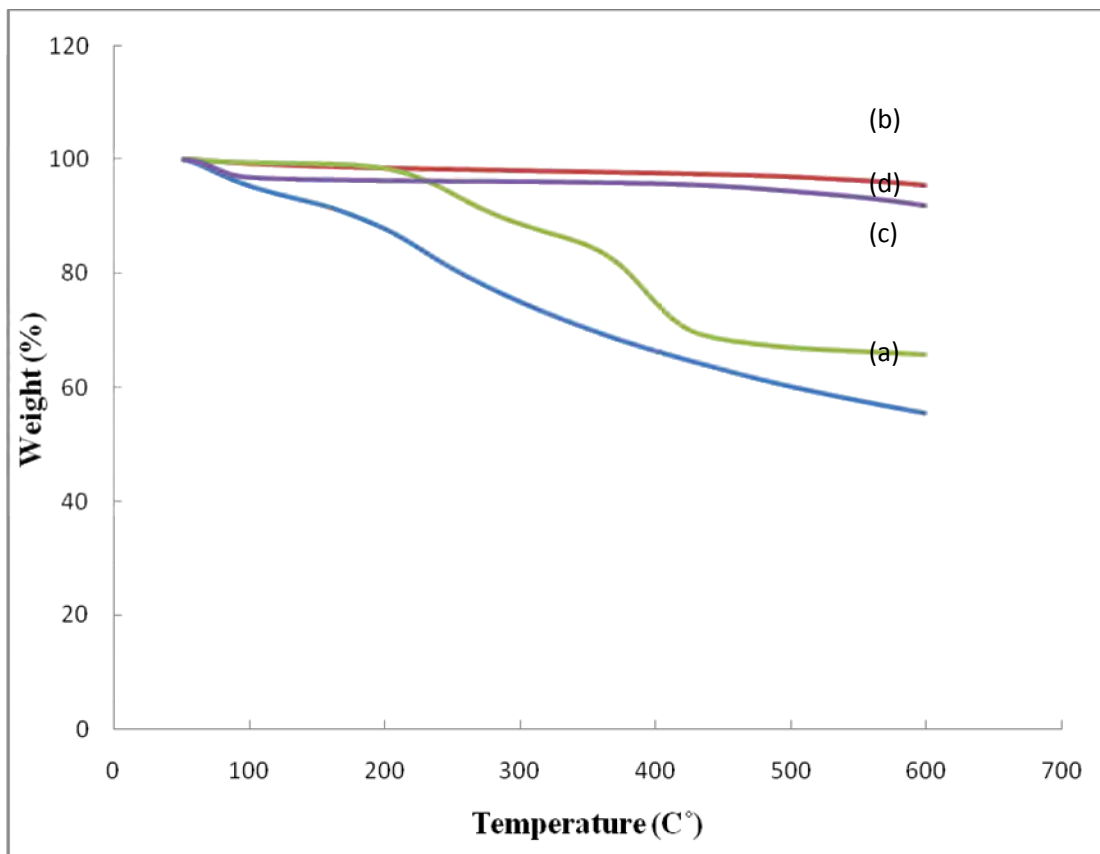


(f) NR/PPy/oMMT-SDBS 15 wt%

**Figure.4.11** SEM micrographs of MMT (a), oMMT-ODA (b), NR/PPy/MMT 15 wt% (c), NR/PPy/oMMT-ODA 15 wt%, and NR/PPy/oMMT-SDBS 15 wt%

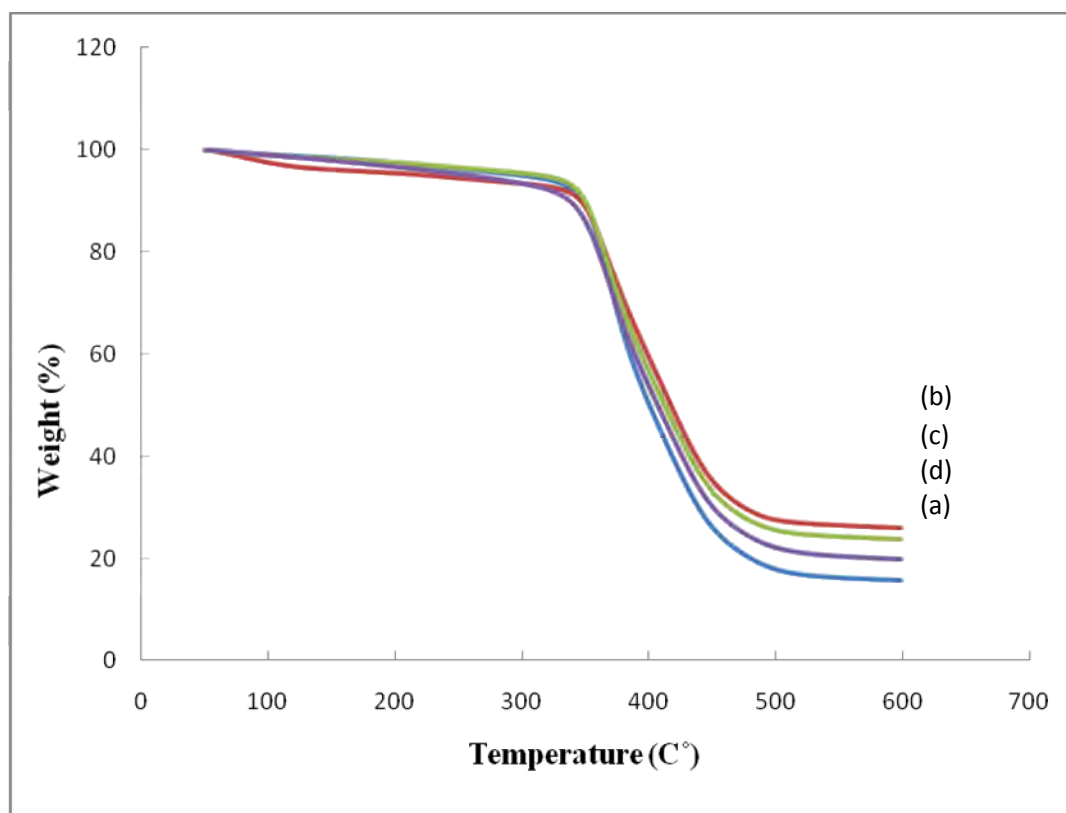
#### **4.4 Thermal stability of natural rubber/polypyrrole/montmorillonite nanocomposites**

Thermogravimetric analysis is capable of measuring changes in weight % of the material as a function of temperature. The result can be used to determine the thermal stability of the composites. The comparison of the degradation behavior by weight % of PPy, NR/PPy composite having 15%wt of pyrrole, and NR/PPy/MMT nanocomposite, having 15%wt of MMT were shown in Figure 4.13(a), 4.14(a), and 4.14 (c), respectively. According to Figure 4.14(a), the NR/PPy composite loses weight slightly at 110 °C, probably due to evaporation of water and the weight loss was more obvious in the range of 350-404 °C. The highest weight loss of 64 wt % occurred at 361 °C. However, the weight loss of NR/PPy/MMT nanocomposite (Fig. 4.14 (b)) followed similar tendency to that of PPy (Fig.4.13(a)) i.e. the slight weight loss was found at 104-270 °C and became more obvious (14 wt%) in the range of 325-450 °C. In the same range, 325-450 °C, the degradation behaviors of all samples were different. PPy kept decomposing while other composites decomposed more slowly than PPy. However, the decomposition rate of NR/PPy/MMT nanocomposite was lower than that of NR/PPy composite. These results demonstrated that NR/PPy/MMT nanocomposites exhibited higher thermal stability than natural NR/PPy composite. This implied that MMT could improve the thermal stability of NR/PPy composite.



**Figure 4.13** The TGA thermograms of PPy (a), MMT (b), oMMT-ODA (c), and oMMT-SDBS (d)





**Figure 4.14** The TGA thermograms of NR/PPy(15 % wt) (a), NR/PPy/MMT (b), NR/PPy/oMMT-ODA (c) and NR/PPy/oMMT-SDBS (d)

## CHAPTER V

### CONCLUSION

#### 5.1 Conclusion

The NR/PPy composites were prepared by chemical oxidative polymerization of pyrrole in natural rubber latex. An electrical conductivity of NR/PPy composite increased with loading PPy. The preparation of nanocomposites using water as solvent gave the conductivity higher than that using 1:1 water/methanol. Addition of SDBS surfactant in the reaction gave higher electrical conductivity of the composite than without. The preparation of NR/PPy composite using water as a solvent and SDBS as surfactant gave the highest electrical conductivity of  $7.16 \text{ Scm}^{-1}$ . Loading MMT in the NR/PPy composite led to an increase in electrical conductivity of the nanocomposite. The use of organic modifier to treat MMT gave higher electrical conductivity of the nanocomposite than without. The electrical conductivity with the addition of SDBS as organic agent was higher than that with ODA. The NR/PPy/MMT nanocomposites prepared with SDBS montmorillonite modifier gave the highest electrical conductivity of  $7.38 \text{ Scm}^{-1}$ . XRD studies showed that d-spacing of MMT increased from 1.26 nm to 1.84 nm and 2.80 nm for NR/PPy/MMT nanocomposite and organically modified MMT, respectively. The NR/PPy, NR/PPy/MMT and NR/PPy/oMMT composites exhibited higher thermal stability than pure PPy.

**Table 5.1** The optimum condition for preparation NR/PPy/MMT nanocomposites

<b>Parameters</b>	<b>Optimum Conditions</b>
Wt % of PPy	15 wt%
Solvent	water
Surfactant (SDBS)	1:5 SDBS/PPy
Organic MMT modifier	10 wt% SDBS

## 5.2 Suggestions for further work

From the observation, with the use of water as solvent, SDBS as surfactant, MMT, and oMMT, the properties of natural rubber can be improved through chemical oxidative polymerization in order to obtain higher electrical conductivity. So that it may be substituted for conductors or semiconductors in a wide varieties of electrical and electronic devices. Potential advantages of conductive or semiconductive polymers lie in their light weight, less brittle, and the ease of manufacturing. Further studies could be carried out in the following aspects;

1. Varying the types of dopant for improving the electrical conductivity of the composite.
2. Varying the the amount of organically modified montmorillonite before polymerization.
3. Try the use of other solvents and surfactants.

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## **APPENDICES**

## APPENDIX A

### Electrical conductivity measurement by Van der Pauw method

Van der Pauw method is the technique for measuring conductivity ( $\sigma$ ) of sample, which has constant thickness but arbitrary shape. First, four ohms contacts are made at the edge of the sample (Figure A-I). Then applied suitable current ( $I_{12}$ ) through contacts 1 and 2 and measured potential difference ( $V_{34}$ ) between contacts 3 and 4. In this case, the suitable current ( $I_{12}$ ) is assigned to the three values by using the resistance 100 K $\Omega$ , 200 K $\Omega$ , and 300 K $\Omega$ , respectively. The obtained data is shown in Table A-I.

**Table A-I** Current and potential data measuring as  $I_{12}$  and  $V_{34}$ , respectively

**V34(3)**

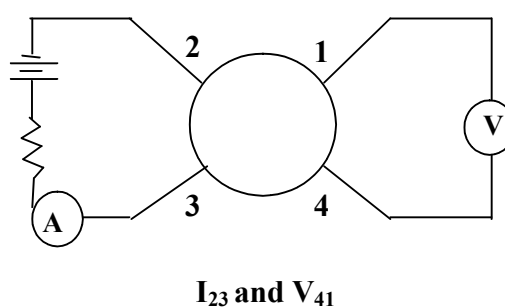
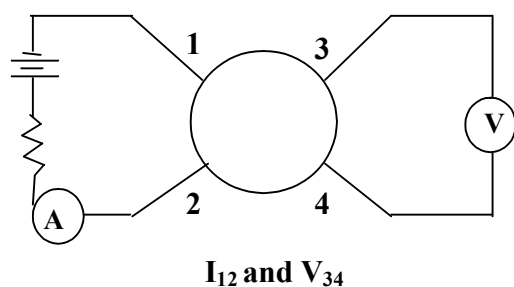
Resistance (K $\Omega$ )	Current (Ampere)	Potential (Volt)
100	$I_{12(1)}$	$V_{34(1)}$
200	$I_{12(2)}$	$V_{34(2)}$
300	$I_{12(3)}$	$V_{34(3)}$

The resistance is obtained by plotting the graph of current and voltage value from Table A- 1. The slope, which is the resistance, is assigned to  $R_1$ . In the other way,  $I_{23}$  is applied through contacts 2 and 3 and potential difference,  $V_{41}$  is measured to obtain the group of the same method, and  $R_2$  is obtained.

Continuously,  $R_1$  and  $R_2$  are taken into the Equation A-I to obtain the electrical conductivity.

$$\text{Exp}^{-\left(\frac{\pi R_1 d}{\sigma}\right)} + \text{Exp}^{-\left(\frac{\pi R_2 d}{\sigma}\right)} = 1 \quad (\text{A -1})$$

Where  $d$  is the thickness of the sample and  $\sigma$  is the electrical conductivity.



**Figure A-1** Conductivity measurement by van der Pauw method

Next, the current electrode is changed around the sample disc, get  $I_{12}$ ,  $I_{23}$ ,  $I_{34}$ ,  $I_{41}$  and corresponding potential difference  $V_{34}$ ,  $V_{41}$ ,  $V_{12}$ ,  $V_{23}$ , respectively. Then calculate  $\sigma_1$ ,  $\sigma_2$ ,  $\sigma_3$ ,  $\sigma_4$  from equation A-1. Finally obtain more accurate conductivity, Equation A-2.

$$\sigma = \frac{(\sigma_1 + \sigma_2 + \sigma_3 + \sigma_4)}{4} \quad (\text{A} - 2)$$

$$\sigma = \text{average conductivity}$$

The main problem in accurate measurement is the contact resistance between the measurement electrodes and the composite sample contact resistance may be reduced by painting electrodes directly on to the surface of the sample. Suitable paints are silver dispersions or Aquadag (an aqueous dispersion of colloidal graphite).

The accuracy of conductivity measurement by van der Pauw method depends on the following condition:

- i) Size of electrical contact points at edge of the sample should be very small compared with the circumference of the sample.
- ii) Sample must have constant density, regular mass and thickness.
- iii) Sample must have no broken.
- iv) In the case of disc sample, separation distance between each contacts should be approximately the same.

### **Calculation of electrical conductivity**

Computer program for calculating conductivity was constructed follow equation A-1 from van der Pauw method by using program "GWbasic" language. The detail of the program is shown below:

Ok

List

```

10 INPUT "SAMPLE THICKNESS = ", D
20 INPUT "Resistance No.1 = ", RI
30 INPUT "Resistance No.2 = ", R2
40 M = 3.141527*D
50 R = RI
60 S = R2
70 A= M*R
80 B = M*S
90 C = (A+B)*0.5
100 X = 0.69314/C
110 I = EXP( -A*X)+EXP( -B*X)
120 IF 1<=0.00001 THEN GOTO 150
130 X = X*I
140 GOTO 110
150 PRINT" Conductivity = ";X

```

Ok

### Example for calculation the electrical conductivity of polymer sample

After the electrical data (V and I) at 4 points of polymer sample were obtained, the slope of the graph plotting between potential and current, R (Resistance), could be obtained by least square fit technique. Then, the resistance values from each sample which have the correct least square fit will be calculated by computer program.

#### Sample

1. Thickness	$d_1 = 0.040$ cm
	$d_2 = 0.042$ cm
	$d_3 = 0.044$ cm
	$d_4 = 0.041$ cm
Average thickness	$d = 0.042$ cm

#### 2. The slope of the graph from V and I data

Group 1  $I_{12}$   $V_{34}$  : 0.79, 0.5; 0.39, 0.3; 0.24, 0.1

Group 2  $I_{23}$   $V_{14}$  : 0.79, 0.8; 0.40, 0.4; 0.25, 0.2

From group 1 we obtained  $R_1 = 0.68$

From group 2 we obtained  $R_2 = 1.09$

#### 3. Calculation program

Run

SAMPLE 1 TICKNESS = 0.042

Resistance No.1 = 0.68

Resistance No.1 = 1.09

Conductivity = 6.050098

Ok

In principle,  $\sigma_1$ ,  $\sigma_2$ ,  $\sigma_3$ ,  $\sigma_4$ , could be calculated by changing the current electrodes around. These values were averaged to obtain the final that was the average conductivity of the sample.

## APPENDIX B

### Electrical conductivity data of natural rubber/polypyrrole composite

**Table B-1** Electrical conductivity data of natural rubber/polypyrrole composites

% Polypyrrole (%wt)	Sample No.	Electrical conductivity (Scm <sup>-1</sup> )					Average
		$\sigma_1$	$\sigma_2$	$\sigma_3$	$\sigma_4$	$\sigma_{ave}$	
100	1	7.93	7.80	7.69	7.97	7.85	7.88
	2	7.95	7.83	7.94	7.65	7.84	
	3	7.87	7.96	8.02	7.94	7.95	
5	1	0.79	0.9	0.88	0.74	0.83	0.84
	2	0.73	0.81	0.87	0.88	0.82	
	3	0.98	0.77	0.84	0.92	0.88	
10	1	2.00	2.04	2.07	2.12	2.06	2.09
	2	2.15	2.16	2.06	2.07	2.11	
	3	2.20	2.20	2.01	2.01	2.11	
15	1	5.01	4.88	4.86	4.87	4.91	4.95
	2	4.93	5.07	4.95	5.06	5.00	
	3	5.06	4.84	4.98	4.89	4.94	
20	1	5.49	5.64	5.67	5.54	5.59	5.56
	2	5.36	5.68	5.75	5.66	5.61	
	3	5.37	5.71	5.41	5.41	5.48	
25	1	6.04	6.09	6.04	5.97	6.04	6.02
	2	6.06	5.97	6.08	5.94	6.01	
	3	6.13	5.99	5.91	6.07	6.03	
30	1	6.12	5.93	6.14	6.35	6.14	6.15
	2	6.23	6.21	6.08	6.24	6.19	
	3	6.13	6.11	6.17	6.09	6.11	

Study in water at 1 hour polymerization time

**Table B-2** Electrical conductivity data of natural rubber/polypyrrole composites

% Polypyrrole (%wt)	Sample No.	Electrical conductivity (Scm <sup>-1</sup> )					Average
		$\sigma_1$	$\sigma_2$	$\sigma_3$	$\sigma_4$	$\sigma_{ave}$	
5	1	0.35	0.51	0.28	0.47	0.41	0.41
	2	0.49	0.33	0.51	0.37	0.41	
	3	0.28	0.49	0.34	0.46	0.42	
10	1	0.89	0.64	0.91	0.69	0.76	0.73
	2	0.65	0.76	0.59	0.77	0.72	
	3	0.73	0.61	0.77	0.69	0.72	
15	1	1.69	1.88	1.62	1.84	1.74	1.74
	2	1.83	1.67	1.77	1.63	1.75	
	3	1.76	1.64	1.81	1.69	1.74	
20	1	2.44	2.24	2.47	2.28	2.36	2.36
	2	2.36	2.48	2.35	2.41	2.36	
	3	2.28	2.37	2.23	2.39	2.37	
25	1	5.08	5.19	5.04	5.18	5.14	5.13
	2	5.13	4.97	5.19	4.9	5.15	
	3	5.17	5.26	5.1	5.29	5.11	
30	1	5.99	5.72	6.03	5.67	5.88	5.88
	2	5.67	5.92	5.74	6.07	5.94	
	3	5.86	6.04	5.84	5.97	5.84	

Study in 1:1 water/methanol at 1 hour polymerization time

**Table B-3** Electrical conductivity data of natural rubber/polypyrrole composites

% Polypyrrole (%wt)	Sample No.	Electrical conductivity (Scm <sup>-1</sup> )					Average
		$\sigma_1$	$\sigma_2$	$\sigma_3$	$\sigma_4$	$\sigma_{ave}$	
5	1	1.12	1.08	1.17	1.19	1.14	1.12
	2	1.16	1.11	1.05	1.13	1.11	
	3	1.09	1.14	1.19	1.04	1.12	
10	1	3.11	2.94	2.97	3.14	3.04	3.09
	2	3.15	3.06	2.96	3.19	3.09	
	3	3.07	3.15	3.13	3.18	3.13	
15	1	4.32	4.28	4.36	4.24	4.30	4.34
	2	4.43	4.39	4.25	4.36	4.36	
	3	4.45	4.37	4.29	4.37	4.37	
20	1	6.04	5.99	6.06	5.97	6.02	6.05
	2	5.96	6.07	6.08	6.04	6.04	
	3	6.07	6.09	6.11	6.13	6.10	
25	1	6.24	6.19	6.24	6.17	6.21	6.2
	2	6.16	6.27	6.18	6.24	6.21	
	3	6.17	6.29	6.14	6.16	6.19	
30	1	6.54	6.49	6.64	6.57	6.56	6.56
	2	6.56	6.67	6.58	6.54	6.59	
	3	6.57	6.49	6.41	6.67	6.54	

Study in 1:1 water/methanol/SDBS at 1 hour polymerization time



**Table B-4** Electrical conductivity data of natural rubber/polypyrrole composites

% Polypyrrole (%wt)	Sample No.	Electrical conductivity (Scm <sup>-1</sup> )					Average
		$\sigma_1$	$\sigma_2$	$\sigma_3$	$\sigma_4$	$\sigma_{ave}$	
5	1	1.72	1.58	1.62	1.64	1.64	1.65
	2	1.63	1.67	1.55	1.58	1.61	
	3	1.66	1.74	1.71	1.74	1.71	
10	1	2.79	2.85	2.88	2.64	2.79	2.84
	2	2.73	2.81	2.77	2.75	2.77	
	3	2.98	2.97	2.94	2.92	2.95	
15	1	4.32	4.53	4.36	4.41	4.41	4.44
	2	4.53	4.39	4.55	4.36	4.46	
	3	4.56	4.49	4.29	4.51	4.46	
20	1	6.44	6.39	6.44	6.47	6.44	6.49
	2	6.56	6.55	6.58	6.44	6.53	
	3	6.57	6.49	6.41	6.59	6.52	
25	1	7.11	7.2	6.96	7.15	7.11	7.06
	2	6.93	7.17	6.89	7.05	7.01	
	3	7.14	7.11	6.98	7.03	7.07	
30	1	7.56	7.42	7.43	7.35	7.44	7.46
	2	7.48	7.47	7.52	7.47	7.49	
	3	7.49	7.59	7.41	7.37	7.47	

Study in water/ SDBS at 1 hour polymerization time

**Table B-5** Electrical conductivity data of natural rubber/polypyrrole/montmorillonite nanocomposites

% MMT (%wt)	Sample No.	Electrical conductivity (Scm <sup>-1</sup> )					Average
		$\sigma_1$	$\sigma_2$	$\sigma_3$	$\sigma_4$	$\sigma_{ave}$	
5	1	6.71	6.57	6.79	6.61	6.67	6.65
	2	6.59	6.82	6.58	6.77	6.69	
	3	6.68	6.53	6.69	6.51	6.60	
10	1	6.83	6.74	6.88	6.69	6.79	6.81
	2	6.95	6.72	6.94	6.69	6.83	
	3	6.68	6.92	6.75	6.89	6.78	
15	1	7.11	7.2	6.96	7.15	7.11	7.09
	2	6.93	7.17	7.02	7.21	7.08	
	3	7.14	7.11	6.98	7.13	7.09	
20	1	7.13	7.19	7.14	7.23	7.17	7.17
	2	7.16	7.27	7.16	7.24	7.21	
	3	7.17	7.11	7.1	7.19	7.14	
25	1	7.29	7.26	7.3	7.23	7.27	7.28
	2	7.32	7.22	7.29	7.26	7.27	
	3	7.31	7.28	7.37	7.27	7.31	

Study in water/SDBS at 1 hour polymerization time

**Table B-6** Electrical conductivity data of natural rubber/polypyrrole/montmorillonite nanocomposites

% MMT (%wt)	Sample No.	Electrical conductivity (S <sub>cm</sub> <sup>-1</sup> )					Average
		$\sigma_1$	$\sigma_2$	$\sigma_3$	$\sigma_4$	$\sigma_{ave}$	
5	1	5.73	5.97	5.79	6.03	5.88	5.89
	2	5.86	5.92	5.81	5.95	5.87	
	3	5.98	5.86	6.01	5.78	5.93	
10	1	6.14	6.26	6.14	6.23	6.19	6.19
	2	6.18	6.27	6.16	6.24	6.21	
	3	6.23	6.11	6.19	6.09	6.16	
15	1	6.83	6.74	6.91	6.78	6.82	6.85
	2	6.95	6.85	6.97	6.87	6.91	
	3	6.86	6.76	6.89	6.8	6.83	
20	1	7.01	7.04	6.96	7.15	7.04	7.03
	2	6.93	7.07	6.89	7.05	6.99	
	3	7.14	7.11	6.98	7.03	7.07	
25	1	7.13	7.09	7.15	7.07	7.11	7.11
	2	7.07	7.15	7.11	7.16	7.12	
	3	7.01	7.18	7.03	7.17	7.10	

Study in 1:1 water/methanol and SDBS at 1 hour polymerization time

**Table B-7** Electrical conductivity data of natural rubber/polypyrrole/organic montmorillonite modifier nanocomposites (ODA)

% MMT (%wt)	Sample No.	Electrical conductivity (Scm <sup>-1</sup> )					Average
		$\sigma_1$	$\sigma_2$	$\sigma_3$	$\sigma_4$	$\sigma_{ave}$	
5	1	6.63	6.84	6.69	6.81	6.74	6.70
	2	6.75	6.61	6.72	6.59	6.67	
	3	6.68	6.76	6.67	6.73	6.71	
10	1	7.01	7.14	6.96	7.15	7.07	7.05
	2	6.93	7.17	6.89	7.05	7.01	
	3	7.09	7.11	6.98	7.13	7.08	
15	1	7.19	7.06	7.25	7.03	7.13	7.13
	2	7.07	7.2	7.11	7.16	7.14	
	3	7.05	7.18	7.09	7.21	7.13	
20	1	7.19	7.29	7.21	7.31	7.25	7.24
	2	7.27	7.12	7.26	7.16	7.20	
	3	7.31	7.28	7.23	7.27	7.27	
25	1	7.22	7.39	7.29	7.41	7.33	7.32
	2	7.47	7.27	7.42	7.23	7.35	
	3	7.21	7.38	7.24	7.33	7.29	

Study in water and SDBS at 1 hour polymerization time

**Table B-8** Electrical conductivity data of natural rubber/polypyrrole/ organic montmorillonite modifier nanocomposites (SDBS)

% MMT (%wt)	Sample No.	Electrical conductivity (Scm <sup>-1</sup> )					Average
		$\sigma_1$	$\sigma_2$	$\sigma_3$	$\sigma_4$	$\sigma_{ave}$	
5	1	6.59	6.69	6.63	6.71	6.66	6.68
	2	6.73	6.61	6.75	6.67	6.69	
	3	6.68	6.76	6.64	6.71	6.70	
10	1	7.08	6.9	7.02	6.92	6.98	7.02
	2	7.01	7.17	7.07	7.19	7.11	
	3	6.94	7.05	6.91	7.03	6.98	
15	1	7.01	7.19	7.06	7.25	7.13	7.15
	2	7.17	7.11	7.22	7.09	7.15	
	3	7.21	7.13	7.23	7.17	7.19	
20	1	7.11	7.29	7.09	7.25	7.19	7.25
	2	7.41	7.19	7.49	7.21	7.33	
	3	7.19	7.31	7.14	7.33	7.24	
25	1	7.28	7.42	7.33	7.46	7.37	7.38
	2	7.38	7.44	7.31	7.49	7.41	
	3	7.4	7.27	7.51	7.32	7.38	

Study in water and SDBS at 1 hour polymerization time

## VITA

Miss Thiyapat Padprom was born on June 19<sup>th</sup>, 1983, in Thailand. She graduated in Bachelor Degree of Science in Chemistry from faculty of Science, Khonkaen University in 2005. Since 2006 she has been graduated student in the Program of Petrochemistry and Polymer Science, Faculty of Science, Chulalongkorn University and graduated in 2009.

Her present address in 343 M.3 Kudsalaos, Kantalaluk, Srisaket, Thailand 11330, Tel 089-627 0709.

A part of this thesis is used to present in International Graduates Congress 2007 (3<sup>rd</sup> MPSGC) on 12<sup>th</sup> – 14<sup>th</sup> December 2007 at University of Malaya, MALAYSIA in the title “Preparation and conductivity of natural rubber/polypyrrole/montmorillonite nanocomposites” and The 10<sup>th</sup> National Graduate Research Conference on 11<sup>st</sup> – 12<sup>nd</sup> September 2008 at Sukhothai Thammathirat Open University, THAILAND in the title “Electrically conductivity of natural rubber / polypyrrole / montmorillonite nanocomposites”