การเตรียมคอมโพสิตของยางธรรมชาติ/พอลิพิโรลโดยพอลิเมอไรเซชันแบบออกซิเดชันทางเคมี

นางสาวรุ่งอรุณ แซ่ลิ้ม

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต
สาขาวิชาปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์
คณะวิทยาศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย
ปีการศึกษา 2548

ISBN 974-14-3274-7

PREPARATION OF NATURAL RUBBER/POLYPYRROLE COMPOSITES BY CHEMICAL OXIDATIVE POLYMERIZATION

Miss Rungaroon Saelim

A Thesis Submitted in Partial Fulfillment of the Requirements for the Degree
of Master of Science Program in Petrochemistry and Polymer Science
Faculty of Science
Chulalongkorn University
Academic year 2005

ISBN 974-14-3274-7

Thesis Title PREPARATION OF NATURAL RUBBER/POLYPYRROLE COMPOSITES BY CHEMICAL OXIDATIVE POLYMERIZATION
By Miss Rungaroon Saelim
Field of Study Petrochemistry and Polymer Science
Thesis Advisor Associate Professor Supawan Tantayanon, Ph.D.

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

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อาจารย์ที่ปรึกษาวิทยานิพนธ์ : รศ.ดร. ศุภวรรณ ตันตยานนท์ ; 91 หน้า. ISBN 974-14-3274-7

การศึกษาครั้งนี้ได้เตรียมยางธรรมชาติ/พอลิพิโรลคอมโพสิต โดยพอลิเมอไรเซชันแบบออกซิเดชันทางเคมีของพิโรลในน้ำยางธรรมชาติ ทำปฏิกิริยาที่อุณหภูมิ 0 องศาเซลเซียส นาน 1 ชั่วโมง โดยใช้สารละลายเฟอริกคลอไรด์เป็นตัวออกซิแดนท์ โดยใช้อัตราส่วนโดยโมลระหว่างตัวออกซิแดนท์และพิโรลคงที่ที่ 2.5 หลังจากหยุดปฏิกิริยา นำคอมโพสิตที่ผ่านการล้างและทำให้แห้งไปชั่งเพื่อหาปริมาณของพอลิพิโรลที่อยู่ในคอมโพสิต วัดค่าการนำไฟฟ้าของคอมโพสิตที่เตรียมได้โดยใช้เครื่องมือโฟร์พร๊อยต์โพรบ ศึกษาปัจจัยต่าง ๆ ที่มีผลต่อค่าการนำไฟฟ้าของคอมโพสิต ได้แก่ ปริมาณและชนิดของน้ำยาง อันดับการเติมพิโรลและเฟอริกคลอไรด์ การเติมสเทบิไรเซอร์และมอนต์มอริลโลไนต์ พบว่าการเติมพิโรลก่อนทำให้คอมโพสิตมีค่าการนำไฟฟ้าสูงกว่าการเติมเฟอริกคลอไรด์ก่อน สภาวะที่เหมาะสมในการเตรียมยางธรรมชาติ/พอลิพิโรลคอมโพสิตคืออัตราส่วนโดยน้ำหนักของเนื้อยางกับพิโรล 0.8 โดยเติมพิโรลก่อนที่จะเติมตัวออกซิแดนท์ ค่าการนำไฟฟ้าของคอมโพสิตจะสูงขึ้น เมื่อใช้ยางธรรมชาติโปรตีนต่ำ แต่เมื่อเติมพอลิเอทิลีนไกลคอลจะทำให้ค่าการนำไฟฟ้าต่ำลง เมื่อมีมอนต์มอริลโลไนต์ คอมโพสิตจะมีค่าการนำไฟฟ้าสูงขึ้นตามปริมาณของมอนต์มอริลโลไนต์ที่เพิ่มขึ้น นอกจากนี้ยังวิเคราะห์สัณฐานวิทยาและเสถียรภาพทางความร้อนของคอมโพสิตอีกด้วย

สาขาวิชา ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์
ปีการศึกษา 2548

ลายมือชื่อ รุ่งอรุณ แซ่ลิ้ม
ลายมือชื่ออาจารย์ที่ปรึกษา
ลายมือชื่ออาจารย์ที่ปรึกษาร่วม

4572453023 : MAJOR PETROCHEMISTRY AND POLYMER SCIENCE
KEY WORD : NATURAL RUBBER / POLYPYRROLE / CONDUCTIVITY / OXIDATIVE POLYMERIZATION / COMPOSITE

RUNGAROON SAELIM : PREPARATION OF NATURAL RUBBER/POLYPYRROLE COMPOSITES BY CHEMICAL OXIDATIVE POLYMERIZATION
THESIS ADVISOR : ASSOC. PROF. SUPAWAN TANTAYANON, Ph.D. 91 pp.
ISBN 974-14-3274-7

In this study, the natural rubber/polypyrrole composites were prepared by the chemical oxidative polymerization of pyrrole in natural rubber latex. The reactions were carried out at 0^{o}C for 1 hour using $FeCl_3$ solution as an oxidant and $FeCl_3$: pyrrole ratio was kept constant at 2.5 by mole. After reaction, the thoroughly washed and dried composites were weighed in order to determine the amount of polypyrrole in the composites. The electrical conductivity of the composites was measured with a home-made four-point probe apparatus. Parameters affecting the electrical conductivity of the composites were studied, i.e. the amount of natural rubber, the types of natural rubber, the addition sequence of pyrrole and ferric chloride, the addition of stabilizer, and the addition of montmorillonite. It was found that pyrrole prior addition gave the composite with higher electrical conductivity than $FeCl_3$ prior addition. The natural rubber/polypyrrole composite at natural rubber to pyrrole ratio of 0.8 (by weight) with pyrrole prior addition was selected to be the most appropriate one. The higher electrical conductivity was obtained when deproteinized protein was used, but the addition of polyethylene glycol gave lower electrical conductivity. In the presence of montmorillonite, the composites exhibited higher electrical conductivity with increasing montmorillonite content. The morphology and thermal stability of the composites were also investigated.

Field of student Petrochemistry and Polymer Science Student's signature Rungaroon Saelim
Academic year 2005 Advisor's signature
Co-advisor's signature

ACKNOWLEDGEMENTS

The author would like to express her sincere thanks to her advisor, Associate Professor Dr.Supawan Tantayanon for their valuable advice and encouragement. She wishes to thank Professor Dr. Pattarapan Prasassarakich, Associate Professor Dr. Nuanphun Chantarasiri, Assistant Professor Dr. Voravee P. Hoven, and Assistant Professor Dr. Warinthorn Chavasiri for their comments and suggestions.

She also likes to thank for the allowance of Chemistry Department for the using of necessary equipment and chemicals. Especially, Assistant Professor Dr. Sanong Ekgasit for the using of ATR FT-IR spectrometer and Associate Professor Dr. Anuvat Sirivat for the using of four-point probe. Thanks to the staffs of Petrochemistry and Polymer Science program for their helpful and suggestion throughout the course of this research.

Grateful acknowledgement is made to the Thai Rubber Latex Corp. (Thailand) PLC. for the support of natural rubber latex and Metallurgy and Materials Science Research Institute for the support of clay. She also thanks all graduate students in her graduated study program, Petrochemistry and Polymer Science, for assistance and good impressiveness from them during study. Great thank goes to her friend, Mr. Sutheerawat Samingprai for everything he have given.

Finally, special gratitude is extended to her family and for their endless love, sympathy, and encouragement.

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LIST OF ABBREVIATIONS

CB : Conduction Band
CPC : Conductive Polymer Composite
$^{\circ}$C : Degree Celsius
DPNR : Deproteinized Natural Rubber
DRC : Dry Rubber Content
eV : Electron Volt
μm : Micrometer
mL : Millimeter
MMT : Montmorillonite
nm : Nanometer
NR : Natural Rubber
PPy : Polypyrrole
SEM : Scanning Electron Microscopy
Scm^{-1} : Siemens per centimeter
TGA : Thermal Gravimetric Analysis
VB : Valence Band

CHAPTER I

INTRODUCTION

1.1 Introduction

Last two decades ago, the conductive polymer composites (CPC) had been widely studied not only their basic knowledge but also their application. Since CPC are prepared by blending the insulating polymer matrix with the conductive filler and their property are very interesting, CPC are used for the intelligent applications such as an electrode for battery, a conductor for electronic device, a capacitor for electrolyte cell, an absorber for sunlight, sensor, and so on [1].

There are several kinds of conductive fillers such as silica, carbon black, metal, and conductive polymer which is a conjugated polymer for instance polyaniline, polythiophene, polypyrrole etc. Especially, polypyrrole (PPy) is very interesting because it resists heat and has high conductivity. However, since pure PPy is brittle, insoluble and infusible, it is hence not processable. To solve this problem, its conductivity and property are improved by producing the polypyrrole composite. For the first trial, CPC was added with the metal particle or pure carbon powder. It was found that its conductivity became higher whereas not only weight of CPC but also cost of the production was higher. To solve the problem, the commodity polymer *i.e.* polypropylene, polyethylene, polyvinyl chloride etc. used as the host polymer (polymer matrix) was coated or mixed with polypyrrole. From this, the properties and processability of CPC were improved.

Natural rubber (*cis*-polyisoprene) can be used as the host polymer because of good flexibility, easily to process, low density, and good chemical resistance. Moreover, it is mostly produced in Thailand. CPC can be applied for the corrosive protector, microwave adsorber, or tire rubber, and so on.

1.2 Objective and scope of research

The purpose of this thesis is to synthesize a highly conducting polypyrrole composite via the chemical oxidative polymerization. Various types of natural rubber are used as host polymers for producing polypyrrole composite. The effects of several parameters such as amount and type of natural rubber, and stabilizer, and the addition sequence of chemicals are investigated. Finally, some instruments like SEM, TGA, ATR FT-IR are used for characterizing the composites.

CHAPTER II

THEORITICAL AND LITERATURE SURVEY

2.1 Conducting Polymer

Electroactive polymers are the materials of increasing scientific and technical interest because of their important high-tech applications on rechargeable batteries, membranes and sensor devices, etc. These conductive materials are usually classified in two large groups, according to the mode of their electric transport:

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

(b) Electronically conducting polymers having conjugated bonds in the macromolecular network, as in polyacetylene (PA), polyaniline (PANI), polypyrrole (PPy), polythiophene (PTh), etc.

2.1.1 Polypyrrole

Polypyrrole is one of the representative conducting polymer. Polypyrrole was firstly synthesized in 1968 [2]. The polymerization of pyrrole was succeeded through α,α'-coupling (2,5-position). The molecular structures of polypyrrole are shown in Figure 2.1.

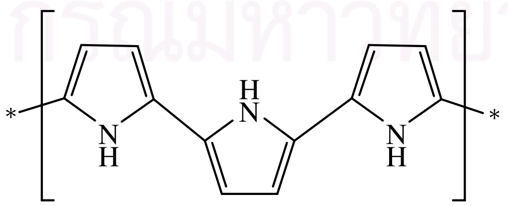


Figure 2.1 The structure of polypyrrole molecule chain

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

In chemical oxidative polymerization, ferric chloride is chosen as an initiator (oxidant). It also acts as the dopant. PPy prepared with this initiator-dopant in the absence of any stabilizer contains about one Cl unit per three-pyrrole unit [3]. The reaction stoichiometry is approximated by Figure 2.2.

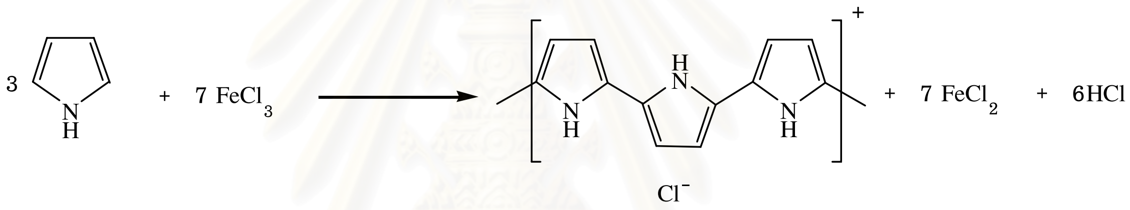


Figure 2.2 Polymerization of pyrrole by using $FeCl_3$ as an oxidant

By this scheme, there are 2.33 moles $FeCl_3$ that is required for the polymerization of one mole of pyrrole. Polymerization in non-aqueous medium requires the use of $FeCl_3$ to pyrrole at mole ratios greater than 2:1 to achieve the highest conductivity. However, in aqueous medium the latter may be obtained using a much lower ratio of $FeCl_3$ to pyrrole, sacrificing the yield, of course.

Polypyrrole is insoluble and infusible and hence difficult to process. The color is black. The electrophysical properties of polypyrrole are determined by the variety of factors such as the degree of polymerization, the nature of dopants and the heteroatom on the molecule. For PPy, the band gap charges from 2.0 eV to 3.2 eV [4], respectively. Furthermore, PPy have two inequivalent structures. Thus, the coupling of electronic excitations to chain distortions leads to polaron and bipolaron as the dominant charged species [5].

2.1.2 Electrical transport of polypyrrole [6]

The electrical transport mechanism in polypyrrole, which has high electrical conductivity, was investigated to understand the band structure on a deformable chain. When polypyrrole was doped by doping oxidant or reductant the polaron and bipolarons are formed. The evolution of the band structure depends on the doping level of dopants. From this, it shows that the formation of polaron and bipolaron are involved the quantity of dopants.

Yakushi and Lauchlan [7] reported the evolution of the optical-adsorption spectrum of polypyrrole as a function of doping level. The concentration of perchlorate anions increases from bottom curve in Figure 2.3.

At low levels of oxidation (lowest curve) there is a strong absorption maximum at 3.2 eV, associates with the interband $\pi \rightarrow \pi^*$ transition. Within the gap region, there are three additional features at 0.7, 1.4, and 2.1 eV. As the level of oxidation increases, the middle 1.4 eV absorption disappears, and the interband transition weakens and shifts to higher energy. In the fully oxidized sample (upper curve), two intense, broad absorption bands are present at 1.0 and 2.7 eV and the interband transition appears as a shoulder at 3.6 eV.

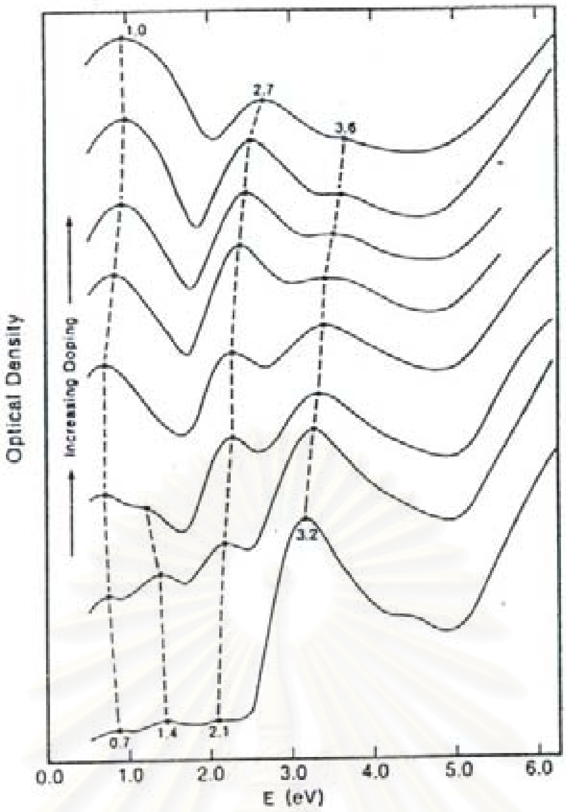


Figure 2.3 Evolution of the optical-absorption spectrum of pyrrole as a function of doping level from bottom curve (almost neutral polypyrrole) to top curve (33 mol% doping level) [6]

In order to interpret these experimental results, they present a theoretical study of the energetics of polaron and bipolaron formation on polypyrrole chains and the band-structure evolution upon oxidation. The result is to demonstrate that the evolution of the absorption spectra upon oxidation can be fully explained in terms of initial polaron formation and then bipolaron formation on the polypyrrole chains. From ESR measurements, the theoretical studies of the absorption spectra indicate that bipolarons are the spinless charge carriers in the highly conducting regime of doped polypyrrole.

The calculation of energetics of polaron and bipolaron formation on polypyrrole chains using tight-binding Huckel theory with σ bond compressability and bond-order-bond length relationships was investigated by Bredas et al. [6] to interprete the experimental results in Figure 2.3. This study using the technique based on a quantum chemical version of adiabatic Su-Schrieffer-Heager Hamiltonian.

The polaron is formed when the increase in π plus σ energy due to the lattice deformation is more than that compensated by a lowering in ionization energy, the difference corresponding to the polaron binding energy. When a single positive charge on the chain, it was obtained the formation of a polaron with a 0.12 eV binding energy, constituting the difference between the 0.49 eV decrease in ionization energy and the 0.37 eV π plus σ energy needed for the change in geometry. The presence of a polaron on the chain introduces two localized electronic levels in the gap: a single occupied bonding polaron state 0.49 eV above the valence band edge an empty antibonding polaron state 0.53 eV below the conduction-band edge (Figure 2.4 (a)). The polaron states in the gap account for the three transitions observed within the gap in very slightly oxidized polypyrrole (lower curve, Figure 2.3). The first absorption peak at 0.7 eV can be related to a transition from the VB to the bonding polaron state. The peak at 1.4 eV is associated with a transition from the bonding to the antibonding polaron state. Finally, the peak at 2.1 eV corresponds to a transition from valence band to the antibonding polaron state. The peak positions indicate that the location of the antibonding polaron state is further away from the conduction band edge than the location of the boding state from the VB edge. This asymmetric location arises because of the different nitrogen orbital contributions to the VB and CB states. The fourth transition, from the bonding polaron state to the CB, should be observed at ~2.5 eV. This energy value unfortunately corresponds to the disorder-broadened edge of the band-gap transition.

As doping level increases, the higher oxidation levels have presented, polaron states start interacting. The two polarons become unstable with respect to the pairing of their spins and the formation of a doubly charged spinless bipolaron in the gap.

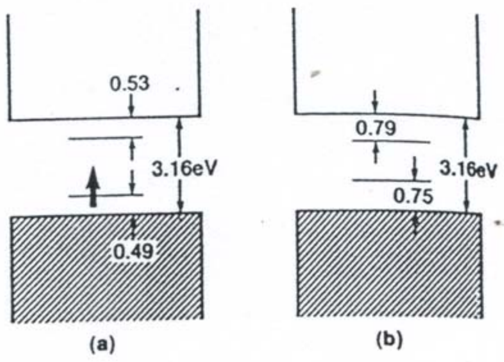


Figure 2.4 Electronic structure diagrams for a polypyrrole chain containing [8]

(a) low doping level, polaron formation

(b) moderate doping level, bipolaron formation

The above picture of polaron recombination to form bipolarons is in full agreement with ESR measurements on polypyrrole chemically doped with oxygen [8] and 0.79 eV below the CB edge (Figure 2.4(b)). Very importantly, the bipolaron bonding state, in contrast to the polaron case, is empty. As a result, only two transitions within the gab are now possible. Thus the emptying of the bonding states in the gap accounts for the loss of the middle 1.4 eV absorption peak when from slightly oxidized polypyrrole.

The band structure of the 33% doping level (highly oxidized) (Figure 2.5) show that the band gap is correctly obtained at 3.56 eV, 0.40 eV larger than in undoped case. The two wide bipolaron bands are present which are calculated to be 0.45 and 0.39 eV, respectively. Furthermore, note that the intensity of lower bipolaron absorption is largest. This is consistent with the oscillator strengths calculated by Fesser, Bishop, and Campbell [9] on the basis of continuum coupled electron-phonon model adapted for nondegenerate ground-state polymers.

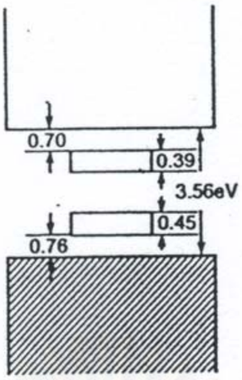


Figure 2.5 Band structure for highly doping level (33 mol%) polypyrrole, showing the presence of two broad bipolaron bands in the gap [9]

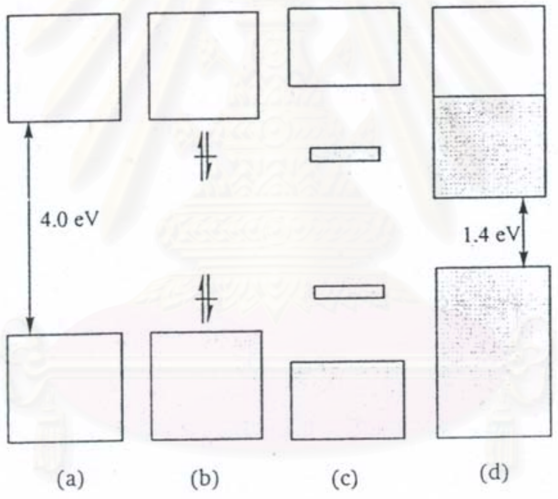


Figure 2.6 The band structure evolution upon (sodium) doping of polypyrrole [9]

(a) undoped

(b) intermediate doping level: non interacting bipolarons present in the chain

(c) per monomer 33% doping level

(d) per monomer 100% doping level

The formation of polaron and bipolaron involving the oxidized doping level is rather complicated beyond understand. The band structures of electrical conductivity in polypyrrole at various doping levels were shown in Figure 2.6.

Picture (a) shows that at undoped polypyrrole the band gap is very wide. At (b) picture, low doping levels, it is expected that polarons (singly charged defects corresponding to radical ions and carrying spin) rather are present on the chain. The recombination among polarons leading to bipolaron formation of bipolaron bands in the gap like in Figure 2.4. If still higher doping level could be achieved, bipolaron bands eventually merge with the CB and VB (Figure 2.6(d)). The band gap energy is low.

Summarized again, theoretical studies on polypyrrole demonstrate that

(1) polarons are formed on the chains at low oxidation level

(2) at higher oxidation levels, polarons combine to form spinless bipolarons

(3) wide bipolaron bands are present in the gap in highly conducting regime

2.2 Polypyrrole composite

Modern conducting composites using polymers only two or more types occurs in this time. Most of the methods have one insulating polymer act as core or smooth plate. The other polymer is the conductive polymer such as polypyrrole, polyaniline, etc., which covers the core or insulating plate. Then, they form the composite. Polymer are considered as highly promising new materials for electronic devices, electrical applications, electrochromic displays, polymer batteries, and polymer modified electrodes, so the different properties of these composite are necessary. In fact, the use of its only one characteristic for various applications is impossible. The changing of polymer composition can improve the disadvantage of each composite. One type of conducting polymer blends with another insulating polymer can use in a wide range of application if the composites designed are appropriated.

Generally, blends of polypyrrole and insulating polymers can be chemically prepared by different methods. The most reported routes include [10]:

(1) Dissolution of the insulating polymer in a solution of an oxidation agent. Stabilized polypyrrole colloidal solutions are obtained by adding pyrrole under stirring [11]. Powder composites are prepared by evaporation of colloidal solutions.

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

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

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

(5) Preparation of blends by mixing the insulating polymer and oxidizing agent solutions, followed by film casting by solvent evaporation. The matrices containing oxidant are subsequently exposed to monomer vapors [18].

Polypyrrole is the most of conducting polymer that is chosen for composite research because its conductivity, air and thermal stability are rather good. Commonly, the combining of polypyrrole with insulating polymer is well known. Different synthesis procedures have been reported. The used of insulating polymer such as polystyrene, poly(vinyl chloride), polypropylene, polyethylene, and poly(methylmethacrylate) [19] to prepare electrical composites was investigated thoroughly. High conductivity of polymer composites, however, has not been exhibited yet. Moreover, the processability is still difficult. Those polymer composites are not good enough for commercial applications. For the above reason, the improvement of composite properties to ease the application for the practical work 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.

2.3 Natural rubber [20-21]

Natural rubber can be isolated from more than a thousand different species of plants, the Para rubber tree (Hevea brasiliensis), is practically the sole source of commercial rubber today. The tree is indigenous to the Amazon valley. Natural rubber has been known to the inhabitants of South America for centuries. Christopher Columbus is considered to be the first European to discover it during his second voyage in 1493-1496, rubber was introduced to the western world by Chareles de la Condamine, who sent samples to France from Peru in 1736 and published the result of his observations in 1745. By the end of the eighteenth century, Europe and America were using a few tons of rubber per year. However, users found it difficult to work with solid rubber. Moreover, articles made from natural rubber turned sticky in hot weather and stiffened in the cold.

Two important developments in the nineteenth century enabled these problems to be solved and laid the foundation for the multibillion-dollar modern rubber industry. In 1820, Thomus Hancock invented a machine called "masticator" that allowed solid rubber to be softened, mixed and shaped. In 1839, Charles Goodyear discovered the process of vulcanization. He found that heating a mixture of rubber and sulfur yielded products that had much better properties than the raw rubber.

The British considered the possibility of cultivating rubber in Asia, the rubber tree arrived in Sri Lanka in 1876 and Malaysia the following year. In 1880 Hevea seeding were widely distributed in Asia. The land used for rubber cultivation and the production of natural rubber has grown steadily as expected since World War II. In 1983, more than 7.5 million metric tons of rubber was produced. The Southeast Asia region accounted for about 82.8% of the total production. Thailand was the biggest producer, followed by Indonesia and Malaysia. The world production of natural rubber is shown in Table 2.1.

Table 2.1 World production of natural rubber (2001-2003)

Production of Natural Rubber						
Country	**2001**		**2002**		**2003**	
	Ton(10^3)	**%**	**Ton(10^3)**	**%**	**Ton(10^3)**	**%**
Thailand	2,319.6	32.3	2,615.1	36.0	2,803.0	37.1
Indonesia	1,607.3	22.4	1,630.0	22.4	1,722.0	22.8
India	631.5	8.8	640.3	8.8	661.0	8.8
Malaysia	547.0	7.6	589.4	8.1	637.0	8.4
China	464.0	6.5	468.0	6.4	471.0	6.2
Vietnam	317.0	4.4	373.0	5.1	385.0	5.1
Ivory Coast	127.9	1.8	120.0	1.7	125.0	1.7
Liberia	107.0	1.5	109.0	1.5	110.0	1.5
Brazil	88.1	1.2	95.9	1.3	96.0	1.3
Sri Lanka	86.2	1.2	90.5	1.2	91.0	1.2
Philippines	69.5	1.0	73.5	1.0	75.0	1.0
Cameroon	60.0	0.8	58.0	0.8	59.0	0.8
Nigeria	50.0	0.7	45.0	0.6	44.5	0.6
Cambodia	46.5	0.6	47.0	0.6	48.0	0.6
Others	668.4	9.3	315.3	4.3	218.5	2.9
Total	7,190.0	100.0	7,270.0	100.0	7,546.0	100.0

Source : IRSG Rubber Statistical Bulletin Vol.58 No. 1, October 2003

2.3.1 Natural Rubber in Thailand [22]

The data from the Industrial Economics & Planning Division, Ministry of Industry showed that in 2003, Thailand produced 2.8 million tons of natural rubber and exported 253,450 metric tons. The remaining 298,699 metric tons was used in the country. Since 1994, Thailand was the biggest producer in world production of natural rubber. The area of Thailand was about 12 million hectares employed for rubber cultivation. In 1995, Thailand produces 1.7 million tons of natural rubber. It is uneconomical to transport preserved field latex over long distances to consumer countries, the normal procedure is to change the latex form before shipment. Therefore, after the natural rubber latex has been collected from the field, it is changed into many forms of rubber, which are showed in Table 2.2.

Table 2.2 The different types of rubber in Thailand 2003.

Types of Rubber	metric tons	%wt
Smoked sheet	1,236,683	43.0
Block rubber	1,035,358	36.0
Crepe rubber	8,627	0.3
Concentrated latex	488,922	17.0
Other rubber	106,415	3.7
total	**2,876,005**	**100**

Source : Southern Industrial Economics Center in Thailand

For Natural rubber latex was 60% dry rubber content by concentration method. In 2003, it expected 488,922 tons and the remaining 79,929 tons was used the country. By it exported to USA, Taiwan, German and Singapore.

2.3.2 Properties of Raw Natural rubber [22]

Natural rubber latex, produced by the tree Hevea brasiliensis, 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 2.3.

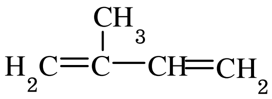
Table 2.3 Typical composition of fresh latex and dry rubber.

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

2.3.3 The Chemical Formula of Natural Rubber [23-24]

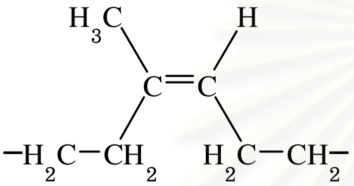
The empirical formula for the natural rubber molecule appears to have been first determine by Faraday who reported his finding in 1826. He concluded that carbon and hydrogen were the only elements present and his results correspond to the formula C_5H_8. While this result was obtained, using a product 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.

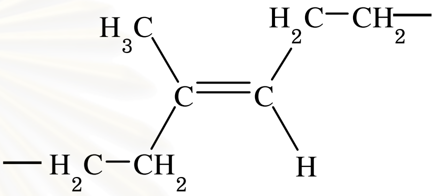


$$H_2C{=}\overset{\overset{\displaystyle CH_3}{|}}{C}{-}CH{=}CH_2$$

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



Cis-

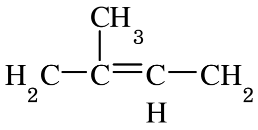


Trans-

It was known that this is the major hydrocarbon component of both gutta percha and balata (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 that of natural rubber. The earlier work of Staudinger suggested that the trans-isomer was natural rubber and gutta percha the cis-. However later 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) which elucidated the structure and unit cell of crystalline stretched rubber molecule.

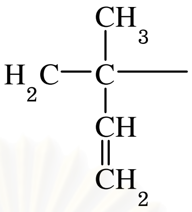
The possibility that the natural rubber molecule might contain a mixture of cis- and trans- groups was considered to be unlikely because such a mixed polymer would have an irregular structure and be unable to crystallize in the manner of natural rubber. Infrared studies have subsequently confirmed that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

cis-1,4-polyisoprene. The absence of measurable amounts of 1,2-structure but an infrared band at 890 cm^{-1} was at one time thought to be due possible to the products of a 3,4-structure.



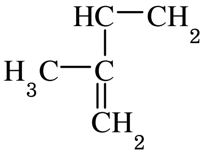
$H_2C-C(CH_3)=CH-CH_2$

1,4-



$H_2C-C(CH_3)(CH=CH_2)-$

1,2-



$H_3C-C(=CH_2)-HC-CH_2$

3,4-

Time-averaging techniques using high resolution NMR which are capable of detecting 3,4-groups at concentrations 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 molecule are more than 99% cis-1,4-polyisoprene. Since all the evidence points to the conclusion 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.

2.4 Clay and Clay Mineral

Clays have been widely used in the last decade to design nanocomposite with increased mechanical, thermal, fireproofing and barrier properties due to their high specific area resulting from their nanometric dispersion [25]. Clay or layered silicate is a natural, 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 contain tetrahedral silicate sheet and octahedral aluminum or magnesium sheet. The clay minerals were 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 organic molecule.

Smectites are 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 upon a type of substituted center cationic atom. Dioctahedral means two of octahedrons are filled with trivalent cation such as Al^{3+} or Fe^{3+}. Trioctahedral means all their octahedrons were filled with divalent Mg^{2+} or Fe^{2+}.

The smectite clay minerals consist of many layers of octahedral aluminates sheets sandwiched between tetrahedral silicate layers. Oxygen atoms reveal the layer edge of tetrahedral site. Illustration in Figure 2.7 is structure of smectite clay.

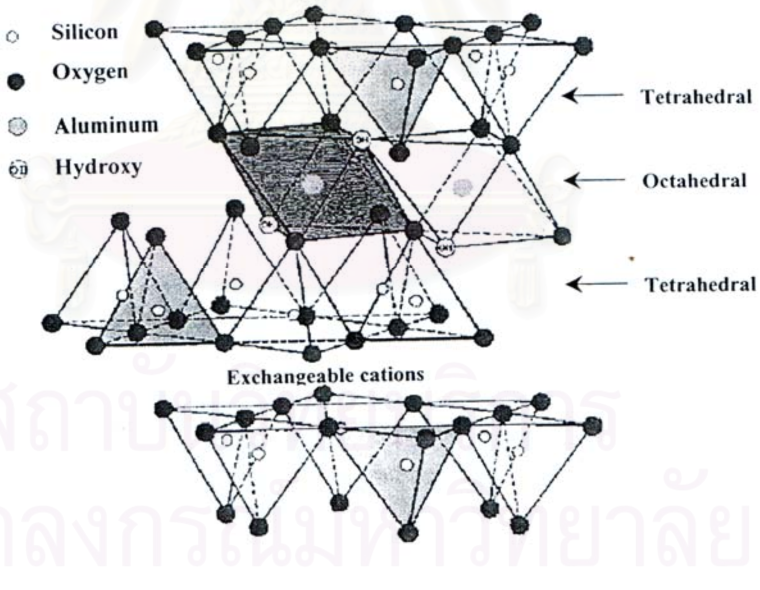


Figure 2.7 Structure of 2:1 phyllosilicates [25]

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

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

Montmorillonite (MMT) is classified smectite group normally applied to polymer nanocomposites because of its have suitable layer charge density.

2.4.1 Montmorillonite

MMT has a low thermal expansion coefficient and a high gas barrier property. Stacking of this structure leads to a regular weak dipolar or Van der Waals interaction between the layers. Isomorphic substitution in each layer generates negative charges that are counterbalanced by hydrated sodium or potassium ions residing in the interlayer spacing. In aqueous suspension, cations in interlayer may exchange with ions in the bulk solution. They are known as exchangeable cations. The total amount of cations adsorbed in the clay interlayer, expressed in miliequivalents per hundred grams of dry clay, is called the cation exchange capacity (CPC). 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 (Figure2.8).

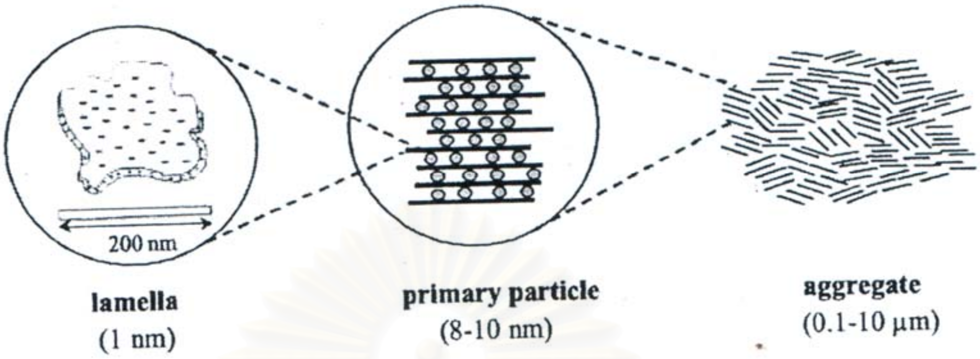


Figure 2.8 Microstructure of montmorillonite [25]

Five to ten lamellae are associated by interlayer ions in primary particles (8-10 nm) in the "transverse" direction which, in turn, form larger irregular aggregates (0.1-10 μm in diameter) giving to the clay its turbostatic structure. Due to this special characteristic, MMT can be easily dispersed in water resulting in a stable colloid.

2.4.2 The structure of the composite

Depending on the nature of the components used (layered silicate, organic cation and polymer matrix) and the method of preparation, three main types of composite may be obtained when layered clay is associated with a polymer (Figure 2.9).

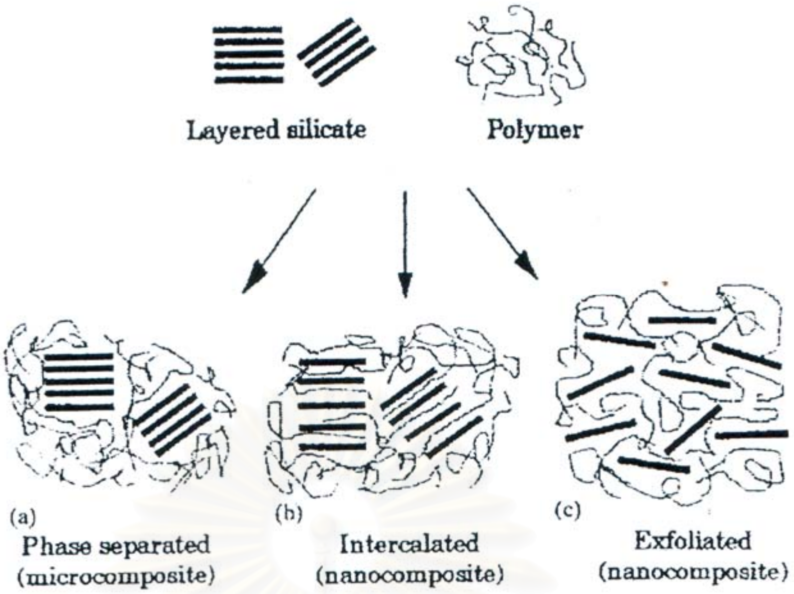


Figure 2.9 The different types of composite arising from the interaction of layered silicates and polymer [25] :

(a) phase separated microcomposite;
(b) intercalated nanocomposite and
(c) exfoliated nanocomposite.

(a) Phase separated microcomposite

In the phase separated microcomposite, the clay acts as conventional filler. When the polymer is unable to intercalate between the silicate sheets, the properties stay in the same range as traditional microcomposites.

(b) Intercalated nanocomposite

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

(c) Exfoliated nanocomposite

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

2.5 Literature survey

The use of polypyrrole in composite forms was studied to improve the advantageous properties. Difficulty in preparing thick film, limited shape led to increases the interesting of polypyrrole composite. Therefore, many methods have been proposed to prepare composites that have sufficiently high conductivities, good mechanical strength and allow easy processability.

Omastova et al. [27] studied the polypyrrole composite of polypropylene (PP). Like another particle composite, 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. In this report, the characterization of elemental analysis, infrared spectroscopy, scanning electrical microscopy (SEM) and thermogravimetric analysis (TGA) were investigated. Additionally, the conductivity of PP/PPy composites was measured to give the ranged value of 10^{-10} to 10^{-20} Scm^{-1}. This value is small compared with that of pure PPy. The report has suggested the applications in antistatic packaging and electromagnetic radiation shielding.

Meng and Chi [28] prepared PPy composites by synthesis of PPy on the surface of poly(vinyl chloride) (PVC) particles, which have the average size 0.10 nm. By this method, PVC particle was covered by PPy (Figure 2.10)

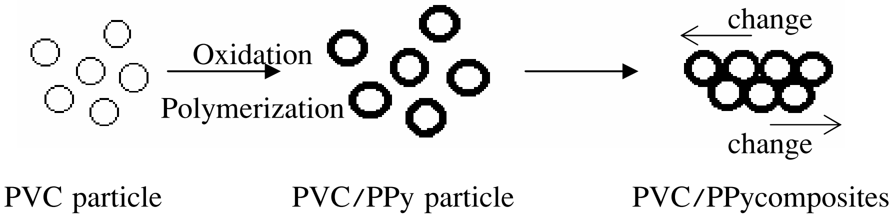


Figure 2.10 Preparation of the compressed PVC/PPy composites [28]

The oxidant solution is $FeCl_3$ in distilled water. The PVC/PPy products was compressed in both hot pressing and cold pressing to give the samples that were measured by conductivity measurement. The PVC/PPy composite samples have the continuous surface after compression. This raises the conductivity along the surface materials. The optimum electrical conductivity is ~10^{-1} Scm^{-1}.

Xie *et al.* [29] synthesized chlorinated polyethylene (CPE)/PPy and natural rubber/PPy composites by *in-situ* oxidation polymerization, using $FeCl_3$ as 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 h. They prepared the PPy/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 about 2 Scm^{-1}.

Cho *et al.* [30] prepared polypyrrole composites by synthesis of PPy on the surface of a zeolite, titanium silicate-1 (TS-1), which have the average size 100 nm surface area of 550 m^2/g. they show schematic representation of core-shell nanocomposites (Figure 2.11). Cetylpyridinium chloride (CPC) was used to form the template, which they suggest that the conducting polymer be formed as a thin layer at surface of the particles. This is the “core-shell” morphology, which was made by dissolving CPC in an aqueous dispersion of the TS-1 zeolite. The conductivity of this composite is about 5 Scm^{-1}, which is 8 wt% of PPy. The report has suggested the applications in the fields of rechargeable batteries and capacitors.

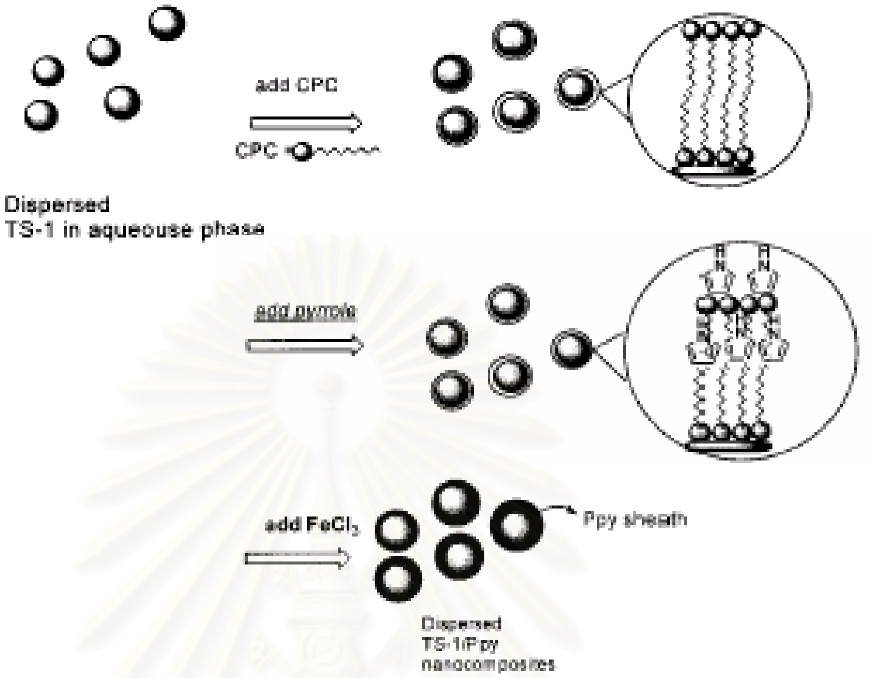


Figure 2.11 Descriptive illustration for preparation of core-shell nanocomposites [30]

Lee *et al.* [31] prepared electrically conducting composite by chemical oxidative polymerization using PPy and polycarbonate (PC) or sulfonated polycarbonate (SPC) in chloroform. The oxidant solution is $FeCl_3$ in methanol. All compounds were stirred for 1 day at room temperature. The product was compressed in hot pressing to give the samples that were measured by a standard four-probe method. The electrical conductivity of PPy/SPC composite was higher than that of PPy/PC composite, which was increased up to 0.82 Scm^{-1} with the amount of PPy. The PPy/SPC composites were very stable in the atmosphere.

Bunsomsit and Magaraphan [32] studied polypyrrole composite by preparing polypyrrole-coated natural rubber latex by admicellar polymerization. In this method, pyrrole monomer was adsolubilized on to the surface of latex particles with surfactant. Concentrating 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 films. After the polymerization had finished, excess surfactant was washed away with water to obtain a thin PPy coating over the latex surfaces. The presence of a small amount of salt, sodium chloride, substantially improves the surfactant adsorption and pyrrole adsolubilization. A polypyrrole-coated natural rubber latex prepared in the absence of surfactant exhibited slightly higher conductivity than a polypyrrole-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 quinone have been used to promote the oxidative polymerization [33]. Shenoy et al [33] prepared conductive polyurethane(PU) foams by first impregnating a PU foam with ferric trifluoromethane sulfonate (ferric triflate) using supercritical carbon dioxide ($scCO_2$) containing 0.2-1.3 vol.% ethanol as a cosolvent, and then exposing the foam to pyrrole vapor. PPy was formed in situ by an chemical oxidative polymerization. The conductivity of the composite foams ranged from 10^{-7} to 10^{-2} Scm^{-1}, depending on the amount of ethanol and impregnation time used.

The improvement of electrical conductivity and the processability of PPy composites have been studied in many reports. The difficulty to combine high conductivity or processability properties with the other is interesting. In this research, by using our condition, it was believed that the improvement of conductivity into PPy coating composite could be achieved.

CHAPTER III

EXPERIMENTAL

3.1 Chemicals

1. Anhydrous ferric chloride, $FeCl_3$	CARLO ERBA
2. Pyrrole	FLUKA
3. Methanal, CH_3OH	MERCK
4. Ethanal,	MERCK
5. Nitrogen, N_2	TIG
6. Natural rubber latex(~60%DRC)	THAI RUBBER LATEX
7. Poly(ethylen glycol)(1500)	FLUKA
8. Tritron-X 100	MERCK
9. Sodium hydroxide, NaOH	CARLO ERBA
10. Montmorillonite	CERAMIC “R” US

3.2 Glasswares and Equipments

1. Beaker
2. Buchner funnel
3. Condenser
4. Glass stopper
5. Gas inlet, outlet tube
6. Magnetic stirrer hotplate
7. Multimeter
8. Three-necked round bottom flask
9. Water bath
10. Water pump
11. Temperature controller bath

3.3 Instruments

1. High speed centrifuge : BACKMAN COULTER J-30I
2. Scanning Electron Microscope (SEM) : JSM-5410LV
3. Thermal Gravimetric Analyser (TGA) : 2960 SDT V3.0F
4. Fourier Transform Infrared Spectrometer (FT-IR) : NICOLET MACNA-IR750
5. X-ray Diffractometer : Rigaku D/MAX 2000 ultima

3.4 Purification and preparation of materials

3.4.1 Deproteinization natural rubber latex by saponification

NR latex was diluted to 10%dry rubber content (DRC) and incubated with NaOH 5%w/v in the presence of triton X-100 0.2 %w/v at 70°C for 3 h. The resulting latex was washed by double centrifugation at 10,000 rpm for 30 min. Cream of saponified latex was than redispersed in triton X-100 solution.

3.4.2 Pyrrole monomer

The pyrrole monomer was distilled at atmospheric pressure as colorless liquid. The distillate was collected in the glass bottle and then sealed instantly. The sealed pyrrole bottle was stored at −4 °C for no more than 1 week before use.

3.4.3 Oxidant solution

To obtain 0.35 M oxidant solution of $FeCl_3$, 5.6774 g of anhydrous ferric chloride was dissolved in 100 ml 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.

3.5 Synthesis of natural rubber/polypyrrole composites

The host polymer (high protein and low protein) and 100 ml 0.35 M $FeCl_3$ solution was added into 250 ml three-necked flask, equipped with a drying tube and gas inlet tube for bubbling nitrogen. The mixture was magnetically stirred while the temperature was kept at 0 °C by using ice and salt bath (Figure 3.1). The reaction was allowed to proceed for 30 minutes before the pyrrole monomer was added and then stirred for another 1 hour. At the end of reaction, 1:1 methanol was added to quench the reaction. The polypyrrole composite was filtered and washed with 1:1 methanol /deionized water until the filtrate was colorless. The polypyrrole composite was then dried in a desiccator at room temperature.

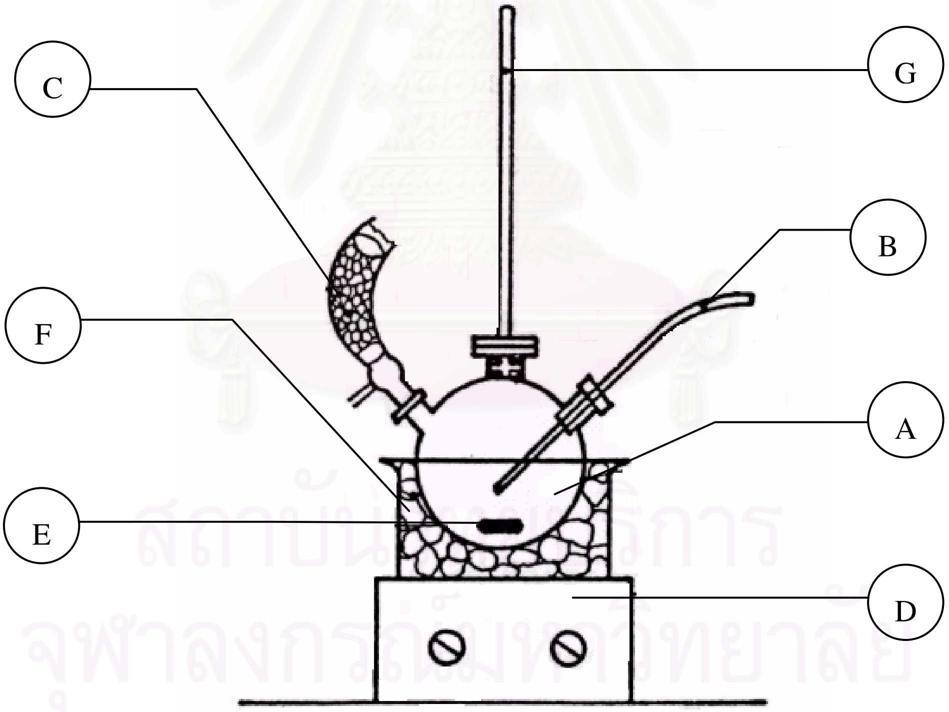


Figure 3.1 Polymerization of polypyrrole composite set up

(A) Three-neck flask	(B) Gas inlet tube	(C) Drying tube
(D) Magnetic stirrer	(E) Magnetic bar	(F) Ice bath
(G) Stand and clamp		

3.6 Determination of condition effects

3.6.1 Amount of natural rubber latex

The polymerization of this section was carried out under the reaction conditions similar to those in section 3.5 natural rubber : pyrrole (by weight) was varied 0.2, 0.5, 0.8, 1.0, and 1.2 to study the effect of the amount of natural rubber latex on the polymerization.

3.6.2 Protein content in natural rubber latex

In the same manner, the polymerization was carried out under the reaction similar to those in section 3.5 High and low protein natural rubber latex were used to study the effect of protein content in natural rubber latex.

3.6.3 Addition sequence of chemicals

The polymerization was carried out under the reaction similar to those in section 3.5. Addition sequence between pyrrole prior addition and $FeCl_3$ prior addition was studied to the effect of addition sequence of chemicals on the occurrence of polymer composites.

3.6.4 Amount of stabilizer

To investigate the effect of the stabilizer, the polymerization was carried out under the reaction conditions similar to those in section 3.5. The stabilizer was changed by the volume of 0.1-2.0 mmol.

3.6.5 Amount of montmorillonite

The natural rubber latex and 1, 2, 3, 4, and 5 g. of montmorillonite was stirred for 30 minutes before the pyrrole was added and the polymerization was carried out under the reaction conditions similar to those in section 3.5. The chemical composition of montmorillonite in weight percentage of oxide is : 13.04% Al, 74.96% Si, 1.03% Fe, 4.82% Na, 0.23% Ti, 3.54% Mg, 0.23% K, and 2.00% Ca. (cations exchange capacity = 0.73 meq/g. clay)

3.7 Characterization

3.7.1 Electrical conductivity measurement

The polypyrrole composites were transformed into a thin disc by pressing under 2000 psi of hydraulic force in evacuable die for 3 minutes. Three samples of each composite was prepared for electrical conductivity measurement. The thickness of samples were measured by micrometer. In general 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, which was clearly described in Appendix A. Three samples were measured under the same contact points and the average value of these measurements was taken.

3.7.2 Scanning electron microscopy

Morphology of polymer particles was investigated by Scanning Electron Microscope technique. Polypyrrole composite samples were prepared by firstly coating with gold in order to discharge the electron from electron beam in electron microscope. The photographs of polymer samples were then taken.

3.7.3 Thermal Gravimetric Analysis

A thermogravimetric analyzing system was used to follow the weight loss of a 10 mg sample between 50-600°C while the system was purged with nitrogen gas. The heating rate was 10°C/min.

3.7.4 Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy

The absorption spectra of polypyrrole/natural rubber composites were obtained by using Attenuated Total Reflectance Fourier Transform Infrared (ATR FT-IR) technique. The frequency range of measurement was 4000-400 cm^{-1} at a resolution of 4.0 cm^{-1} and the number of scans was 128. Using Nicolet Magna-IR750 FT-IR Spectrometer equipped with a liquid-nitrogen-cooled mercury-cadmium-telluride (MCT) detector. A single attenuated total reflection accessory with 45° germanium (Ge) IRE (spectra Tech, USA) was employed for all ATR spectral acquisitions. The measurement controlled by Omnic software.

3.7.5 X-ray powder Diffraction

X-ray diffractometer used in this study is Rigaku D/MAX 2000 ultima with CuKα radiation (1.5406 Å). The voltage and the current of X-ray tubes were 40 kV and 30 mA respectively. The scanning was done by step scanning with a step size of 0.02 degree 2 theta.

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Preliminary study on preparation of natural rubber/polypyrrole composites

In this study, the natural rubber/polypyrrole (NR/PPy) composites were prepared via chemical oxidative polymerization in the natural rubber latex using $FeCl_3$ as the oxidant at 0°C. The resulting natural rubber/polypyrrole composite was then washed exhaustedly with 1:1 methanol until the mother liquor was colorless to ensure that there was no pyrrole, ferric chloride and ferrous chloride salt in the composite. The resulting composite was then identified by Attenuated Total Reflectance (ATR FT-IR) technique because it was not translucent. This technique allows the measurement of the functional group on sample surface. Figure 4.1 shows the ATR FT-IR spectra of natural rubber/polypyrrole composite prepared from natural rubber and pyrrole at 1.2:1 by dry weight, comparing to polypyrrole and natural rubber latex. The ATR FT-IR spectrum (Figure 4.1(b)) shows the characteristic absorption bands of polypyrrole. The band at 1546 cm^{-1} is assigned to pyrrole ring, *i.e.*, the combination of C=C and C-C stretching vibrations. The peak at 1446 cm^{-1} is associated with the C-N stretching vibrations. The peaks at 1301 and 1167 cm^{-1} are attributed to the in-plain vibrations of C-H which were characteristics of polypyrrole. The N-H stretching vibration of the pyrrole ring does not appear at about 3400 cm^{-1}. It has been reported that its absence has been attributed to its masking by the charge carrier absorption band, which was also active in this range. The ATR FT-IR spectrum of natural rubber (Figure 4.1(c)) shows the absorption bands of CH_3 asymmetric stretching, CH_2 asymmetric stretching and CH_3 symmetric stretching at 2956, 2918, and 2848 cm^{-1}, respectively, C=C stretching of cis isomer at 1661 cm^{-1}, CH_3 asymmetric deformation at 1448 cm^{-1}, CH_3 symmetric deformation at 1375 cm^{-1}, and C-H rocking at 836 cm^{-1} which were characteristics of natural rubber. It can be seen clearly that the spectrum of natural rubber/polypyrrole composite shown in

Figure 4.1(a) was the combination of those two spectra which indicated that the polymer composite was composed of polypyrrole and natural rubber.

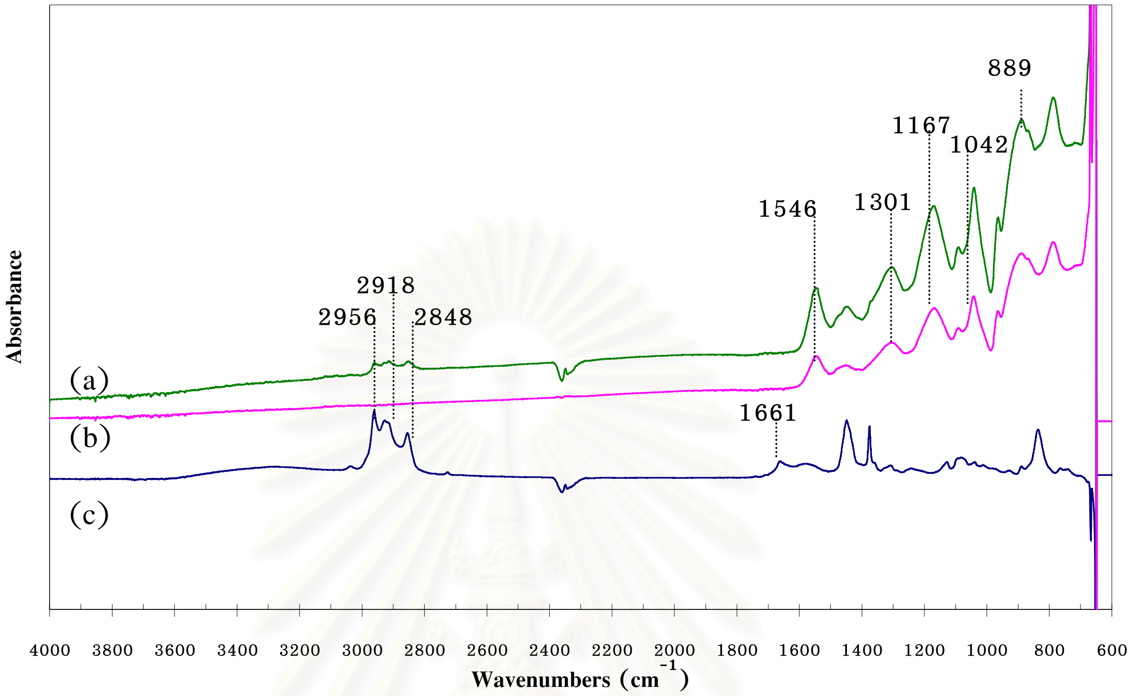


Figure 4.1 ATR FT-IR spectra of natural rubber/polypyrrole composite (natural rubber : pyrrole 1.2:1 by weight)(a), polypyrrole (b), and natural rubber (c)

4.2 Parameters affecting the preparation of natural rubber/polypyrrole composites

In order to determine the optimal condition for preparing natural rubber/polypyrrole composite with high electrical conductivity, various polymerization conditions were studied. However, the molar ratio of $FeCl_3$/pyrrole was kept constant at 2.5 and pyrrole 1 mL was used in every polymerization reaction throughout this study. Other parameters were varied as follows:

4.2.1 The amount of natural rubber latex

The amount of natural rubber latex was varied in terms of natural rubber : pyrrole ratio (by weight). The reaction temperature was controlled at 0^{o}C for 1 hour polymerization time. After reaction, the resulting product was thoroughly washed with 1 : 1 methanol and dried. It was then pressed into pellet for electrical conductivity measurement. Polypyrrole without natural rubber was also prepared for comparison.

It is worth to mention that pressed sample of polypyrrole was brittle while all the composites were softer and more flexible. The electrical conductivity measurement was performed using a home-made four-point probe apparatus. The measurement was repeated by using a more fancy four-point probe apparatus in order to ensure the electrical conductivity value.

Table 4.1 shows the electrical conductivity of natural rubber/polypyrrole composites and polypyrrole measured by using these two apparatus, A and B.

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

NR : pyrrole (by weight)	Sample code	Electrical conductivity* (Scm^{-1})		
		apparatus A	**apparatus B**	**difference**
_	PPy	4.74 ± 0.04	5.46 ± 0.08	0.68 ± 0.09
0.2	NPa	3.60 ± 0.06	4.35 ± 0.10	0.75 ± 0.11
0.5	NPb	3.52 ± 0.06	4.28 ± 0.10	0.76 ± 0.11
0.8	NPc	3.45 ± 0.08	4.26 ± 0.06	0.81 ± 0.10
1.0	NPd	2.63 ± 0.10	3.43 ± 0.12	0.80 ± 0.15
1.2	NPe	1.69 ± 0.06	2.48 ± 0.04	0.79 ± 0.07

NP = natural rubber/polypyrrole composite
Apparatus A = a home-made four-point probe apparatus
Apparatus B = a more fancy four-point probe apparatus
*electrical conductivity data were shown in Appendix B

It was found that the electrical conductivity measured with apparatus B was higher than the one measured with apparatus A in the range of 0.7-0.8 Scm^{-1} for every sample. However, using apparatus A was more convenient and required three times less amount of sample than apparatus B. In addition, the evaluation of the electrical conductivity of natural rubber/polypyrrole composite would be considered in the relative trend rather than the true value. Hereafter, the electrical conductivity of all samples was measured by using apparatus A.

The electrical conductivity of polypyrrole prepared at this specific condition was found to be 4.74 Scm^{-1}. The natural rubber/polypyrrole composite showed less electrical conductivity than polypyrrole. Furthermore, the electrical conductivity of natural rubber/polypyrrole composite decreased as the amount of natural rubber in the composite increased. This was probably due to the insulating natural rubber which could interrupt polypyrrole network.

Figure 4.2 is a plot between electrical conductivity and natural rubber : pyrrole ratio (by weight). At 0.2 to 0.8 natural rubber : pyrrole ratio (by weight), the electrical conductivity was about the same. It could be explained that more pyrrole in the reaction and the more core-shell like material can be formed. Charge transport can then occur through the material without significant interference from the underlying electrically insulating natural rubber component. The similar results were obtained for polystyrene/polypyrrole and polypropylene/polypyrrole composites studied by Lascelles [34] and Omastova [27].

When natural rubber : pyrrole ratio was higher than 0.8, lower electrical conductivity was detected. This was the contrast effect of the amount of natural rubber interfering the charge transport in polypyrrole network.

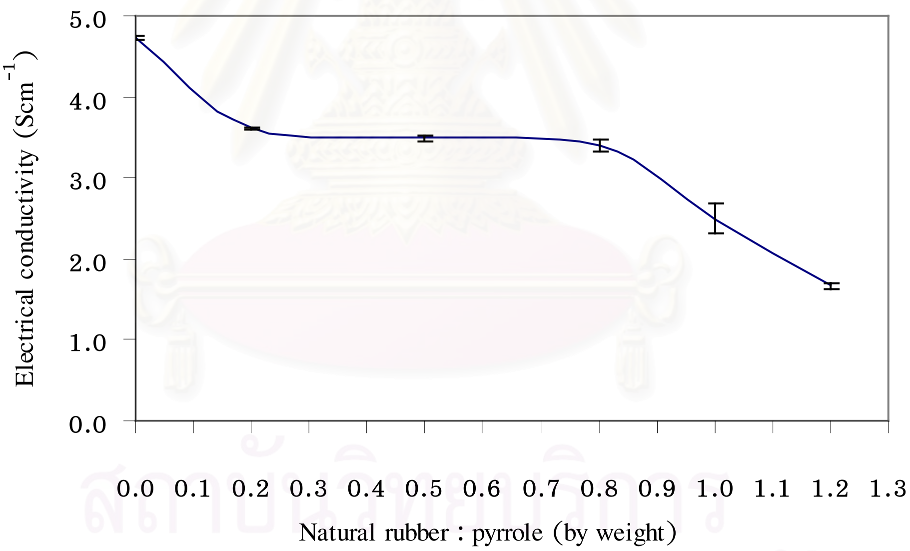


Figure 4.2 The electrical conductivity of natural rubber/polypyrrole composites at different ratio of natural rubber and pyrrole (with apparatus A)

4.2.2 The addition sequence of chemicals

In section 4.2.1, natural rubber/polypyrrole composites were prepared by firstly stirring natural rubber latex and $FeCl_3$ solution for a half hour then adding pyrrole dropwise into the mixture called procedure I. It should be noted that once pyrrole was dropped into the solution mixture, a black powder formed almost instantaneously and black thin film was gradually developed on the inner wall of reaction flask. At the same time the color of solution turned from rusty orange at the beginning to green and rapidly changed to yellow.

In this section, natural rubber latex was mixed with pyrrole first and $FeCl_3$ solution was added dropwise later called procedure II. It was observed that the formation of black thin film on the inner wall of reaction flask was slower as compared to the other way of addition mentioned above. From these observations, it was postulated that homopolymerization of pyrrole competed with the formation of natural rubber / polypyrrole composites.

Table 4.2 Effect of addition sequence of chemicals on electrical conductivity of natural rubber/polypyrrole composites

Natural rubber : pyrrole (by weight)	Sample code	Procedure I		Sample code	Procedure II	
		Weight of PPy in the composite (g.)	σ (Scm^{-1})		Weight of PPy in the composite (g.)	σ (Scm^{-1})
0.0	PPy	0.615 ± 0.024	4.73 ± 0.04	PPy	0.683 ± 0.053	7.13 ± 0.10
0.2	NP1	0.619 ± 0.016	3.61 ± 0.03	NP6	0.718 ± 0.052	6.20 ± 0.12
0.5	NP2	0.621 ± 0.015	3.49 ± 0.08	NP7	0.720 ± 0.050	5.32 ± 0.14
0.8	NP3	0.622 ± 0.014	3.40 ± 0.14	NP8	0.722 ± 0.050	5.20 ± 0.14
1.0	NP4	0.622 ± 0.013	2.50 ± 0.18	NP9	0.720 ± 0.048	3.08 ± 0.16
1.2	NP5	0.622 ± 0.012	1.67 ± 0.07	NP10	0.721 ± 0.048	2.06 ± 0.10

Table 4.2 exhibits the weight of polypyrrole in composites and the electrical conductivity of the natural rubber/polypyrrole composites obtained from both cases comparing to polypyrrole. It was found that polypyrrole prepared by $FeCl_3$ prior addition weighted approximately 0.615 g which was less than polypyrrole prepared by pyrrole prior addition. For natural rubber/polypyrrole composites, the weight of polypyrrole in composites was approximately the same for both cases regardless of the increase of natural rubber, 0.620 g for $FeCl_3$ prior addition and 0.720 g for pyrrole prior addition.

Since pyrrole 0.9370 g was used in all reactions, less weight of polypyrrole was formed due to the black film developed on the inner wall of reaction flask and unreacted pyrrole. It should be noted that all polymerization were carried out for the same length of time of 1 hour which was expected to be optimal reaction time. However, it was noticed that methanol washings of the resulting product turned black after a few hours. This observation indicated that polymerization of pyrrole was not completed and the remaining pyrrole was washed down to methanol washing which could be further polymerized. The electrical conductivity of every natural rubber/polypyrrole composite was lower than polypyrrole. When natural rubber in composite increased, the electrical conductivity of composites prepared by both procedures ($FeCl_3$ prior addition(I) and pyrrole prior addition(II)) decreased. The same explanation as discussed in section 4.2.1, about the interference of insulating natural rubber, can be applied for these results. Furthermore, the electrical conductivity of natural rubber/polypyrrole composites obtained from the reaction with pyrrole prior addition had higher electrical conductivity than the composites obtained from the reaction with $FeCl_3$ prior addition at every natural rubber : pyrrole ratio (by weight). The reasonable explanation that more pyrrole could be adsorbed and perhaps penetrate into the inner part of the natural rubber particles. When the $FeCl_3$ was added, the pyrrole started to polymerize both on the surface and in the inner part of the natural rubber particles, resulting in more uniform distribution of polypyrrole in the composite.

Figure 4.3. showed that the high electrical conductivity of the composites was attained up to the natural rubber : pyrrole ratio of 0.8 in both cases. Beyond that ratio, the electrical conductivity was dropped. Accordingly, the further study used by the natural rubber : pyrrole ratio of 0.8 with pyrrole prior addition.

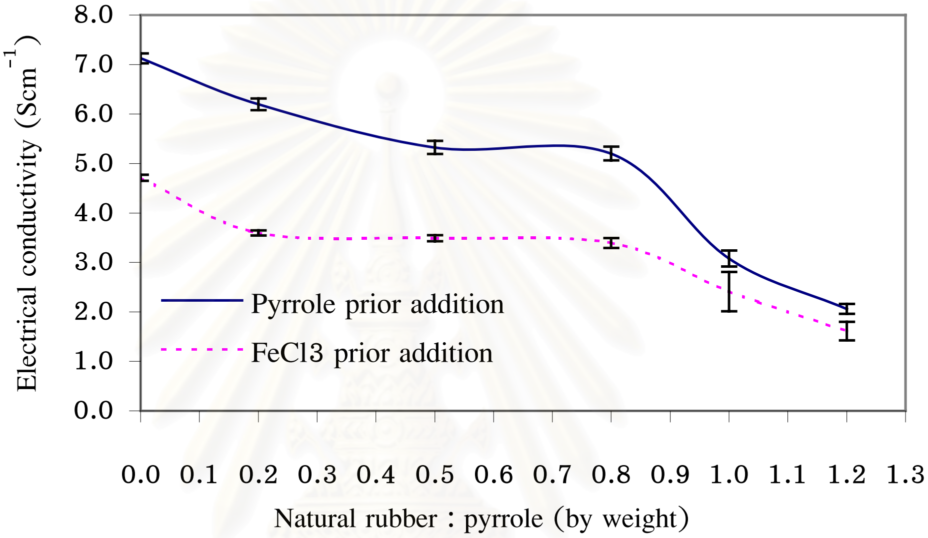


Figure 4.3 The electrical conductivity of natural rubber/polypyrrole composite at different ratio of natural rubber : pyrrole (by weight)

4.2.3 Effect of stabilizer

Recent study also showed that the addition of the water-soluble polymer during the preparation of polypyrrole could influence the electrical conductivity of the polypyrrole [1 cited in 35]. Kang and coworkers [35] reported that the electrical conductivity of polypyrrole prepared by chemical oxidative polymerization in the presence of poly(ethylene glycol)(PEG) was higher than polypyrrole synthesized in the absence of poly(ethylene glycol). Therefore, poly(ethylene glycol) was also used in this research.

From observation and the above mention in section 4.2.2, the powder of natural rubber/polypyrrole composite was coagulation and it clearly indicated that the electrical conductivity decreased when the natural rubber content in natural rubber/polypyrrole composite increased. To solve this drawback, the poly(ethylene glycol) powder was dissolved in water and mixed thoroughly with natural rubber latex before adding $FeCl_3$ solution to initialize the polymerization process. It was expected that natural rubber particle was solvated with poly(ethylene glycol) acting as a colloidal stabilizer. Then pyrrole was polymerized on the solvated natural rubber particle surface.

To study the effect of poly(ethylene glycol) on electrical conductivity of natural rubber/polypyrrole composite, the amount of poly(ethylene glycol) were varied as shown in Table 4.3.

Table 4.3 Effect of the amount of poly(ethylene glycol) on electrical conductivity of natural rubber/polypyrrole composites

Sample code	Amount of PEG (mmol)	Electrical conductivity (Scm^{-1})
NP8	_	5.20 ± 0.14
NP11	0.2	3.50 ± 0.06
NP12	0.4	2.22 ± 0.04
NP13	0.6	1.86 ± 0.04
NP14	0.8	1.80 ± 0.12
NP15	1.0	1.73 ± 0.10
NP16	1.2	1.63 ± 0.14
NP17	1.4	1.44 ± 0.04
NP18	1.6	1.20 ± 0.06
NP19	1.8	1.05 ± 0.06
NP20	2.0	0.98 ± 0.04

Remark : natural rubber : pyrrole at ratio 0.8 (by weight) were used for preparing all these composites

According to Table 4.3, the electrical conductivity of natural rubber/polypyrrole composite prepared in the presence of poly(ethylene glycol) additive was found to be lower than those of natural rubber/polypyrrole composite synthesized without additive. While the amount of poly(ethylene glycol) increased, the electrical conductivity slowly decreased. This phenomenon may be explained by the poly(ethylene glycol) causes more dissolution of pyrrole in the aqueous phase and more polypyrrole particles formed in the aqueous phase, resulting in less uniform distribution of polypyrrole in the composite and less electrical conductivity.

4.2.4 Protein content in natural rubber latex

In general, protein in natural rubber acts as emulsifier. Protein easily to denatured not only by acid-base level but also by solvent and heat. Thus the protein was necessary to get rid of from rubber latex. Moreover, the non-ionic surfactant was used instead of protein for stabilizing the colloid system.

To study the effect of protein content in natural rubber latex on the electrical conductivity of natural rubber/polypyrrole composites, low protein natural rubber latex was used. It was prepared by saponification technique called deproteinization [36]. The deproteinized natural rubber was redispersed in triton X-100 solution which is non-ionic surfactant to attain colloidal stability. Deproteinized natural rubber prepared from this process would theoretically allowed polypyrrole formation on the surface and in the inner parts of rubber particles.

Indeed, this experimental results clearly demonstrated that the deproteinized natural rubber/polypyrrole composites had higher electrical conductivity than the composite obtained from normal natural rubber despite the fact that a small increase in electrical conductivity was observed. It implied that more polypyrrole was in the composite prepared from deproteinized natural rubber. Another evidence supporting this observation was the higher weight of polypyrrole in the deproteinized natural rubber/polypyrrole composite. It could be explained by when the non-ionic surfactant was adsorbed on the surface of the natural rubber latex, it prevents the coagulation of latex particles and favors the *in-situ* polymerization of pyrrole on the surface and in the inner part of the natural rubber particles, resulting in more uniform distribution of polypyrrole in the composite and higher electrical conductivity of the composite.

Table 4.4 Electrical conductivity of natural rubber/polypyrrole composites prepared from deproteinized natural rubber and virgin natural rubber

Natural rubber : pyrrole (by weight)	Deproteinized natural rubber /polypyrrole composite			Natural rubber/polypyrrole composite		
	Sample code	weight of PPy in composite(g)	σ (Scm^{-1})	Sample code	weight of PPy in composite(g)	σ (Scm^{-1})
0.2	NP21	0.764 ± 0.015	6.52 ± 0.09	NP6	0.718 ± 0.052	6.20 ± 0.12
0.5	NP22	0.766 ± 0.018	5.61 ± 0.07	NP7	0.720 ± 0.050	5.32 ± 0.14
0.8	NP23	0.768 ± 0.018	5.43 ± 0.09	NP8	0.722 ± 0.050	5.20 ± 0.14
1.0	NP24	0.768 ± 0.017	3.32 ± 0.10	NP9	0.720 ± 0.048	3.08 ± 0.16
1.2	NP25	0.768 ± 0.017	2.26 ± 0.11	NP10	0.721 ± 0.048	2.06 ± 0.10

According to Table 4.4, the electrical conductivity of deproteinized natural rubber/polypyrrole composite depended on the amount of natural rubber. The electrical conductivity of deproteinized natural rubber/polypyrrole composite decreased as the amount of deproteinized natural rubber increased. Its electrical conductivity with various deproteinized natural rubber : pyrrole ratios (by weight) was leveled off after 0.8 of natural rubber : pyrrole ratio (by weight). This behavior was similar to the case of normal natural rubber/polypyrrole composite that too high rubber content in the composites interfered the charge transport in polymer network.

4.3 Preparation of natural rubber/polypyrrole/montmorillonite composites

In this study, montmorillonite (MMT) was added to natural rubber latex. The mixture was stirred well for a half hour to ensure better exfoliation of montmorillonite. Then the chemical oxidative polymerization of pyrrole was started with pyrrole prior addition. Surprisingly, no black film developed on the inner wall of the reaction flask for every reaction. The electrical conductivity and the weight of polypyrrole in natural rubber/polypyrrole/montmorillonite composites are shown in Table 4.5.

Interestingly, the weight of polypyrrole in the natural rubber / polypyrrole / montmorillonite composites was found to be significantly, higher then the composite without montmorillonite. When the amount of montmorillonite increased, the weight of polypyrrole composite was gradually higher. The highest weight of polypyrrole, 0.885 g, was detected. It meant that only 0.052 g of pyrrole was lost in this case. In other words, nearly all pyrrole was polymerized to form natural rubber / polypyrrole / montmorillonite composites

Table 4.5 Effect of the amount of montmorillonite on electrical conductivity of natural rubber/polypyrrole/montmorillonite composites

Sample code	Ratio of natural rubber : pyrrole : MMT (by weight)	Weight of PPy in the composite (g)	Electrical conductivity (Scm^{-1})
NP8	0.8 : 1 : 0	0.722 ± 0.050	5.20 ± 0.14
NPM1	0.8 : 1 : 1.1	0.847 ± 0.014	6.05 ± 0.16
NPM2	0.8 : 1 : 2.1	0.855 ± 0.014	6.30 ± 0.12
NPM3	0.8 : 1 : 3.2	0.865 ± 0.013	6.58 ± 0.06
NPM4	0.8 : 1 : 4.3	0.876 ± 0.012	6.81 ± 0.08
NPM5	0.8 : 1 : 5.3	0.885 ± 0.010	7.28 ± 0.08

The natural rubber/polypyrrole/montmorillonite composites always exhibit higher electrical conductivity than the composite without montmorillonite. Furthermore, the electrical conductivity of natural rubber/polypyrrole/montmorillonite composites increased with increasing montmorillonite content. These results conformed very well with the increasing weight of polypyrrole in the composites. Accordingly, it obviously indicated that the electrical conductivity of natural rubber/polypyrrole/montmorillonite composites depended on the polypyrrole loading. In addition, it was also implied that the structure of montmorillonite influenced the electrical conductivity of the composites.

Insertion of the natural rubber and polypyrrole into the layer of montmorillonite was also examined by an XRD, which confirmed that natural rubber and polypyrrole chain was intercalated with the layer of montmorillonite. Figure 4.4 represents XRD patterns of the montmorillonite and natural rubber/polypyrrole/montmorillonite sample. A shift in the natural rubber/polypyrrole/montmorillonite spectra to lower angles was found, corresponding to the increase of interlayer spacing d(001) from 1.26 nm for original montmorillonite to 1.84 nm of natural rubber/polypyrrole/montmorillonite composite. The variation of d-spacing was estimated by using Bragg formula $n\lambda=2d\sin\theta$.

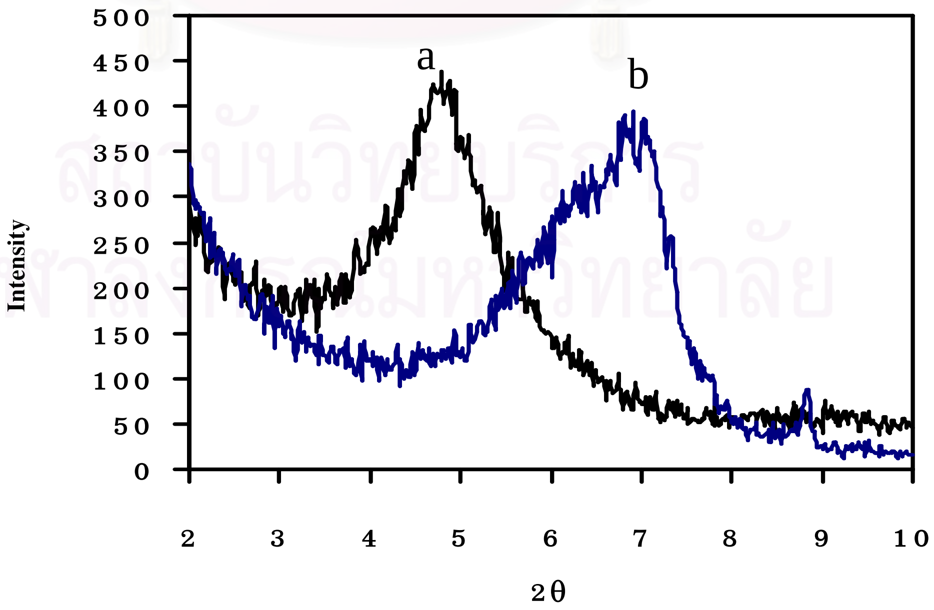
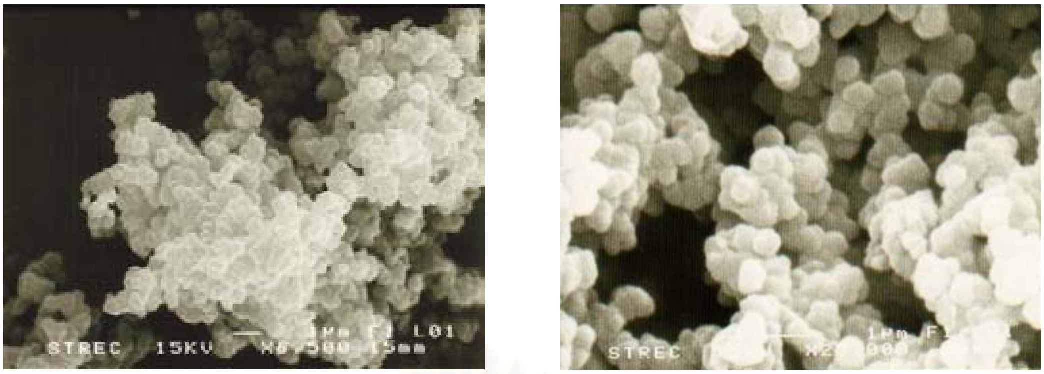


Figure 4.4 XRD patterns of a) 0.8 : 1 : 5.3 natural rubber/polypyrrole/montmorillonite composite and b) montmorillonite

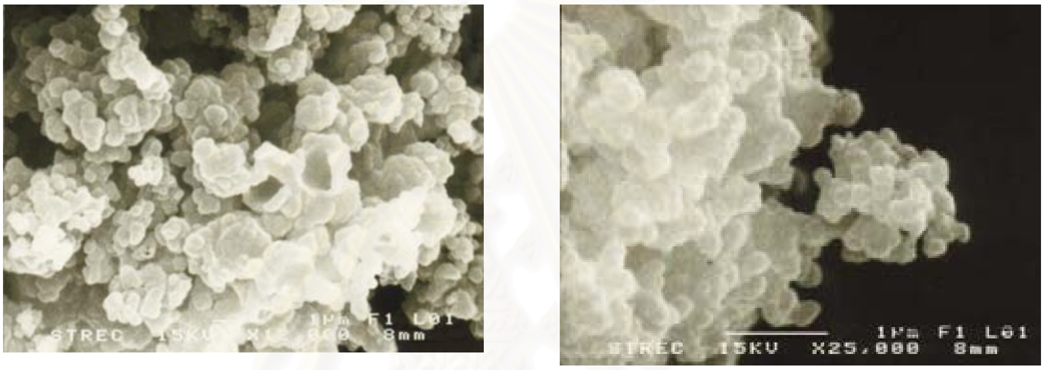
4.4 The morphology of natural rubber/polypyrrole composite

The scanning electron microscopy was employed to investigate the morphology of natural rubber/polypyrrole composites. In Figures 4.5 (b), (c), (d), (e), and (f), the morphology of the prepared composites at 0.2, 0.5, 0.8, 1.0, and 1.2 natural rubber : pyrrole ratio (by weight), respectively, were shown. For comparison, polypyrrole was also shown in Figure 4.5(a).

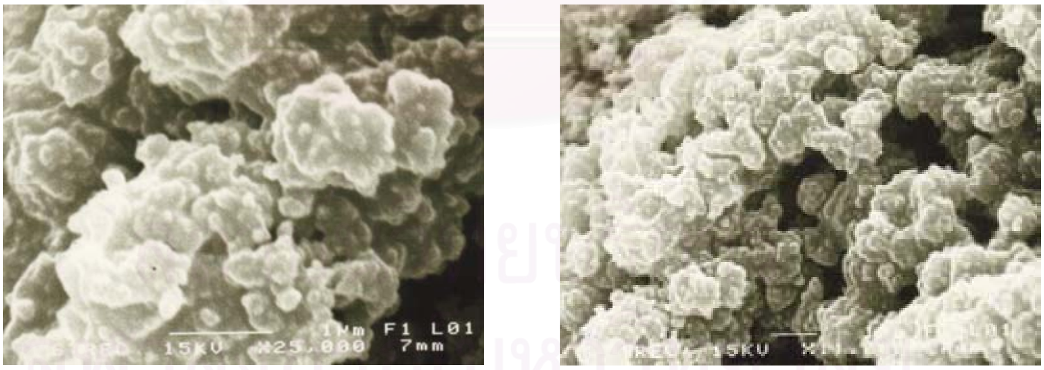
The SEMs clearly demonstrated that at lower amount of natural rubber, polypyrrole appeared as a spherical particle but at higher amount of natural rubber, the polypyrrole embeded in the natural rubber matrix. The results that polypyrrole was interfered by natural rubber it confirmed that electrical conductivity decreased as natural rubber increased.



(a) polypyrrole (b) 0.2 natural rubber : pyrrole



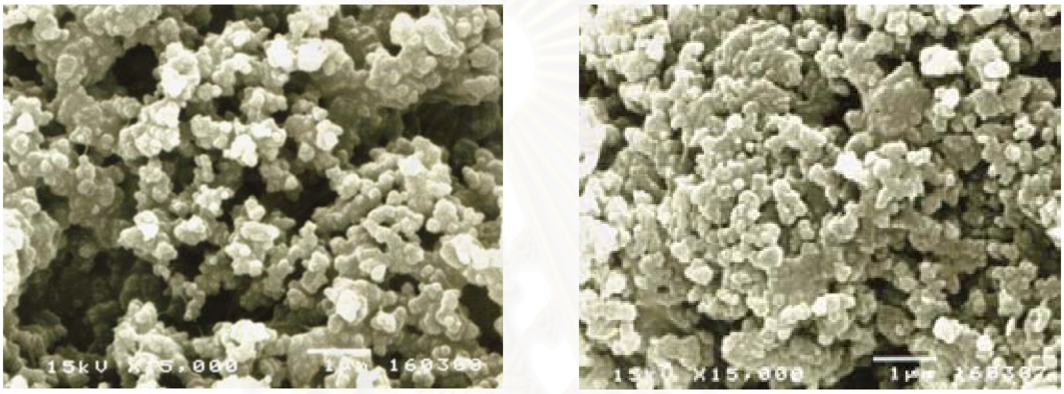
(c) 0.5 natural rubber : pyrrole (d) 0.8 natural rubber : pyrrole



(e) 1.0 natural rubber : pyrrole (f) 1.2 natural rubber : pyrrole

Figure 4.5 Scanning electron micrographs of natural rubber/polypyrrole composite at different ratio of natural rubber : pyrrole (by weight)

The scanning electron micrographs of natural rubber/polypyrrole composite which was prepared in the presence of 0.2, 1.0 mmol poly(ethylene glycol) were also shown in Figure 4.6(a) and (b). It can be observed that at higher poly(ethylene glycol), the natural rubber/polypyrrole composite appeared more agglomerated than at lower poly(ethylene glycol). It could be explained that the polypyrrole homopolymerized in the phase of poly(ethylene glycol) resulting in non-uniform formation of polypyrrole on the surface of natural rubber.



(a) (b)

Figure 4.6 Scanning electron micrographs of natural rubber/polypyrrole composite prepared with (a) 0.2 mmol poly(ethylene glycol) (b) 1.0 mmol poly(ethylene glycol)

The morphology of natural rubber/polypyrrole/montmorillonite composite and montmorillonite were shown in Figure 4.7(a) and (b). It could be seen that polypyrrole exhibits submicrometer-sized, bright globular particles. The morphology of the natural rubber/polypyrrole/montmorillonite composite (Figure 4.7(a)) slightly differs from that of the original montmorillonite (Figure 4.7(b)) because the particles had some rearrangement of the original montmorillonite flakes. Moreover, the surface exhibits some bright inclusions that could be assigned to polypyrrole as judged from Figure 4.5(a).

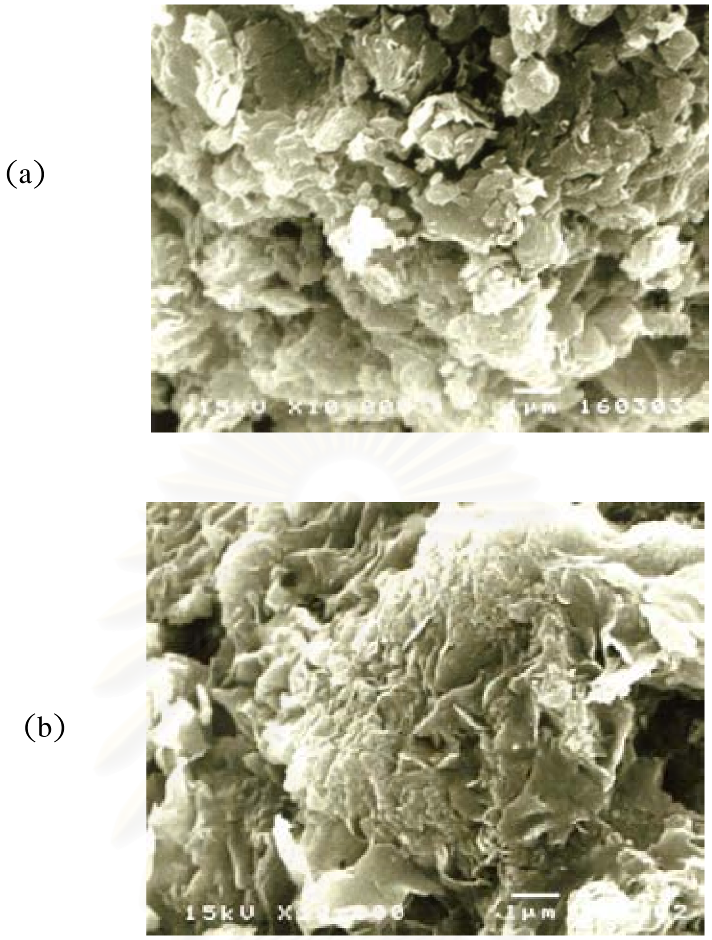


Figure 4.7 Scanning electron micrographs of natural rubber/polypyrrole/montmorillonite composite (a) and montmorillonite (b)

4.5 The electrically conductive stability of natural rubber/polypyrrole composites

In order to determine the electrically conductive stability of the composites, some composites were selected as the representatives for electrical conductivity measurement as a function of storing time. The electrical conductivity of 0.5 and 0.8 natural rubber : pyrrole, NP2 and NP3, deproteinized natural rubber/polypyrrole composites with 0.5 and 0.8 deproteinized natural rubber : pyrrole, NP22 and NP23, and 0.8 : 1 : 5.3 natural rubber/polypyrrole/montmorillonite, NPM5 were analyzed. The measurement was performed every 2 weeks for a total of 10 weeks comparing to polypyrrole. The results were shown in Figure 4.8.

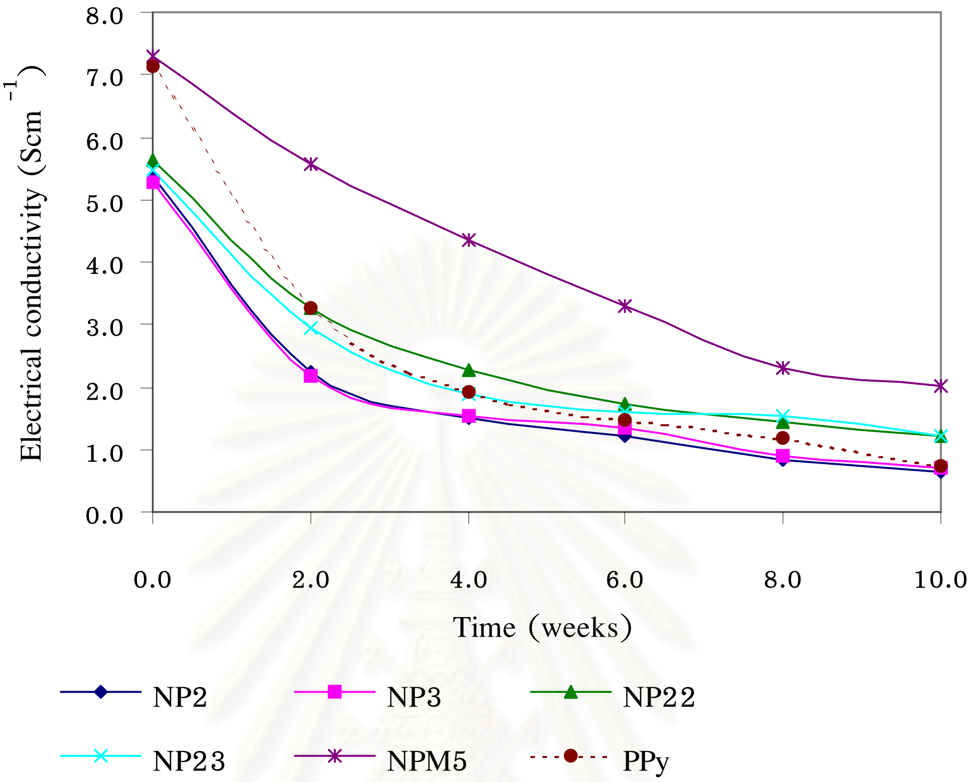


Figure 4.8 the electrical conductivity of natural rubber/polypyrrole composites as storing time

From Figure 4.8, it can be seen that the electrical conductivity of all samples decreased rapidly in the first few weeks and then became nearly constant. Interestingly among all composites, 0.8 : 1 : 5.3 natural rubber/polypyrrole/montmorillonite composite exhibited the highest electrical conductivity. This behavior was postulated that the possibility of chloride anions on the surface of the polymer matrix were less than those hold below the surface due to the interference of moisture or temperature. The presence of electrical conductivity after 10 weeks was due to the presence of trapped chloride ions within the sample disc. The electrical conductivity of natural rubber/polypyrrole without montmorillonite show the decreasing rate as similar to trend of the deproteinized natural rubber/polypyrrole composite. The highest electrical conductivity was obtained at 0.8 natural rubber : pyrrole ratio(by weight) of deproteinized natural rubber/polypyrrole composite, NP23. However, this sample was not the best because the electrical conductivity of natural rubber/polypyrrole prepared in the presence of montmorillonite, NPM5, was the most stable. It can be seen that the electrical conductivity of NPM5 was the highest even after 10 weeks.

4.6 Thermal stability of natural rubber/polypyrrole composites

Thermogravimetric analysis is capable of measuring changes in 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 polypyrrole, natural rubber/polypyrrole composite having 0.8 : 1 of natural rubber : pyrrole ratio (by weight), and natural rubber/polypyrrole/montmorillonite composite having 0.8 : 1 : 5.3 of natural rubber : pyrrole : montmorillonite ratio (by weight) were shown in Figure 4.9(a), (b), and (c), respectively. According to Figure 4.9(b), the natural rubber/polypyrrole composite loses weight slightly at 110°C, probably due to volatilization of water and the weight loses was more obvious in the range of 350-404°C. The highest weight loss rate occurs at 361°C. It lost about 64 %wt. However, the natural rubber/polypyrrole/montmorillonite composite followed a similar tendency to that of polypyrrole. It showed that the lost weight slightly at 104-270°C and obviously in the range of 325-450°C. It lost about 14 %wt. At the same range, 325-450°C, it indicated obviously that the degradation behavior of all sample was different. Polypyrrole was kept decomposing whereas the rest was the decomposition rate of less than polypyrrole. However, the decomposition rate of natural rubber/polypyrrole /montmorillonite composite was lower than natural rubber/polypyrrole composite. Thus, these results demonstrated that the natural rubber/polypyrrole/montmorillonite composites exhibited higher thermal stability than natural rubber/polypyrrole composite.

It can be implied that montmorillonite could improve the thermal stability of natural rubber/polypyrrole composite.

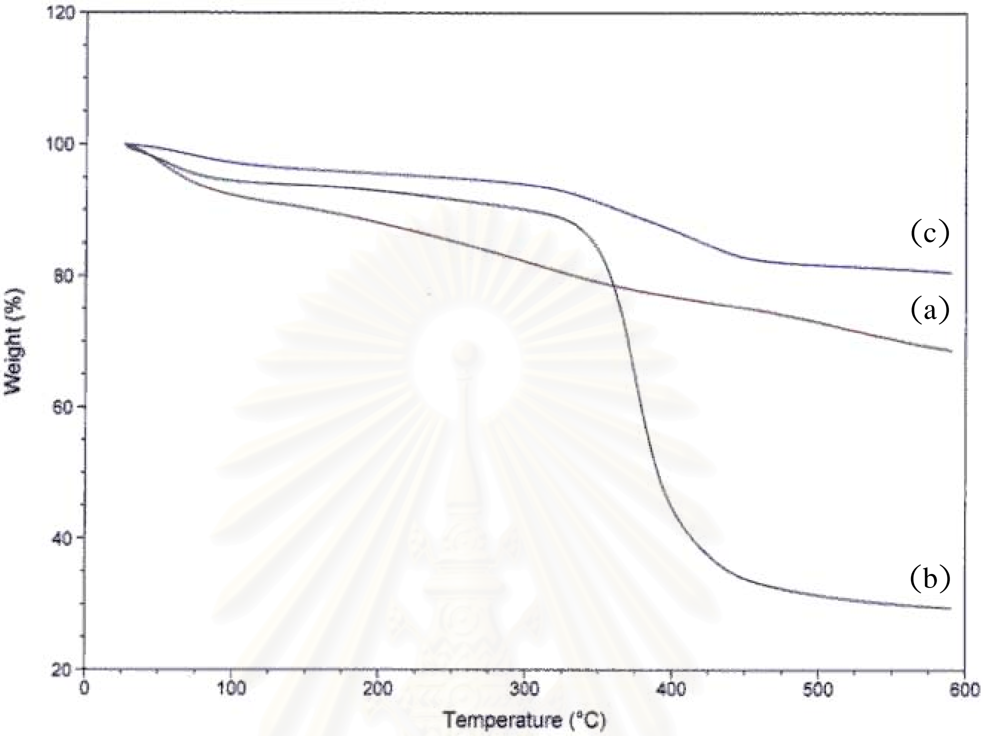


Figure 4.9 The TGA thermograms of polypyrrole (a), 0.8 natural rubber : pyrrole ratio (by weight) of natural rubber/polypyrrole composite (b), and 0.8 : 1 : 5.3 natural rubber : pyrrole : montmorillonite ratio (by weight) of natural rubber/polypyrrole/ montmorillonite composite (c)

CHAPTER V

CONCLUSION

5.1 Conclusion

The natural rubber/polypyrrole composites were prepared by chemical oxidative polymerization of pyrrole in natural rubber latex. The natural rubber content in the composites interrupted the polypyrrole network and caused the decrease in electrical conductivity. After compressing into thin disks the resulting composites were, however, less brittle and more flexible comparing to polypyrrole. Using deproteinized natural rubber insignificantly improved the electrical conductivity of the composites. Interestingly, when montmorillonite was included in the reaction, the resulting ternary composites exhibited higher electrical conductivity than polypyrrole and natural rubber/polypyrrole composites. When the amount of montmorillonite increased, higher electrical conductivity of the composites as well as the weight of polypyrrole in the composites were increased. These results indicated that a good network of polypyrrole in the composites was important for high electrical conductivity. Furthermore, the presence of montmorillonite also maintained the stability of electrical conductivity of the composites very well.

5.2 Suggestions for further work

From the observation, it is suggested that, the properties of natural rubber can be improved through chemical oxidative polymerization in order to obtain higher electrical conductivity. So that it may be substitute for conductor or semiconductors in a wide variety of electrical and electronic devices. Potential advantages of conductive or semiconductive polymer lie in their light weight less brittle and ease of manufacturing can be accomplished. It should be further studied in the following aspect;

1. Varying the dopant for improving the electrical conductivity of the composite
2. Varying the modified montmorillonite before polymerization. It will improve the properties of the composite.
3. Testing the mechanical properties of the composite

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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 (σ) of sample, which has constant thickness but arbitrary shape. First, four ohms contacts are made at the edge of the sample (Figure A-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 by using the resistance 100 KΩ, 200 KΩ, and 300 KΩ, respectively. The obtained data is shown in Table A-1.

Table A-1 Current and potential data measuring as I_{12} and V_{34}, respectively

Resistance (KΩ)	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-1 to obtain the electrical conductivity.

$$\exp^{(-\pi R_1 d\sigma)} + \exp^{(-\pi R_2 d\sigma)} = 1 \qquad (A-1)$$

Where d is the thickness of the sample and σ is the electrical conductivity.

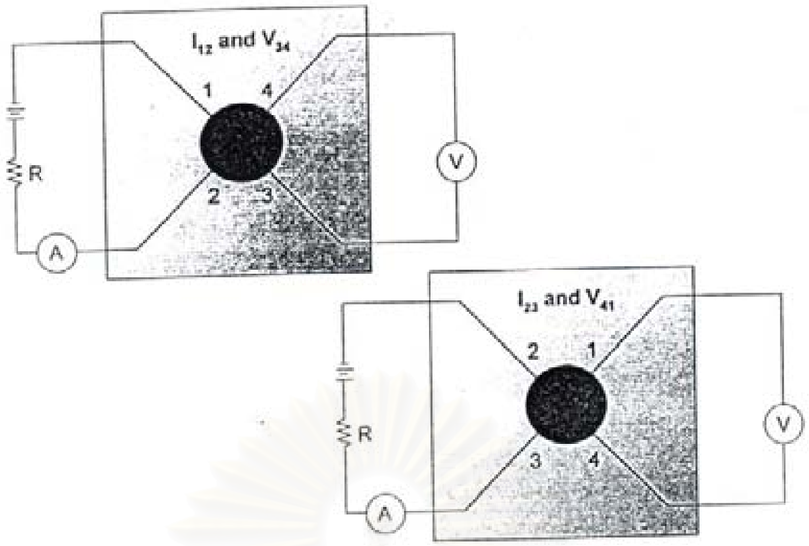

Figure A-1 Conductivity measurement by van der Pauw method

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.

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

σ = 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 = ”, R1
30     INPUT “Resistance No.2 = ”, R2
40     M = 3.141527*D
50     R = R1
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 I<=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 THICKNESS          = 0.042
Resistance No.1           = 0.68
Resistance No.1           = 1.09
Conductivity              = 6.050098
Ok
```

In principle, σ_1, σ_2, σ_3, σ_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 composites

Table B-1 Electrical conductivity data of natural rubber/polypyrrole composites (The first trial)

Sample code	Natural rubber : pyrrole ratio	Sample No.	Electrical conductivity (Scm^{-1})					
			σ_1	σ_2	σ_3	σ_4	$\sigma_{ave.}$	Average
PPy	–	1	4.73	4.74	4.69	4.70	4.72	4.71
		2	4.75	4.72	4.64	4.65	4.69	
		3	4.68	4.76	4.69	4.75	4.72	
NP1	0.2	1	3.64	3.59	3.64	3.57	3.61	3.62
		2	3.56	3.67	3.68	3.54	3.61	
		3	3.57	3.69	3.61	3.67	3.64	
NP2	0.5	1	3.46	3.48	3.51	3.45	3.48	3.46
		2	3.52	3.43	3.47	3.49	3.48	
		3	3.48	3.44	3.42	3.41	3.44	
NP3	0.8	1	3.32	3.38	3.36	3.34	3.35	3.35
		2	3.33	3.37	3.35	3.37	3.36	
		3	3.36	3.34	3.29	3.39	3.35	
NP4	1.0	1	2.39	2.34	2.37	2.34	2.36	2.37
		2	2.36	2.38	2.35	2.36	2.36	
		3	2.37	2.40	2.41	2.41	2.40	
NP5	1.2	1	1.59	1.65	1.68	1.64	1.64	1.64
		2	1.63	1.61	1.67	1.65	1.64	
		3	1.68	1.67	1.64	1.62	1.65	

Study in aqueous medium at 1 hour polymerization time and $FeCl_3$ prior addition

Table B-2 Electrical conductivity data of natural rubber/polypyrrole composites (The second trial)

Sample code	Natural rubber : pyrrole ratio	Sample No.	Electrical conductivity (Scm^{-1})					
			σ_1	σ_2	σ_3	σ_4	$\sigma_{ave.}$	Average
Ppy	_	1	4.73	4.76	4.75	4.74	4.75	4.74
		2	4.72	4.73	4.76	4.75	4.74	
		3	4.71	4.74	4.73	4.75	4.73	
NP1 (NPa)	0.2	1	3.58	3.61	3.62	3.57	3.60	3.60
		2	3.57	3.63	3.65	3.58	3.61	
		3	3.64	3.59	3.61	3.57	3.60	
NP2 (NPb)	0.5	1	3.52	3.54	3.51	3.49	3.52	3.52
		2	3.56	3.52	3.53	3.51	3.53	
		3	3.54	3.53	3.47	3.52	3.52	
NP3 (NPc)	0.8	1	3.43	3.50	3.44	3.39	3.44	3.45
		2	3.46	3.38	3.42	3.51	3.44	
		3	3.45	3.42	3.46	3.48	3.45	
NP4 (NPd)	1.0	1	2.67	2.74	2.63	2.61	2.66	2.63
		2	2.64	2.57	2.69	2.58	2.62	
		3	2.61	2.59	2.62	2.64	2.62	
NP5 (NPe)	1.2	1	1.65	1.63	1.68	1.71	1.67	1.69
		2	1.73	1.72	1.74	1.69	1.72	
		3	1.66	1.68	1.72	1.71	1.69	

Study in aqueous medium at 1 hour polymerization time and $FeCl_3$ prior addition

Table B-3 Electrical conductivity data of natural rubber/polypyrrole composites (The first trial)

Sample code	Natural rubber : pyrrole ratio	Sample No.	Electrical conductivity (Scm^{-1})					
			σ_1	σ_2	σ_3	σ_4	$\sigma_{ave.}$	Average
PPy	-	1	7.12	7.17	7.18	7.14	7.15	7.16
		2	7.16	7.15	7.18	7.13	7.16	
		3	7.13	7.18	7.16	7.19	7.17	
NP6	0.2	1	6.18	6.15	6.20	6.21	6.19	6.19
		2	6.21	6.23	6.24	6.19	6.22	
		3	6.22	6.14	6.17	6.17	6.18	
NP7	0.5	1	5.34	5.36	5.32	5.34	5.34	5.32
		2	5.31	5.29	5.27	5.28	5.29	
		3	5.32	5.33	5.35	5.29	5.32	
NP8	0.8	1	5.19	5.16	5.21	5.23	5.20	5.20
		2	5.18	5.22	5.23	5.17	5.20	
		3	5.24	5.21	5.18	5.19	5.21	
NP9	1.0	1	3.09	3.08	3.12	3.13	3.11	3.11
		2	3.07	3.09	3.11	3.14	3.10	
		3	3.13	3.12	3.16	3.08	3.12	
NP10	1.2	1	2.04	2.06	2.03	2.07	2.05	2.06
		2	2.03	2.07	2.05	2.09	2.06	
		3	2.11	2.09	2.04	2.08	2.08	

Study in aqueous medium at 1 hour polymerization time and pyrrole prior addition

Table B-4 Electrical conductivity data of natural rubber/polypyrrole composites (The second trial)

Sample code	Natural rubber : pyrrole ratio	Sample No.	Electrical conductivity (Scm^{-1})					
			σ_1	σ_2	σ_3	σ_4	$\sigma_{ave.}$	Average
PPy	_	1	7.03	7.06	7.08	7.11	7.07	7.07
		2	7.14	7.02	7.05	7.13	7.09	
		3	7.04	7.06	7.05	7.08	7.06	
NP6	0.2	1	6.17	6.13	6.14	6.18	6.16	6.14
		2	6.12	6.11	6.15	6.13	6.13	
		3	6.19	6.12	6.11	6.09	6.13	
NP7	0.5	1	5.31	5.27	5.24	5.23	5.26	5.26
		2	5.29	5.23	5.21	5.24	5.24	
		3	5.26	5.24	5.25	5.29	5.26	
NP8	0.8	1	5.10	5.16	5.14	5.18	5.15	5.13
		2	5.17	5.09	5.12	5.14	5.13	
		3	5.08	5.12	5.18	5.07	5.11	
NP9	1.0	1	3.01	3.05	3.04	3.03	3.03	2.99
		2	2.96	2.94	2.93	2.91	2.94	
		3	2.98	3.02	3.03	3.00	3.01	
NP10	1.2	1	2.03	2.04	1.99	1.98	2.01	2.01
		2	1.99	1.98	1.97	2.02	1.99	
		3	2.01	2.04	2.03	1.99	2.02	

Study in aqueous medium at 1 hour polymerization time and pyrrole prior addition

Table B-5 Electrical conductivity data of natural rubber/polypyrrole composites (The third trial)

Sample code	Natural rubber : pyrrole ratio	Sample No.	Electrical conductivity (Scm^{-1})					
			σ_1	σ_2	σ_3	σ_4	$\sigma_{ave.}$	Average
PPy	-	1	7.19	7.13	7.14	7.12	7.15	7.15
		2	7.16	7.12	7.13	7.15	7.14	
		3	7.18	7.12	7.14	7.16	7.15	
NP6	0.2	1	6.23	6.28	6.24	6.29	6.26	6.26
		2	6.27	6.23	6.25	6.28	6.26	
		3	6.22	6.27	6.23	6.29	6.25	
NP7	0.5	1	5.41	5.42	5.38	5.34	5.39	5.39
		2	5.36	5.37	5.43	5.42	5.40	
		3	5.39	5.35	5.36	5.40	5.38	
NP8	0.8	1	5.23	5.29	5.27	5.26	5.26	5.27
		2	5.28	5.24	5.27	5.25	5.26	
		3	5.30	5.28	5.24	5.27	5.27	
NP9	1.0	1	3.12	3.18	3.17	3.13	3.15	3.14
		2	3.14	3.13	3.16	3.15	3.15	
		3	3.19	3.11	3.12	3.11	3.13	
NP10	1.2	1	2.15	2.14	2.12	2.14	2.14	2.11
		2	2.09	2.07	2.06	2.07	2.07	
		3	2.08	2.09	2.14	2.13	2.11	

Study in aqueous medium at 1 hour polymerization time and pyrrole prior addition

Table B-6 Electrical conductivity data of natural rubber/polypyrrole composites (The first trial)

Sample code	Amount of PEG (mmol)	Sample No.	Electrical conductivity (Scm^{-1})					
			σ_1	σ_2	σ_3	σ_4	$\sigma_{ave.}$	Average
NP11	0.2	1	3.57	3.56	3.52	3.51	3.54	3.53
		2	3.53	3.51	3.54	3.56	3.54	
		3	3.54	3.55	3.49	3.51	3.52	
NP12	0.4	1	2.23	2.21	2.17	2.22	2.21	2.20
		2	2.18	2.17	2.23	2.19	2.19	
		3	2.21	2.25	2.19	2.18	2.21	
NP13	0.6	1	1.84	1.87	1.91	1.92	1.89	1.88
		2	1.86	1.88	1.93	1.91	1.90	
		3	1.86	1.85	1.84	1.89	1.86	
NP14	0.8	1	1.83	1.82	1.81	1.88	1.84	1.85
		2	1.87	1.89	1.85	1.84	1.86	
		3	1.86	1.87	1.86	1.84	1.86	
NP15	1.0	1	1.73	1.76	1.78	1.74	1.75	1.77
		2	1.77	1.78	1.74	1.73	1.76	
		3	1.80	1.79	1.81	1.82	1.81	
NP16	1.2	1	1.73	1.74	1.71	1.71	1.72	1.69
		2	1.67	1.65	1.66	1.68	1.67	
		3	1.64	1.69	1.72	1.73	1.70	
NP17	1.4	1	1.48	1.50	1.46	1.47	1.48	1.46
		2	1.43	1.45	1.46	1.45	1.45	
		3	1.48	1.49	1.43	1.45	1.46	
NP18	1.6	1	1.21	1.24	1.26	1.22	1.23	1.23
		2	1.23	1.25	1.21	1.24	1.23	
		3	1.25	1.24	1.23	1.22	1.24	
NP19	1.8	1	1.05	1.11	1.05	1.04	1.06	1.09
		2	1.06	1.09	1.12	1.13	1.10	
		3	1.12	1.08	1.07	1.11	1.10	
NP20	2.0	1	0.93	0.97	0.96	0.99	0.96	0.97
		2	1.01	0.96	0.98	0.99	0.99	
		3	0.96	0.98	0.97	0.95	0.97	

Study in aqueous medium at 1 hour polymerization time and pyrrole prior addition various the amount of PEG

Table B-7 Electrical conductivity data of natural rubber/polypyrrole composites (The second trial)

Sample code	Amount of PEG (mmol)	Sample No.	Electrical conductivity (Scm^{-1})					
			σ_1	σ_2	σ_3	σ_4	$\sigma_{ave.}$	Average
NP11	0.2	1	3.50	3.48	3.46	3.51	3.49	3.47
		2	3.49	3.46	3.47	3.5	3.48	
		3	3.42	3.43	3.46	3.45	3.44	
NP12	0.4	1	2.21	2.25	2.23	2.26	2.24	2.24
		2	2.23	2.27	2.28	2.24	2.26	
		3	2.26	2.19	2.25	2.23	2.23	
NP13	0.6	1	1.84	1.83	1.90	1.89	1.87	1.85
		2	1.85	1.88	1.86	1.85	1.86	
		3	1.87	1.83	1.82	1.82	1.84	
NP14	0.8	1	1.71	1.73	1.72	1.74	1.73	1.73
		2	1.69	1.73	1.74	1.76	1.73	
		3	1.72	1.75	1.74	1.68	1.72	
NP15	1.0	1	1.72	1.70	1.66	1.64	1.68	1.68
		2	1.67	1.65	1.68	1.71	1.68	
		3	1.68	1.73	1.72	1.64	1.69	
NP16	1.2	1	1.60	1.59	1.57	1.56	1.58	1.56
		2	1.54	1.53	1.56	1.57	1.55	
		3	1.61	1.55	1.53	1.54	1.56	
NP17	1.4	1	1.39	1.39	1.42	1.43	1.41	1.42
		2	1.38	1.43	1.42	1.39	1.41	
		3	1.42	1.43	1.44	1.45	1.44	
NP18	1.6	1	1.16	1.19	1.20	1.18	1.18	1.17
		2	1.17	1.16	1.16	1.15	1.16	
		3	1.16	1.15	1.18	1.19	1.17	
NP19	1.8	1	1.05	1.02	1.03	1.04	1.04	1.03
		2	0.99	1.04	1.01	1.02	1.02	
		3	1.06	1.02	0.99	1.03	1.03	
NP20	2.0	1	0.94	0.97	0.95	1.00	0.97	0.97
		2	0.99	0.98	1.01	0.99	0.99	
		3	0.98	0.96	0.95	0.94	0.96	

Study in aqueous medium at 1 hour polymerization time and pyrrole prior addition various the amount of PEG

Table B-8 Electrical conductivity data of natural rubber/polypyrrole composites (The second trial)

Sample code	Amount of PEG (mmol)	Sample No.	Electrical conductivity (Scm^{-1})					
			σ_1	σ_2	σ_3	σ_4	$\sigma_{ave.}$	Average
NP11	0.2	1	3.52	3.52	3.50	3.49	3.51	3.51
		2	3.48	3.52	3.49	3.51	3.50	
		3	3.49	3.51	3.51	3.52	3.51	
NP12	0.4	1	2.23	2.21	2.18	2.22	2.21	2.21
		2	2.22	2.21	2.23	2.23	2.22	
		3	2.20	2.19	2.17	2.19	2.19	
NP13	0.6	1	1.84	1.83	1.87	1.87	1.85	1.86
		2	1.86	1.86	1.87	1.88	1.87	
		3	1.84	1.86	1.85	1.85	1.85	
NP14	0.8	1	1.82	1.84	1.84	1.83	1.83	1.83
		2	1.85	1.83	1.82	1.84	1.84	
		3	1.83	1.82	1.85	1.83	1.83	
NP15	1.0	1	1.72	1.73	1.73	1.74	1.73	1.74
		2	1.71	1.74	1.75	1.75	1.74	
		3	1.76	1.76	1.73	1.73	1.75	
NP16	1.2	1	1.63	1.64	1.65	1.64	1.64	1.65
		2	1.67	1.67	1.63	1.64	1.65	
		3	1.66	1.65	1.66	1.67	1.66	
NP17	1.4	1	1.41	1.43	1.44	1.43	1.43	1.43
		2	1.42	1.44	1.43	1.39	1.42	
		3	1.45	1.42	1.43	1.45	1.44	
NP18	1.6	1	1.20	1.19	1.20	1.17	1.19	1.19
		2	1.18	1.2	1.21	1.21	1.20	
		3	1.16	1.17	1.17	1.19	1.17	
NP19	1.8	1	1.06	1.03	1.02	1.05	1.04	1.04
		2	1.05	1.02	1.03	1.04	1.04	
		3	1.04	1.04	1.03	1.05	1.04	
NP20	2.0	1	0.99	0.97	0.98	1.00	0.99	1.01
		2	1.02	1.01	1.01	1.03	1.02	
		3	1.02	1.02	1.03	1.03	1.03	

Study in aqueous medium at 1 hour polymerization time and pyrrole prior addition various the amount of PEG

Table B-9 Electrical conductivity data of deproteinized natural rubber/polypyrrole composites (The first trial)

Sample code	Deproteinized natural rubber : pyrrole ratio	Sample No.	Electrical conductivity (Scm^{-1})					
			σ_1	σ_2	σ_3	σ_4	$\sigma_{ave.}$	Average
NP21	0.2	1	6.46	6.47	6.46	6.48	6.47	6.48
		2	6.50	6.49	6.47	6.47	6.48	
		3	6.46	6.48	6.49	6.48	6.48	
NP22	0.5	1	5.59	5.56	5.56	5.57	5.57	5.57
		2	5.58	5.57	5.56	5.58	5.57	
		3	5.56	5.54	5.54	5.58	5.56	
NP23	0.8	1	5.38	5.41	5.38	5.39	5.39	5.39
		2	5.37	5.38	5.41	5.42	5.40	
		3	5.39	5.42	5.41	5.37	5.40	
NP24	1.0	1	3.26	3.28	3.30	3.26	3.28	3.27
		2	3.25	3.24	3.26	3.28	3.26	
		3	3.29	3.28	3.29	3.27	3.28	
NP25	1.2	1	2.23	2.23	2.21	2.22	2.22	2.21
		2	2.22	2.23	2.23	2.24	2.23	
		3	2.19	2.18	2.19	2.18	2.19	

Study in aqueous medium at 1 hour polymerization time and pyrrole prior addition

Table B-10 Electrical conductivity data of deproteinized natural rubber/polypyrrole composites (The second trial)

Sample code	Deproteinized natural rubber : pyrrole ratio	Sample No.	Electrical conductivity (Scm^{-1})					
			σ_1	σ_2	σ_3	σ_4	$\sigma_{ave.}$	Average
NP21	0.2	1	6.49	6.48	6.49	6.50	6.49	6.51
		2	6.52	6.52	6.53	6.51	6.52	
		3	6.49	6.51	6.51	6.52	6.51	
NP22	0.5	1	5.62	5.61	5.61	5.62	5.62	5.62
		2	5.63	5.65	5.65	5.64	5.64	
		3	5.62	5.61	5.62	5.60	5.61	
NP23	0.8	1	5.43	5.41	5.42	5.43	5.42	5.42
		2	5.44	5.44	5.43	5.43	5.44	
		3	5.41	5.41	5.39	5.39	5.40	
NP24	1.0	1	3.34	3.32	3.33	3.33	3.33	3.32
		2	3.31	3.31	3.35	3.32	3.32	
		3	3.32	3.33	3.30	3.30	3.31	
NP25	1.2	1	2.23	2.26	2.26	2.22	2.24	2.25
		2	2.26	2.27	2.27	2.25	2.26	
		3	2.24	2.26	2.28	2.23	2.25	

Study in aqueous medium at 1 hour polymerization time and pyrrole prior addition

Table B-11 Electrical conductivity data of deproteinized natural rubber/polypyrrole composites (The third trial)

Sample code	Deproteinized natural rubber : pyrrole ratio	Sample No.	Electrical conductivity (Scm^{-1})					
			σ_1	σ_2	σ_3	σ_4	$\sigma_{ave.}$	Average
NP21	0.2	1	6.60	6.59	6.57	6.57	6.58	6.57
		2	6.58	6.56	6.56	6.58	6.57	
		3	6.55	6.57	6.55	6.54	6.55	
NP22	0.5	1	5.63	5.65	5.65	5.64	5.64	5.64
		2	5.67	5.68	5.65	5.64	5.66	
		3	5.63	5.63	5.62	5.62	5.63	
NP23	0.8	1	5.50	5.50	5.49	5.49	5.50	5.48
		2	5.46	5.46	5.48	5.48	5.47	
		3	5.48	5.48	5.49	5.47	5.48	
NP24	1.0	1	3.38	3.39	3.37	3.39	3.38	3.37
		2	3.36	3.35	3.36	3.37	3.36	
		3	3.38	3.36	3.37	3.36	3.37	
NP25	1.2	1	2.31	2.34	2.31	2.33	2.32	2.32
		2	2.35	2.33	2.33	2.34	2.34	
		3	2.32	2.31	2.31	2.31	2.31	

Study in aqueous medium at 1 hour polymerization time and pyrrole prior addition

Table B-12 Electrical conductivity data of natural rubber/polypyrrole/montmorillonite composites (The first trial)

Sample code	Ratio of natural rubber : pyrrole : MMT (by weight)	Sample No.	Electrical conductivity (Scm^{-1})					
			σ_1	σ_2	σ_3	σ_4	$\sigma_{ave.}$	Average
NPM1	0.8 : 1 : 1.1	1	6.05	6.06	6.06	6.07	6.06	6.08
		2	6.10	6.09	6.09	6.11	6.10	
		3	6.07	6.08	6.09	6.08	6.08	
NPM2	0.8 : 1 : 2.1	1	6.29	6.28	6.28	6.27	6.28	6.26
		2	6.23	6.23	6.25	6.24	6.24	
		3	6.27	6.25	6.23	6.25	6.25	
NPM3	0.8 : 1 : 3.2	1	6.54	6.53	6.56	6.56	6.55	6.57
		2	6.60	6.56	6.56	6.55	6.57	
		3	6.58	6.59	6.59	6.58	6.59	
NPM4	0.8 : 1 : 4.3	1	6.79	6.79	6.80	6.80	6.80	6.81
		2	6.83	6.82	6.82	6.81	6.82	
		3	6.78	6.78	6.82	6.82	6.80	
NPM5	0.8 : 1 : 5.3	1	7.28	7.31	7.30	7.28	7.29	7.29
		2	7.27	7.27	7.31	7.30	7.29	
		3	7.32	7.31	7.28	7.27	7.30	

Study in aqueous medium at 1 hour polymerization time and pyrrole prior addition

Table B-13 Electrical conductivity data of natural rubber/polypyrrole/montmorillonite composites (The second trial)

Sample code	Ratio of natural rubber : pyrrole : MMT (by weight)	Sample No.	Electrical conductivity (Scm^{-1})					
			σ_1	σ_2	σ_3	σ_4	$\sigma_{ave.}$	Average
NPM1	0.8 : 1 : 1.1	1	5.95	5.94	5.95	5.93	5.94	5.96
		2	6.00	5.97	5.97	5.98	5.98	
		3	5.98	5.98	5.96	5.96	5.97	
NPM2	0.8 : 1 : 2.1	1	6.26	6.25	6.25	6.26	6.26	6.28
		2	6.27	6.29	6.29	6.28	6.28	
		3	6.29	6.30	6.30	6.30	6.30	
NPM3	0.8 : 1 : 3.2	1	6.54	6.57	6.57	6.58	6.57	6.56
		2	6.56	6.58	6.58	6.57	6.57	
		3	6.53	6.54	6.54	6.58	6.55	
NPM4	0.8 : 1 : 4.3	1	6.78	6.76	6.75	6.75	6.76	6.77
		2	6.77	6.78	6.74	6.74	6.76	
		3	6.79	6.79	6.76	6.78	6.78	
NPM5	0.8 : 1 : 5.3	1	7.26	7.25	7.25	7.26	7.26	7.24
		2	7.28	7.23	7.24	7.24	7.25	
		3	7.23	7.22	7.22	7.22	7.22	

Study in aqueous medium at 1 hour polymerization time and pyrrole prior addition

Table B-14 Electrical conductivity data of natural rubber/polypyrrole/montmorillonite composites (The third trial)

Sample code	Ratio of natural rubber : pyrrole : MMT (by weight)	Sample No.	Electrical conductivity (Scm^{-1})					
			σ_1	σ_2	σ_3	σ_4	$\sigma_{ave.}$	Average
NMP1	0.8 : 1 : 1.1	1	6.09	6.08	6.11	6.12	6.10	6.11
		2	6.12	6.12	6.13	6.13	6.13	
		3	6.09	6.09	6.10	6.10	6.10	
NPM2	0.8 : 1 : 2.1	1	6.41	6.39	6.39	6.40	6.40	6.37
		2	6.35	6.36	6.35	6.34	6.35	
		3	6.34	6.36	6.35	6.34	6.35	
NPM3	0.8 : 1 : 3.2	1	6.59	6.60	6.61	6.61	6.60	6.62
		2	6.63	6.63	6.64	6.64	6.64	
		3	6.62	6.65	6.63	6.62	6.63	
NPM4	0.8 : 1 : 4.3	1	6.85	6.84	6.84	6.83	6.84	6.84
		2	6.83	6.83	6.82	6.87	6.84	
		3	6.82	6.86	6.85	6.82	6.84	
NPM5	0.8 : 1 : 5.3	1	7.29	7.29	7.30	7.28	7.29	7.31
		2	7.32	7.33	7.32	7.32	7.32	
		3	7.29	7.31	7.29	7.32	7.30	

Study in aqueous medium at 1 hour polymerization time and pyrrole prior addition

Table B-15 Electrical conductive stability of natural rubber/polypyrrole composites (the third trial)

Sample code	Storing time (week)	Electrical conductivity (Scm^{-1})			
		#1	#2	#3	Average
PPy	0	7.15	7.14	7.15	7.15
	2	3.28	3.25	3.27	3.27
	4	1.94	1.90	1.93	1.92
	6	1.47	1.44	1.47	1.46
	8	1.20	1.18	1.19	1.19
	10	0.74	0.71	0.73	0.73
NP6	0	6.26	6.26	6.25	6.26
	2	2.52	2.51	2.51	2.51
	4	1.64	1.63	1.62	1.63
	6	1.24	1.24	1.23	1.24
	8	0.97	0.96	0.95	0.96
	10	0.68	0.67	0.67	0.67
NP7	0	5.39	5.40	5.38	5.39
	2	2.22	2.26	2.23	2.24
	4	1.52	1.54	1.48	1.51
	6	1.21	1.25	1.20	1.22
	8	0.83	0.86	0.81	0.83
	10	0.64	0.69	0.62	0.65
NP8	0	5.26	5.26	5.27	5.27
	2	2.17	2.17	2.18	2.17
	4	1.53	1.52	1.56	1.54
	6	1.35	1.35	1.37	1.36
	8	0.89	0.92	0.91	0.91
	10	0.70	0.71	0.74	0.72
NP9	0	3.15	3.15	3.13	3.14
	2	1.08	1.09	1.07	1.08
	4	0.69	0.65	0.66	0.67
	6	0.44	0.43	0.42	0.43
	8	0.21	0.22	0.19	0.21
	10	0.14	0.13	0.11	0.13
NP10	0	2.14	2.07	2.11	2.11
	2	0.59	0.47	0.57	0.54
	4	0.36	0.31	0.33	0.33
	6	0.15	0.10	0.12	0.12
	8	0.06	0.03	0.04	0.04
	10	0.01	0.01	0.01	0.01

Table B-16 Electrical conductive stability of deproteinized natural rubber/polypyrrole composites (the third trial)

Sample code	Storing time (week)	Electrical conductivity (Scm^{-1})			
		#1	#2	#3	Average
NP21	0	6.58	6.57	6.55	6.57
	2	3.50	3.48	3.46	3.48
	4	2.54	2.50	2.49	2.51
	6	1.85	1.82	1.80	1.82
	8	1.52	1.48	1.47	1.49
	10	1.34	1.32	1.31	1.32
NP22	0	5.64	5.66	5.63	5.64
	2	3.25	3.26	3.26	3.26
	4	2.26	2.29	2.25	2.27
	6	1.71	1.75	1.76	1.74
	8	1.44	1.43	1.42	1.43
	10	1.23	1.19	1.21	1.21
NP23	0	5.50	5.47	5.48	5.48
	2	2.97	2.93	2.95	2.95
	4	1.94	1.85	1.89	1.89
	6	1.65	1.54	1.63	1.61
	8	1.58	1.46	1.59	1.54
	10	1.26	1.18	1.23	1.22
NP24	0	3.38	3.36	3.37	3.37
	2	1.44	1.41	1.43	1.43
	4	0.73	0.70	0.72	0.72
	6	0.57	0.58	0.58	0.58
	8	0.46	0.42	0.46	0.45
	10	0.31	0.28	0.27	0.29
NP25	0	2.32	2.34	2.31	2.32
	2	0.63	0.65	0.64	0.64
	4	0.35	0.34	0.31	0.33
	6	0.14	0.15	0.15	0.15
	8	0.06	0.05	0.06	0.06
	10	0.01	0.02	0.02	0.02

Table B-17 Electrical conductive stability of natural rubber/polypyrrole/montmorillonite composites (the third trial)

Sample code	Storing time (week)	Electrical conductivity (Scm^{-1})			
		#1	#2	#3	Average
NP26	0	6.10	6.13	6.10	6.11
	2	3.46	3.48	3.46	3.47
	4	2.37	2.36	2.37	2.37
	6	1.73	1.73	1.72	1.73
	8	1.28	1.29	1.28	1.28
	10	1.02	1.03	1.02	1.02
NP27	0	6.40	6.35	6.35	6.37
	2	3.81	3.76	3.76	3.78
	4	2.54	2.49	2.49	2.51
	6	1.84	1.83	1.83	1.83
	8	1.35	1.31	1.31	1.32
	10	1.13	1.14	1.14	1.14
NP28	0	6.60	6.64	6.63	6.62
	2	4.18	4.14	4.14	4.15
	4	2.89	2.86	2.87	2.87
	6	2.14	2.13	2.13	2.13
	8	1.59	1.58	1.59	1.59
	10	1.27	1.24	1.26	1.26
NP29	0	6.84	6.84	6.84	6.84
	2	4.76	4.75	4.75	4.75
	4	3.42	3.41	3.40	3.41
	6	2.63	2.62	2.61	2.62
	8	2.06	2.07	2.07	2.07
	10	1.68	1.68	1.67	1.68
NP30	0	7.29	7.32	7.30	7.31
	2	5.55	5.57	5.56	5.56
	4	4.36	4.34	4.33	4.34
	6	3.27	3.31	3.28	3.29
	8	2.31	2.34	2.29	2.31
	10	1.99	2.03	2.01	2.01

APPENDIX C

Attenuated Total Reflectance
Fourier Transform Infrared Spectroscopy (ATR FT-IR)

The attenuated total reflectance FT-IR spectroscopy is a sampling technique based on internal reflection spectroscopy (IRS). The ATR technique rely on the intimate contact of a sample with the surface of a high refractive index, infrared transparent character or ATR prism, see Figure C-1. IR radiation entering the prism. Its energy was attenuated by absorption of the sample attached to the prism [37].

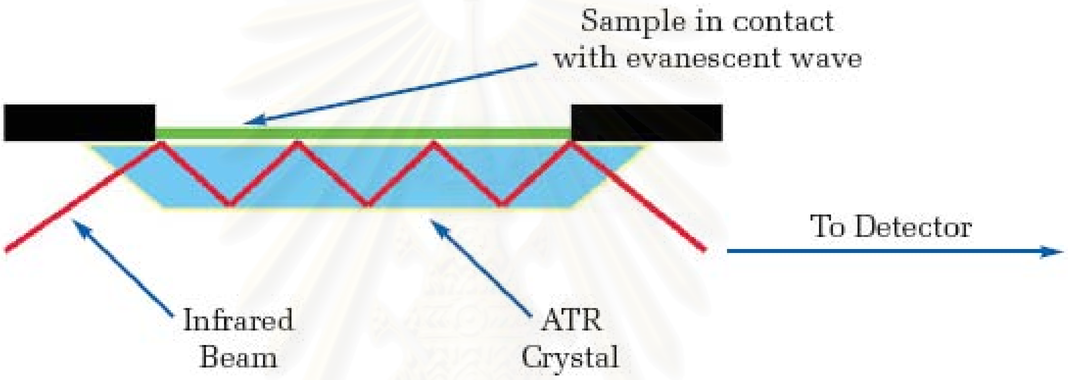

Figure C-1 Schematic diagram of internal reflection spectroscopy

Powders of the sample can be placed directly onto the IRE with application of a pressure plate clamp to achieve good contact. The sample on the surface of the ATR prism was analyzed by ATR FT-IR spectroscopy. The incident angle is important for obtaining absorption band. If the incident angle is small, the inner layer of polymer sample will be detected. Thus, in this investigation an incident angle of 45^{o} was employed to observe the outer layer only of polymer composite.

APPENDIX D

ATR FT-IR Spectra

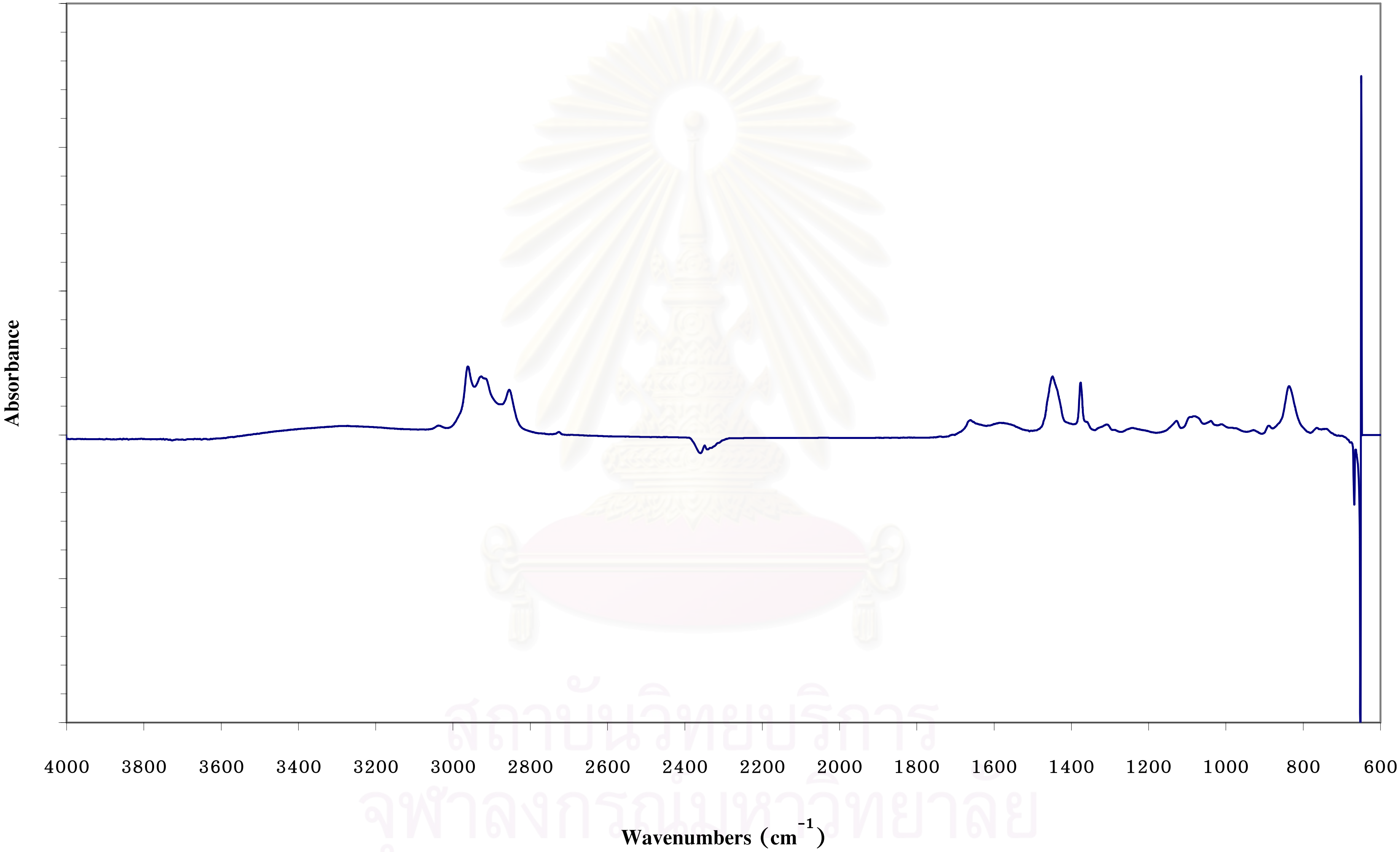

Figure D-1 ATR FT-IR spectrum of Natural rubber latex

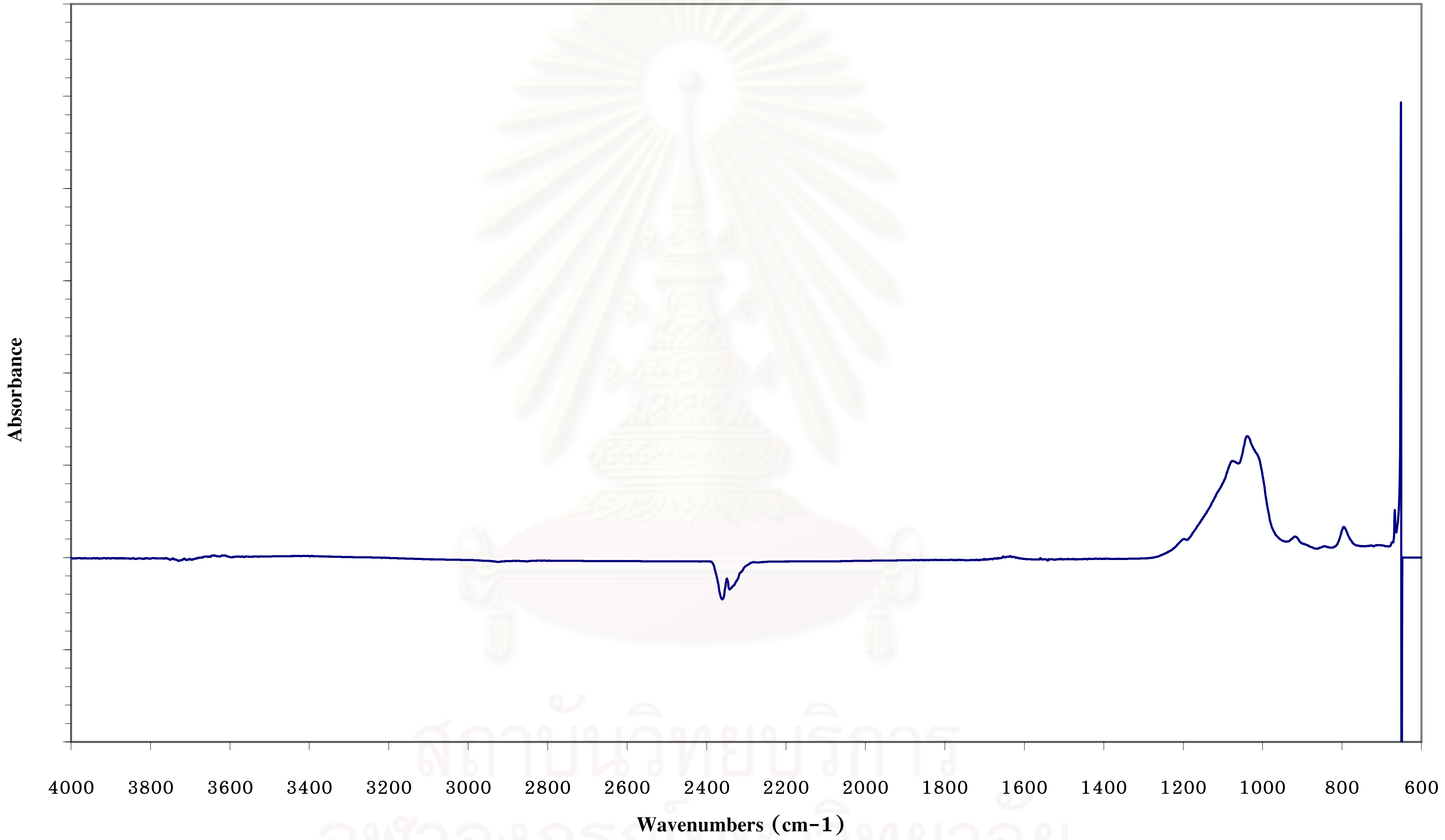

Figure D-2 ATR FT-IR spectrum of Montmorillonite

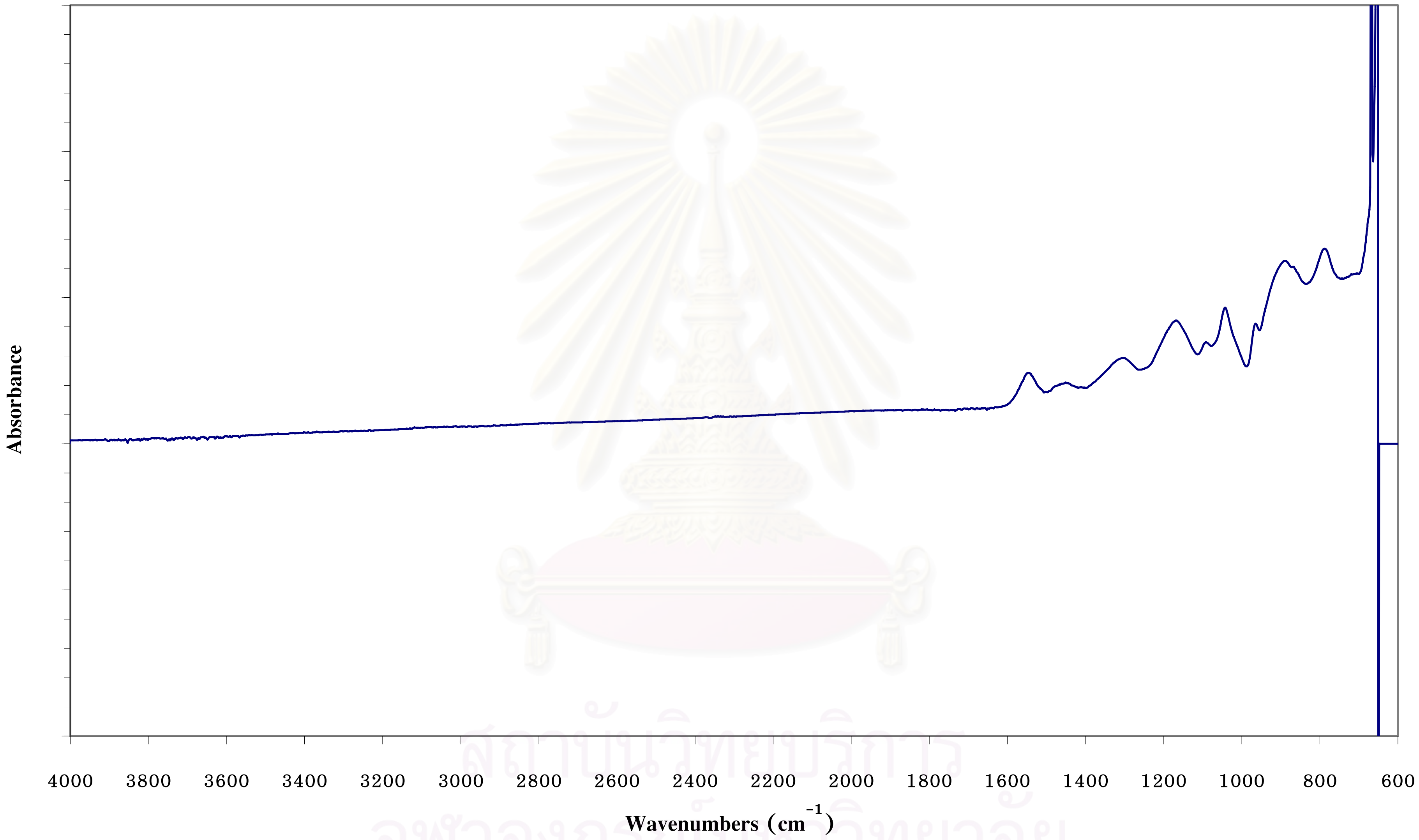

Figure D-3 ATR FT-IR spectrum of Polypyrrole

VITA

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