ฟิล์มพอลิพิโรลคอมโพสิตนำไฟฟ้าโดยพอลิเมอไรเซชันแบบไอเคมี

นางสาวอุทัยรัตน์ จิรพัฒนพงศ์

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต
สาขาวิชาปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์
หลักสูตรปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์
คณะวิทยาศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย
ปีการศึกษา 2542

ISBN 974-334-509-4

CONDUCTIVE POLYPYRROLE COMPOSITE FILMS BY CHEMICAL VAPOR POLYMERIZATION

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A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Science in Petrochemistry and Polymer Science
Program of Petrochemistry and Polymer Science
Faculty of Science Chulalongkorn University
Academic Year 1999

ISBN 974-334-509-4

Thesis title	Conductive Polypyrrole Composite Films By Chemical Vapor Polymerization
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อาจารย์ที่ปรึกษาวิทยานิพนธ์ : รศ.ดร. ศุภวรรณ ตันตยานนท์,

อาจารย์ที่ปรึกษาวิทยานิพนธ์ร่วม : รศ.ดร. อนันตสิน เตชะกำพุช, 105 หน้า. ISBN 974-334-509-4

การเตรียมฟิล์มพอลิพิโรลคอมโพสิตโดยวิธีการออกซิเดชันทางเคมีแบบไอของโมโนเมอร์มี 2 วิธีคือ วิธีการละลายและวิธีการบวมตัว วิธีแรกละลายพอลิเมอร์รองรับในสารละลายเฟอริกคลอไรด์โดยมีเตตระไฮโดรฟูแรนด์เป็นตัวทำละลายจากนั้นทำการหล่อขึ้นรูปแผ่นฟิล์มแล้วนำไปสัมผัสไอของพิโรล วิธีที่สองแช่ฟิล์มพอลิเมอร์รองรับในสารละลายเฟอริกคลอไรด์โดยมีเตตระไฮโดรฟูแรนด์เป็นตัวทำละลายเพื่อให้เกิดการบวมตัวจากนั้นนำไปสัมผัสไอของพิโรล ฟิล์มคอมโพสิตสามารถวิเคราะห์ด้วยเทคนิคอินฟราเรด สเปกโตรสโคปี ค่าการนำไฟฟ้าวัดได้โดยใช้วิธี วาน เดอ พาว ในกรณีที่ใช้วิธีการละลายได้ใช้ความหนาของฟิล์มคอมโพสิตในการคำนวนสภาพนำไฟฟ้าของฟิล์มคอมโพสิต และมีการศึกษาถึงปัจจัยต่างๆ ที่มีผลต่อค่าการนำไฟฟ้า เช่น ความเข้มข้นของสารละลายเฟอริกคลอไรด์ อุณหภูมิในการทำปฏิกิริยาและเวลาที่ใช้ในการทำปฏิกิริยา พบว่าค่าการนำไฟฟ้าเพิ่มขึ้นเมื่ออุณหภูมิในการทำปฏิกิริยาต่ำ เวลาที่ใช้ในการทำปฏิกิริยาลดลงและความเข้มข้นของสารละลายเฟอริกคลอไรด์เพิ่มขึ้น ฟิล์มพอลิพิโรลคอมโพสิตที่เตรียมจากวิธีการละลายสามารถ ยืนยันได้จากการตรวจวิเคราะห์ทาง สแกนนิงอิเลกตรอนไมโครสโคปี และ ทรานสมิสชันอิเลกตรอนไมโครสโคปี ว่าพอลิพิโรลสามารถกระจายตัวในพอลิเมอร์รองรับได้ดีกว่าฟิล์มพอลิพิโรลคอมโพสิตที่เตรียมจากวิธีการบวมตัว นอกจากนั้นมีการศึกษาถึงความสามารถในการคงตัวต่อความร้อนและความสามารถในการคงตัวต่อเวลาของฟิล์มคอมโพสิต

สาขาวิชา...ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์... ลายมือชื่อนิสิต...
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ปีการศึกษา...2542... ลายมือชื่ออาจารย์ที่ปรึกษาร่วม...

4072470223 : MAJOR PETROCHEMISTRY AND POLYMER SCIENCE
KEY WORD: POLYPYRROLE / POLYVINYL CHLORIDE / POLYSTYRENE / POLY(SODIUM 4-STYRENE SULFONATE) / VAPOR POLYMERIZATION

UTHAIRAT JIRAPATANAPONG : CONDUCTIVE POLYPYRROLE COMPOSITE FILMS BY CHEMICAL VAPOR POLYMERIZATION
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105 pp. ISBN 974-334-509-4

Polypyrrole composite films were prepared by chemical oxidation of the vapor monomer using two different methods, dissolving and swelling method. In the first method, polymeric matrices were dissolved with $FeCl_3$/THF solution, then casting as film, and exposed to pyrrole vapor. In the second method, polymeric matrices films were swollen in an $FeCl_3$/THF solution and exposed to pyrrole vapor. The composite films were characterized by FT-IR spectroscopy. Their conductivity was determined by Van der Pauw method. In case of the dissolving method, it was assumed that the thickness of the composite film was the thickness of polypyrrole layer. Several factors influenced on conductivity were investigated such as $FeCl_3$ concentration, reaction temperature and reaction time. The conductivity of the polypyrrole composite films increased by decreasing polymerization temperature, decreasing polymerization time and increasing $FeCl_3$ concentration. It was found that polypyrrole composite film obtained by dissolving method, polypyrrole could disperse into matrix better than one obtained by swelling method as revealed by SEM and TEM. Mechanical property, thermal stability and time-decay of the composite films were also investigated.

สาขาวิชา ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์ ลายมือชื่อนิสิต..........
หลักสูตร ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์ ลายมือชื่ออาจารย์ที่ปรึกษา..........
ปีการศึกษา 2542 ลายมือชื่ออาจารย์ที่ปรึกษาร่วม..........

ACKNOWLEDGEMENTS

The author would like to express her deepest gratitude to her advisor, Associate Professor Supawan Tantayanon, Ph.D., for her advice, concern and encouragement throughout this research. She is grateful to Associate Professor Anantasin Techagumpuch, Ph.D. for his guidance and valuable advice.

In addition, She is also grateful to the chairman and members of the thesis committee for their valuable suggestions and comments.

Thanks go towards everyone who has contributed suggestions and supports throughout this work. Finally, She is very deep and thanks to her family for their love, support and encouragement.

CONTENTS

CHAPTER

CONTENTS (continued)

CONTENTS (continued)

CONTENTS (continued)

PAGE

CONTENTS (continued)

LIST OF TABLES

LIST OF TABLES (continued)

LIST OF TABLES (continued)

LIST OF FIGURES

FIGURE PAGE

LIST OF FIGURES (continued)

PAGE

LIST OF FIGURES (continued)

ABBRAVIATIONS

°C	degree Celsius
cm	centimeter
d	thickness of sample
R	resistivity
V	potential difference
I	current
σ	conductivity
mA	milliampere
mV	millivolt
M	mole per litter
PVC	polyvinyl chloride
PS	polystyrene
PSS	poly(sodium-4-styrene sulfonate)
Scm^{-1}	siemens per centimeter

CHAPTER I

INTRODUCTION

1.1 Development of conducting polymer

Electrical conductivity is fundamental property which distinguishes metal from polymer. The value of conductivity for metal is the order of 10^4-10^6 S/cm, whereas for insulating polymer this value does not exceed 10^{-14} S/cm. However, after the development of electrically conducting polymer nearly two decades ago, the line dividing electrical properties of metals, semiconductors and polymers has become less distinguishable. Thus some polymers can be used as electrical material.

The advantage of conducting polymer are electrical conductivity, light weight, strong, inert, greater workability and low temperature processing capability. Intrinsically conductive polymers present very interesting properties which have potential their application in several technological sectors [1,2], such as rechargeable batteries, electrochromic displays, electronic devices as schottky type diodes, field effect transistors, electrochemical sensors, electrical shielding for information-carrying cables, electromagnetic interference (EMI), electrical insulator (no electricity passes through them), membrane separation that is in-situ control of molecular interaction act as molecular gates, using as appropriate electrical stimuli, selected ion, controlled release, sensor.

The term conducting polymer originated over a decade ago with the discovery of polyacetylene. The most important structural feature of polyacetylene is its highly conjugated carbon backbone composed of an array of alternating single and double bonds. The conjugated backbone is the key of conductivity, therefore, organic conducting polymer, based on similar fundamentals, have been generated in the 1980s. Conducting polymer is conjugated polymeric backbone which allow electron transfer when the materials are in certain oxidation states. Examples of conducting polymers are polypyrrole, polythiophene, polyaniline, etc.

However, polyacetylene is unstable under ambient condition, but polypyrrole, polyaniline and polythiophene have stability. High electrical conductivity and the stability of conducting polymer are important for their applications. Polypyrrole is one of the most widely studied conducting polymer due to its easy synthesis and overall interesting properties. Polypyrrole was shown to be a conducting polymer in 1968 [3]. It was prepared by oxidation of pyrrole in sulfuric acid and was black powder. The five member ring of pyrrole polymerizes through 2,5-position, Figure 1.1.

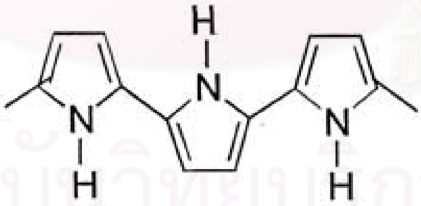


Figure 1.1 The structure of polypyrrole molecular chain

Polypyrrole can be produced in the form of powders, coatings or a film and is intrinsically conductive. The synthesis of polypyrrole was studied to obtain high conductivity both in electrochemical polymerization and chemical polymerization method. Electrochemical polymerization gives pure, high molecular weight polypyrrole and eliminate the need for strong oxidizing or hazardous agent but it has low yield. Chemical polymerization gives large quantities polypyrrole but the product is insoluble, infusible. So that it is difficult to use in industry processing. Although polypyrrole has high conductivity and rather stable in atmosphere, it is hard and brittle material. Many factors for preparation such as reaction time, reaction temperature, dopant affect properties of polypyrrole.

1.2 Conducting polymer composite

Disadvantages of polypyrrole are insoluble in any solvent, high melting point, their poor mechanical properties and processability constitute major obstacles to their extensive application. Some procedure has used to avoid these problems, the preparation of conducting polymer composite is one of other method to improve the mechanical properties and processability. Composites are available by a variety of blending techniques as well as by synthesis of the conducting polymer within a host matrix [4].

Mechanical properties are usually determined by the matrix of non-conducting polymer so long as the fraction of the conducting phase is low enough. But the appropriate system consisting of a non-conducting matrix and a conducting phase be available in such a way that the non-conducting matrix allows the penetration of conducting species. Improved structural order as achieved by stretching leads to material with higher conductivity and stability. While intrinsically conducting polymers embedded in matrix of non-conducting polymer is a possible method to introduce flexibility and toughness into conducting material. Good mechanical properties can be achieved if the content of the intrinsically conducting polymer is kept as low as possible.

The simplest conducting composites consists of a fine metal or carbon powders dispersed uniformly throughout an insulating plastic matrix were investigated. Polypyrrole is chosen for composite research because conductivity and stability of polypyrrole are good. Generally, blends of polypyrrole and insulating polymers can be chemically prepared by different methods [5].

1. An insulating polymer is dissolved in a solution of an oxidizing agent, then pyrrole is added under stirring [6,7]. Stabilized polypyrrole colloidal solution is evaporated for giving powder composite .

2. Polymeric films or textiles are covered by polypyrrole, the insulating matrix is immersed in a mixture of oxidizing agent and pyrrole [8].

3. An insulating polymer is used for separating a monomer solution and solution of an oxidizing agent. The monomer and oxidant diffuse across the matrix and interfacial polymerization occurs [9,10].

4. An insulating polymer is swollen in an oxidizing agent, followed by exposure to pyrrole vapor [11-14].

5. An insulating polymer and oxidizing agent are mixed, following by film casting by solvent evaporation. The matrix containing oxidant are subsequently exposed to monomer vapor [15,16].

The insulating polymers such as polystyrene, poly(vinyl chloride) and poly(methyl methacrylate) were investigated. However, conductivity of polymer composites has not been exhibited yet and polymer composites are not good enough for commercial applications. Materials that present conductivities in the range of 1 to 10 S/cm, are very efficient in electromagnetic shielding [2]. Blends containing a conductive and an insulating polymer have an overall conductivity lower than that of the pure conductive polymer. It is possible to obtain blends which associate a reasonable electrical conductivity with suitable mechanical properties, making possible their utilization for electromagnetic radiation shielding and anti-static pakaging.

So the improvement of composite properties to ease the application work is very important. This research is a study of parameter effect on conductivity, stability and processability of polymer composite.

1.3 Objective of research

The purpose of research is to prepare a highly conductive polypyrrole composite films by chemical vapor polymerization. Various type of insulating polymer are used to produce conductive polypyrrole composite. The major conditions such as ferric chloride concentration, reaction temperature and reaction time, that influence the quality of polymer composite are investigated. Electrical conductivities of polypyrrole composites are measured by Van der Pauw method. Some instruments are used to characterize the properties of polymer composites.

CHAPTER II

THEORETICAL BACKGROUND AND LITERATURE REVIEW

The electrical properties of any material are determined by the extent of occupation of the energy bands and the magnitude of the band gap so that band theory is the essential basic concept for understanding the electrical conduction of polymer.

2.1 The classical theory for electrical conductive material

Band theory [17] is the main information for explaining electrical conduction behavior in materials. According to the theory, the lowest-energy orbital is bonding (valence band; VB) and the highest-energy orbital is anti-bonding (conduction band; CB).

1. Metal

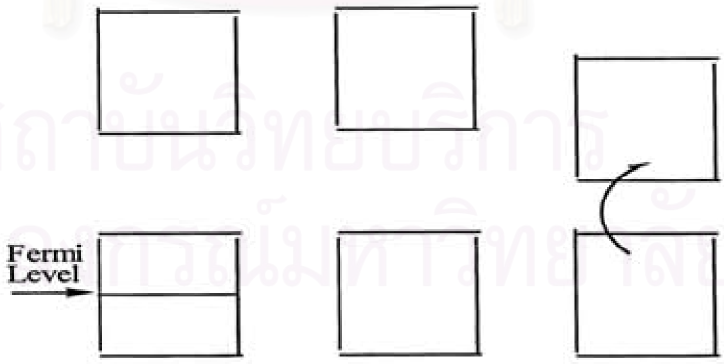
The simple model is shown in Figure 2.1 (a). The orbital in the band is so close together, electrons close to the top of the filled orbital. The energy level of the empty orbital is very close to that of lined orbital. Some of the electrons are, therefore, very mobile, and give rise to electrical conductivity.

2. Insulator

In these materials, show in Figure 2.1 (b), the valence band is completely filled and an energy gap exists between the band and the next higher energy band. The energy gap is very large, the chance of electrons to be excited into an empty conduction band is very small.

3. Semi-conductor

In semi-conductor materials, the energy gap is small, some electron can be easily excited into the CB. In some cases, when the impurity atoms are added into the materials, although the band gap is wide, it may be possible to establish level within the gap those facilitates the movement of electrons into CB. Another way of forming carriers is to introduce impurities in ultra-pure material. If these impurities can withdraw electrons from the full band, leaving holes which permit conduction; this is p-type semi-conductivity. Alternatively, the impurity might carry excess electrons and these electrons swim in the empty bands, giving n-type semi-conductivity.



(a) (b) (c)

Figure 2.1 Band filling (a) metal, (b) insulator, (c) semi-conductor

The previous description presents the concept of electrical conductivity in ordinary materials, which are used in worldwide application for long time ago. This concept, however, is not quite correct for the new materials, which have long molecular chain, such as polymer, the feature of electrical transport in these materials is very complicated and different from the traditional conductive materials.

2.2 Electrical conductive polymer [18-21]

Each monomer unit of polymer consists of molecular orbitals of the molecule, thus bonding and anti-bonding molecular unit orbitals lead to polymer valence bands and conduction bands, respectively. Organic materials exhibit semi-conducting electrical behavior because in the solid state, organic molecules interact weakly as molecular van der Waals or electrostatic forces. In a linear polymer electron interactions within a given macromolecular chain are much stronger than interaction between chains. Therefore, most polymers, the macromolecules are not packed into perfect single crystals.

Conjugated polymer without doping (i.e. oxidation and reduction) are insulators or semiconductors at best. The chain is thermodynamically more stable by lowering its free energy through the transition from the resonance structure of identical bond length to the alternating short and long bonds, which in effect will destroy the electronic delocalization that can take place along the backbone.

When conjugated polymer is doped, it occurs carrier transport. The initial species formed on ionization of a conjugated polymer is radical ion which possesses both spin and charge, the radical ion is referred to polaron. A polaron is either radical cation or radical anion. If another electron is remove from the already oxidized polymer containing the polaron, electron could come from either a different segment of the polymer chain, thus creating another independent polaron, or from the first polaron level (remove the unpaired electron) to create a special dication, it is called bipolaron. A bipolaron is a pair of charges.

Polypyrrole possess a non-degenerate ground state since ground state corresponds to aromatic-like. A quinoid-like resonance structure can be envisioned but has a higher total energy. The quinoid structure has a larger electron affinity than the aromatic structure. On doping, geometry relaxes toward the quinoid structure, following Figure 2.2.

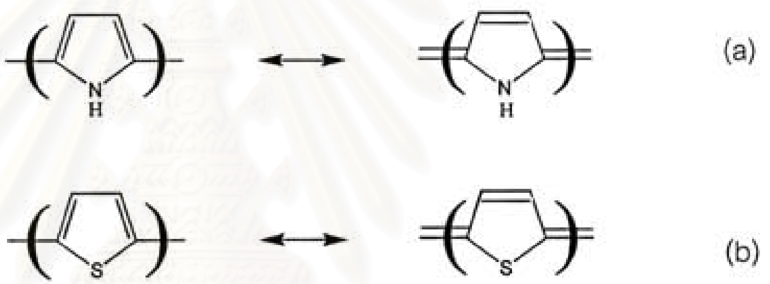


Figure 2.2 Aromatic and quinoid like geometric structure for (a) polypyrrole (b) polythiophene

PPy without doping is a poorly conducting material with a band gap of 3.2 *eV* between the conduction and valence bands. Oxidation removes one electron to form a polaron (radical cation). When further oxidation removes a second electron from the backbone, a bipolaron (dication) is formed. A bipolaron is thermodynamically more stable that of two polarons. The formation of polaron and bipolaron creates new electronic states in the interband gap, and leads to a structural change of the polymer to quinoid form extending over four monomer units. Both polarons and bipolarons can move along the conjugated backbone by the rearrangement of the double bonds and single bonds.

Thus, polarons and bipolarons behave as the charge carriers in the electrical conduction of PPy. As quantum chemical calculations of the structure of PPy suggest that the quinoid form is a more conductive species than the benzoid form, the association of the quinoid structure with the formation of polaron and bipolaron is not a mere structural coincidence. On dedoping (reducing) PPy, the conductivity of the polymer decreases very rapidly with the dedoping time due to the loss of polarons and bipolarons.

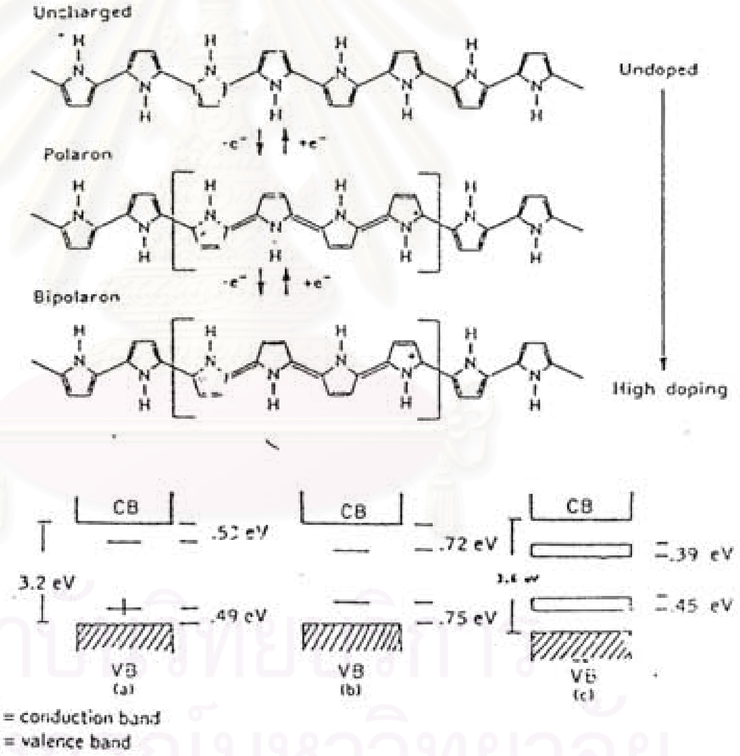


Figure 2.3 Evolution of the electronic structure of PPy following the formation of polaron and bipolaron along the backbone, (a) low doping, polaron formation: (b) moderate doping, bipolaron formation, (c) high doping formation of bipolaron bands

Theoretical studies on polypyrrole, demonstrate that

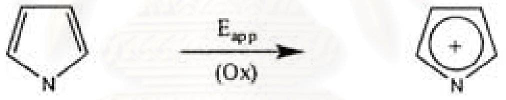
1. polarons are formed on the chains at low oxidation level
2. wide bipolaron bands are present in the gap in the highly oxidation level.

2.3 Synthesis of polypyrrole

2.3.1 Electrochemical polymerization [1]

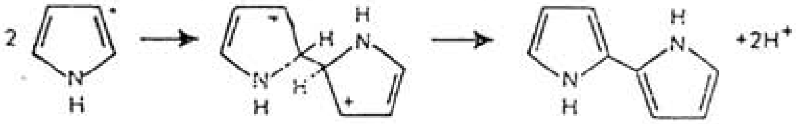
Conducting polymer is obtained by anode oxidation or cathode reduction of monomer which is involved in supporting electrolyte. Steps of this method are very complicated and shown in Figure 2.4.

1. Monomer oxidation



2. Resonance forms

3. Radical-radical coupling



4. Chain propagation

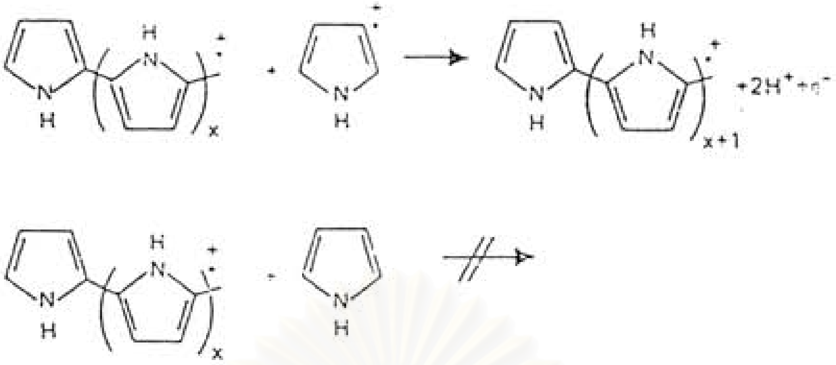


Figure 2.4 Steps in the electropolymerization of pyrrole

Polypyrrole is formed in solution at electrode surface and operated free-standing film. The polymerization reaction proceeds until dopant is incorporated and eventually the solubility of polypyrrole in solution is exceeded, causing deposition onto the electrode. Polypyrrole grows at active site on the electrode and provides a unique opportunity, in that a wide range of counterions (A^-) can be incorporated. Counterions are cation and anion (e.g. ClO_4^-). Interaction types of polypyrrole and counterion are ionic, ionic-dipole, H-bonding, dipole induction. One or more of molecular interaction can be encouraged by incorporation appropriate counterion.

Electrochemical polymerization gives pure, high molecular weight polypyrrole and eliminates the need for strong oxidizing or hazardous agent but it has low yield. The electrochemical polymerization approach provides polypyrrole in the matrix of thermoplastic polymer with higher conductivity, a technical possibility here is the electrochemical of monomer-swollen matrix coated as film onto an anode, but disadvantage is low penetration of monomer into insulating polymeric substrate. Therefore, the procedure is limited to very thin film.

2.3.2 Chemical polymerization in solution [22]

This method can be used to produce conductive electroactive polymer. Polymerization is readily initiated, using a chemical oxidant such as $FeCl_3$, $AgNO_3$, $Fe(NO_3)_3$, etc. Mole ratio of $FeCl_3$/pyrrole is 2.33/1. Steps of chemical polymerization are shown in Figure 2.5.

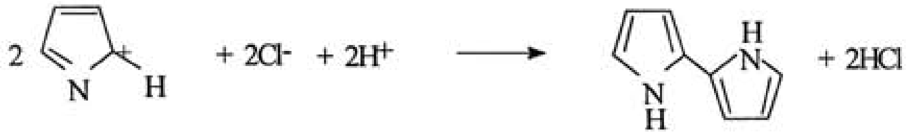
1. Dissociation of $FeCl_3$

$$FeCl_3 \longrightarrow Fe^{3+} + 3Cl^-$$

2. Monomer oxidation

3. Resonance forms

4. Pyrrole ion coupling



5. Reaction stoichiometries of pyrrole

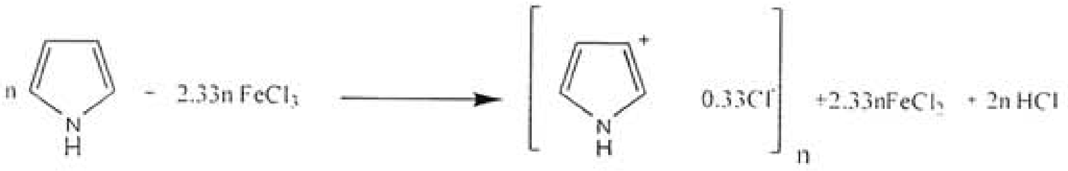


Figure 2.5 Steps of chemical polymerization of polypyrrole

Figure 2.5 shows that 2.33 mole $FeCl_3$ is required for the polymerization of one mole of pyrrole. Polypyrrole in large quantity can be prepared by this method.

2.3.3 Chemical vapor polymerization [23]

Takeaki et al. prepared firstly the conducting composite films of polypyrrole by exposing polymeric matrix film containing ferric chloride to pyrrole vapor. The composite film are highly transparent under the appropriate preparation condition. Poly(vinyl alcohol) (PVA) was used as polymeric matrix. $FeCl_3$ was an oxidizing agent for the polymerization. After dissolving PVA and $FeCl_3$ in the water, the solution was casted on a poly(ethylene terephthalate) (PET) film substrate. The preparation of pyrrole-PVA composite films was carried out in a desiccator at –15 °C by exposing PVA films containing $FeCl_3$ on the PET film to the pyrrole and H_2O vapors which had been deoxygenated sufficiently. The polymerization period was from 30 minutes to 24 hours. The composite films were then dried under vacuum at room temperature. At optimum condition, the composite film shows about 10 S/cm conductivity.

2.4 Literature review

Many polypyrrole composites were synthesized to improve properties i.e., high conductivity, good mechanical strength and easy processability.

Kurachi et al. [24] prepared polypyrrole/polyethylene (PPy/PE) composite films by the vapor-phase polymerization of pyrrole. PE porous films (average thickness of 10-12 μm, average pore size of 0.03 μm) were impregnated with appropriate oxidant e.g. $FeCl_3$ or $Fe(ClO_4)$ and evaporating the solvent in the air. The conductivity of the composite films increased by lowering polymerization temperature. A strong function of the oxidation potential of oxidant solutions which was impregnated into the PE films prior to the polymerization of pyrrole affected on conductivity. Maximum conductivity was obtained using short chain alcohol as solvent. Conductivity value was about 0.1-10 S/cm. It was found that the composite film have excellent mechanical properties compared to PPy.

Yang et al. [25] prepared polypyrrole/polypropylene (PPy/PP) composite films using a two direction permeation diffusion polymerization method. PP microporous films were fixed between pyrrole solution and $FeCl_3$ solution in u-type reactor. The maximum conductivity was 6.0 S/cm. The mechanical properties of the composite films were better than PPy film which synthesized by electrochemical polymerization in aqueous solution.

Kang et al. [11] studied polypyrrole/polyvinyl chloride (PPy/PVC) composite films. Pyrrole had been diffused into PVC matrix in the swelling medium of n-hexane and acetone mixture. The oxidative polymerization of the diffused pyrrole in the binary solvent system of acetonitrile and methanol gave high conductivity of the PPy as well as the good penetration of the oxidant into the PVC matrix. The mole ratio of acetonitrile to methanol in the binary solvent system with 1.0 mole of $FeCl_3$ showed optimum in range of 0.80 to 0.85. The thickness of the conducting layer was measured to be about 1.0 μm. The electrical conductivity was measured as high as 20 S/cm.

Mano et al. [26] prepared PPy/PVC composite films. PVC films which impregnated with $FeCl_3$ were obtained by casting a tetrahydrofuran (THF) solution containing PVC and $FeCl_3$. THF was evaporated at 45 °C and the films were dried in vacuum at ambient temperature. The PPy/PVC films were obtained by exposure of $FeCl_3$/PVC films to pyrrole vapor. Conductivity of composite films varied from 10^{-4} to 10^{-1} S/cm.

Kise et al. [27] prepared a composite film of PPy and PVC by oxidative polymerization of pyrrole at the interface between an aqueous oxidant (Fe (III) salts) solution and an organic phase consisting of a benzene or toluene solution of pyrrole separated by a thin PVC film (thickness 90-100 μm). The reactants diffuse across the film polymerizing pyrrole in or at the surface of the film. The nature of the oxidant-deriving anions influences strongly the conductivity of the composite films.

Jousse et al. [28] prepared a composite film of PPy and PVC. Those thermoplastic composites reach conductivity in the range between 10^{-5} and 1 S/cm already for polypyrrole concentrations less than 15%. As describing elsewhere, parameters such as solvent and nature of the oxidizing agent determine the properties like structure and conductivity of the composite.

Fabianowski et al. [29] studied polypyrrole/polyvinyl alcohol (PPy/PVA) composite film. Values of conductivity close to that of pure pyrrole are reported exposing films of PVA treated with $K_3Fe(CN)_6$ to pyrrole vapor. A relationship between the reaction time and the amount of incorporated polypyrrole and the conductivity of the composite is investigated. $FeCl_3$ and $Fe(ClO)_4)_3$ give composites with higher conductivity than those obtained with $Fe(SO_4)_3$ or $Fe(NO_3)_3$ but $Fe(ClO)_4)_3$ as oxidant gave hard and brittle composites. Decrease of reaction temperature causes the content of pyrrole to decrease but the conductivity of the composite to increase. High electrical conductivity of composite films were 15 S/cm.

He et al. [30] studied polypyrrole/polyurethane composite foam. Polyurethane foam was impregnated with $FeCl_3$ in methanol and dried in vacuum. The foam was exposed to pyrrole vapor. Conductivity increased with increase in oxidant content in polyurethane. Lower reaction temperatures were preferable for higher conductivity of 10^{-3} S/cm.

Zoppi et al. [2] studied elastomeric blends based on EPDM-rubber/polypyrrole. Rubber and oxidant were mixed by calendering. $CuCl_2$-containing matrix of the rubber are accessible by sorption of pyrrole vapor. The particle size of the oxidant influences significantly the weight fraction of polypyrrole in the blend if the value is kept below 106 nm whereas no significant influence of the oxidant concentration and the polymerization time on the polypyrrole weight fraction is measured. After 72 hours of exposure to pyrrole vapor at high oxidant concentration (50%), only a slight increase in the Young's Modulus from 2.2 to 3.9 MPa and the conductivity from 10^{-9} to 10^{-7} S/cm was measured.

Tieke et al. [31] studied electrical conductivity with high thermal stability up to 350 °C is combined in polypyrrole/polyimide composite films, which are prepared either by electrochemical polymerization of pyrrole on a polyimide coated electrode or by exposing polyimide films containing $FeCl_3$ as oxidant to pyrrole vapor. Films prepared by the electrochemical route consist of sequence of three layers with the polyimide sandwiched between the layers of the polypyrrole. These films show maximum conductivity of about 10 S/cm. The chemically manufactured films consist of polyimide containing finely dispersed polypyrrole particles of 10 to 500 nm in diameter with a maximum conductivity of $5X10^{-4}$ S/cm.

However, previous researches were limited by diffusing of oxidant inside the film. This obstacle could be partly avoided by the use of insulating films, in which the ionic dopant was already bound to the polymer backbone, viz ionomers

Zinger et al. [32] prepared polypyrrole/polyethylene-base films grafted with poly(styrene sulphonic acid) (PPy/PE-*g*-PSSA) composite films. PE films were grafted with polystyrene (PS) then PE-*g*-PS films were sulfonated by sulphuric acid. PE-PSSA films were immersed in a $FeCl_3$ solution and polymerized with pyrrole. Electrical conductivity varied range of 0.1-10 S/cm. Mechanical properties were improved.

De Jesus et al. [33] studied polypyrrole/polystyrene sulfonate (PPy/PSS) composite films. Electrically conductive composite surfaces were prepared by diffusion-controlled in-situ polymerization of pyrrole in the surface layer of sulfonated polystyrene ionomer films. Premolded films of the ionomer sulfonic acid derivative were sequentially immersed in aqueous solutions of pyrrole and $FeCl_3$. The penetration of the PPy into the film was controlled by varying the immersion time in monomer solution. Surface conductivity of 10^{-4}-10^{-1} S/cm was achieved.

Somchoke Lauhasurayothin [37] prepared polypyrrole (PPy) composites. PPy was synthesized by chemical oxidation method in the presence of PS particle using

$FeCl_3$ as the oxidant. PPy was covered on PS and analyzed by attenuated total reflectance spectroscopy. The other host polymers were attempted including polyvinyl chloride (PVC), polyethylene (PE) and polypropylene (PP). The results indicated that PPy/PS composite and PPy/PVC composite have the conductivity as high as 10 S/cm.

CHAPTER III

EXPERIMENT

3.1 Instruments

1. Fourier Transform Infrared Spectrometer (FT-IR); Nicolet Impact 410
2. Thermogravimetric Analyser (TGA); Perkin Elmer
3. Transmission Electron Microscope (TEM); JEOL-JEM-200 CX
4. Scanning Electron Microscope (SEM); JEOL-JSM-6400

3.2 Materials and chemicals

1. Polyvinyl chloride powder K-61 (PVC)	APAC Plastic co.,.Ltd.
2. Polyvinyl chloride films K-61	APAC Plastic co., Ltd.
3. Polystyrene films MI 8 (PS)	Thai Modern co., Ltd.
4. Polystyrene pellet MW 100,000	Eternal Resin co., Ltd.
5. Poly(sodium 4-styrene sulfonate) MW 70,000 (PSS)	Aldrich
6. Pyrrole	Merck
7. Anhydrous ferric chloride ($FeCl_3$)	Fluka
8. Tetrahydrofuran (THF)	Unilab
9. Methanol (CH_3OH)	Analar

3.3 Glasswares and equipments

1. Beaker
2. Vacuum Desiccator dimension 11 cm
3. Digital Multimeter
4. Water Pump
5. Refrigerator

3.4 Preparation of materials

3.4.1 Pyrrole monomer

Pyrrole was distilled at 110-120 °C as colorless liquid. The distillate was stored at 4 °C for not more than 1 week.

3.4.2 Oxidation solution

Ferric chloride ($FeCl_3$) was dissolved in tetrahydrofuran (THF) and filtered before use. Concentration of $FeCl_3$ solution was varied 0.01-1.00 M in case of dissolving method and 0.10-1.25 M for swelling method.

3.4.3 Preparation of poly(sodium 4-styrene sulfonate) films

To obtain poly(sodium 4-styrene sulfonate) films, with 380 μm thickness, 1.03 g of poly(sodium 4-styrene sulfonate) powder was dissolved in 5 ml distilled water. This solution was casted on a glass plate, with rim height 5 mm, then evaporated at 50 °C for 48 hours.

3.4.4 Preparation of polypyrrole composite films by dissolving polymeric matrices in $FeCl_3$ solution

Polymeric matrices were dissolved in $FeCl_3$ solution. Polymeric matrices and $FeCl_3$ solution were pipetted about 0.5 ml and casted on glass plate, with rim height 1 mm. The casting solution was evaporated at 50 °C in oven about 15 minutes then peeled it from glass plate. Films were yellow-orange transparency films.

Distilled pyrrole was injected to a beaker in desiccator. After that desiccator was evacuated and composite films prepared by dissolving polymeric matrices in $FeCl_3$ solution were polymerized at 10 °C for 2 hours. Green films were formed instantaneous when desiccator was evacuated. Black films were formed after polymerization. The polymerization reaction was quenched by opening stopcock. Polypyrrole composite films prepared by dissolving polymeric matrices in $FeCl_3$ solution were washed several times with methanol until solvent remained colorless and dried in air for 12 hours.

3.4.5 Preparation of polypyrrole composite films by swelling polymeric matrices in $FeCl_3$ solution

Polymeric matrices films were swollen in $FeCl_3$ solution by immersing films into solution, then evaporated at 50 °C in oven about 15 minutes. This procedure of polymerization is similar to the preparation of polypyrrole composite films by dissolving in $FeCl_3$ solution (Section 3.4.4).

3.5 Determination of condition effect

Polypyrrole composite films prepared by dissolving polymeric matrices in $FeCl_3$ solution and ones by swelling polymeric matrices in $FeCl_3$ solution were varied condition effect, as following;

3.5.1 Types of polymeric matrices

Polyvinyl chloride (PVC), polystyrene (PS), and poly(sodium 4-styrene sulfonate) (PSS) were used to study their effect on conductivity. The polymerization was carried out under the reaction conditions similar to Section 3.4.4.

3.5.2 Immersion time in $FeCl_3$ solution

Only polypyrrole composite films prepared by swelling polymeric matrices in $FeCl_3$ solution were varied immersion time from 1 to 20 seconds. In the same manner, the polymerization was administrated under the reaction conditions similar to Section 3.4.4.

3.5.3 $FeCl_3$ concentration

To study effect of $FeCl_3$ concentration on conductivity, polypyrrole composite films prepared by dissolving polymeric matrices in $FeCl_3$ solution, concentration of $FeCl_3$ was used at the concentration between 0.01 to 1.00 M and polypyrrole composite films prepared by swelling polymeric matrices in $FeCl_3$ solution, $FeCl_3$ were used at the concentration between 0.10 to 1.25 M. The polymerization of this section was carried out under reaction conditions similar to Section 3.4.4.

3.5.4 Reaction temperature

To investigate the effect of reaction temperature on conductivity, the polymerization was accomplished similar to Section 3.4.4 but temperature was changed from –15 °C to 45 °C. The temperature of reaction was controlled by various techniques. The temperatures of –15 °C and 10 °C were fixed by using refrigerator. Moreover the 30 °C temperature (room temperature) and the 45 °C were controlled by oven.

3.5.5 Reaction time

The polymerization was carried out under the same manner as in Section 3.4.4. The other parameters were kept constant except the reaction time was varied from 1 to 72 hours, for studying effect of reaction time on conductivity of polypyrrole composite films.

3.6 Characterization

3.6.1 Electrical conductivity measurement

Each sample was size 2.5X3.5 cm. Van der Pauw method is technique for measuring conductivity (σ) of samples. Four contacts are made at edge of the sample, Figure 3.1.

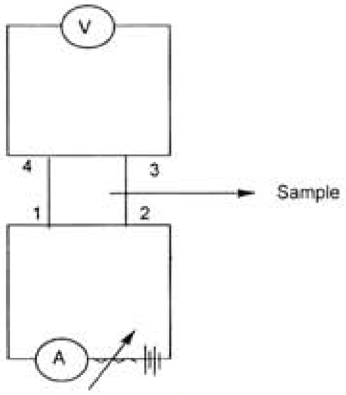


Figure 3.1 Conductivity measurement by Van der Pauw method

Current (I_{12}) applied through contacts 1 and 2 and potential difference (V_{34}) between contacts 3 and 4 were measured. Applied current was changed to get I_{12}, I_{23}, I_{34}, I_{41} and potential difference V_{34}, V_{41}, V_{12}, V_{23} was measured, respectively. From these measurements and from measured thickness d of the film, four values of conductivity of sample were obtained by Van der Pauw method (Appendix A) and the average value of the measurements was taken as conductivity of the sample.

3.6.2 Time-decay of polypyrrole composite films

Some of polypyrrole composite films were subjected to conductivity measurement at several interval time using Van der Pauw method. Polypyrrole composite films were suddenly measured conductivity after polymerized. They were next measured conductivity several times later, i.e. 3, 5, 10, 15, 30, 45, 60 and 90 days. These measurements show the stability of electrical conductivity.

3.6.3 Fourier transform infrared spectroscopy

The absorption spectra of polypyrrole composite films were obtained by using FT-IR. FT-IR is used to compare between pyrrole composite films and polymeric matrix.

3.6.4 Thermogravimetric analysis

Thermal stability of polypyrrole composite films was measured by thermogravimetric analysis (TGA). Sample weight is about 3-10 mg. Range of temperature is about 50-800 °C, for studying polymer decomposition.

3.6.5 Tensile strength

Toughness of polypyrrole composite film was tested by tensile strength. Standard method of test of tensile properties of polypyrrole composite films is ASTM D882. This test is used for thin film. Dimension is dumbell specimen. Length of narrow section is 5 cm and width of narrow section is 0.4 cm.

3.6.6 Transmission electron microscopy

Morphology of polypyrrole composite films was indicated by transmission electron microscopy (TEM). Samples were immersed in osmium solution for coating pigment on double bond of polymer.

3.6.7 Scanning electron microscopy

Morphology of polypyrrole composite films was investigated by scanning electron microscopy (SEM). Polypyrrole composite films were prepared by firstly coating with gold in order to discharge the electron from electron beam in electron microscope.

CHAPTER IV

RESULTS AND DISCUSSION

4.1 PPy/PVC composite films

Much work on the preparation of PPy/PVC composite films by electrochemical polymerization of pyrrole onto the electrodes coated with PVC film has been reported [4]. The electrical conductivity of those composite films were as low as 10^{-5} S/cm [28] up to the highest one of 50 S/cm [34]. Even though the electrochemical polymerization method would provide some composite films with high conductivity, it has disadvantage when a large quantity of product is required. On the other hand polypyrrole could be prepared by the chemical polymerization in a large quantity at one time.

There are two common ways of chemical oxidation i.e., polymerization in the presence of host matrix which is powder in an oxidant solution [35-37] and vapor polymerization onto the substrate which is a film containing an oxidant [11,26]. The latter method seems to have more advantages than the former one such as it is easier to manipulate the polymerization and the product is more ready for use due to the feature of composite in a film form. From the literature review, PVC containing oxidant was prepared by two different procedures, i.e., swelling of PVC film in a solution of monomer, followed by immersing it into oxidizing solution [11] and dissolving PVC in oxidizing solution, followed by casting and solvent evaporation [26], the matrices containing oxidant were subsequently exposed to monomer vapor. The conductivity of those composite films was reported to be from 10^{-4} to 20 S/cm [11,26]. Among these, the highest conductivity of PPy/PVC composite film prepared by dissolving was reported to be 10^{-1} S/cm [26], while by swelling method was 20 S/cm [11]. Although, the conductivity of PPy/PVC composite film prepared by dissolving method was lower than the one prepared by swelling method, in dissolving method PPy could be better incorporated into PVC than the other thus significantly improve the mechanical property of PVC matrix.

4.1.1 PPy/PVC composite films prepared by dissolving PVC in $FeCl_3$ solution

4.1.1.1 Preliminary investigation

Only the solvents in which PVC could dissolve were chosen in this study. Therefore PVC powder was dissolved in 0.25 M $FeCl_3$ solution in different solvents, i.e. chloroform, dichloromethane and THF at room temperature, then casted into thin films. It was observed that THF was the most suitable solvent for film forming, since discontinuous films were obtained when chloroform and dichloromethane were used as solvent. In this experiment, the film was exposed to pyrrole vapor at 10 °C. After 2 hours, it was observed that the yellow film turned black indicating that polymerization of pyrrole occurred on the surface of those films. The conductivity of the film was measured by Van der Pauw method which was found to be 0.10 S/cm, equal to the one reported by Mano et al. [26]. Mano et al. had prepared PPy/PVC composite film by dissolving PVC in $FeCl_3$ in THF, then casting as film and exposing to pyrrole vapor at room temperature. To improve the electrical conductivity of PPy/PVC composite film, several factors on preparation were thus investigated such as $FeCl_3$ concentration, reaction temperature and reaction time.

4.1.1.2 Effect of $FeCl_3$ concentration

In this study, $FeCl_3$ concentration in THF was varied from 0.01-1.00 M. At $FeCl_3$ concentration higher than 1.00 M, it was observed that PVC powder could not dissolve well. Figure 4.1 shows that the conductivity of PPy/PVC composite films increase with the $FeCl_3$ concentration.

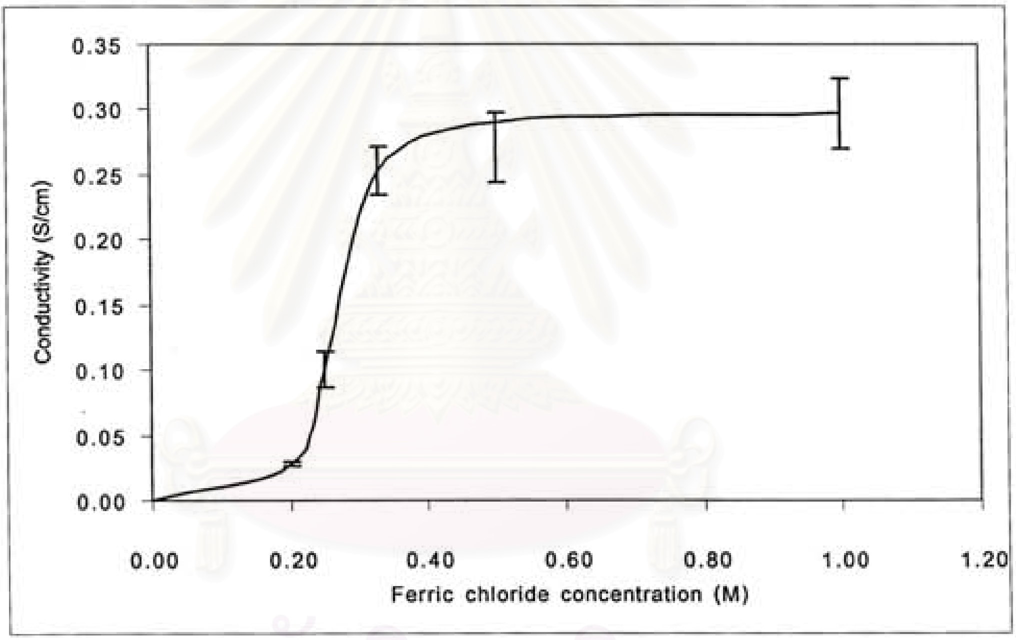


Figure 4.1 Effect of $FeCl_3$ concentration on the conductivity of PPy/PVC composite films prepared by dissolving method using 10 °C polymerization temperature and 2 hours polymerization time.

This can be explained by the fact that higher concentration of $FeCl_3$ results in higher polymerization rate. In addition, at higher concentration of $FeCl_3$ polypyrrole could have long conjugation and higher level of doping in the molecule.

This observation was similar to the one obtained by Bi et al. [38] who prepared polypyrrole/poly(*p*-phenylene terepthalated) composite fiber by continuous vapor phase polymerization, at temperature 40 °C. They reported that the increasing concentration of oxidize agent from 10 to 40% w/w improved the polymerization rate, conjugation length, the doping level of PPy and resulted in an increase of electrical conductivity from 0.08 to 0.68 S/cm. Moreover Mandel et al. [39] prepared polypyrrole/poly(vinyl methyl ether) (PVME) composites by oxidative polymerization of pyrrole in ethanol using 2.5 M $FeCl_3$ in the presence of PVME at 20 °C. They reported that conductivity of the composites increased greatly with increasing in $FeCl_3$ concentration.

However, PPy/PVC composite films developed at high $FeCl_3$ concentration have rough surfaces. The optimum $FeCl_3$ concentration which provided smooth PPy/PVC composite film was at 0.33 M which yielded the film with conductivity of 0.25 S/cm. It should be noted that the determination of electrical conductivity of the film by Van der Pauw method involved the thickness of polypyrrole layer as shown in Appendix A. For PPy/PVC composite films prepared by dissolving method polypyrrole was incorporated into PVC matrix. The conductivity of the films was thus calculated by using total thickness of PPy/PVC composite films.

4.1.1.3 Effect of reaction temperature

In this research group, it was reported previously that the optimum polymerization temperature for preparing polypyrrole with high conductivity was at 0 °C [37,40]. They reported that reaction temperature affected on intrinsic conductivity of PPy. In this work, the reaction temperature was varied from –15 °C to 45 °C. Figure 4.2

shows that conductivity of PPy/PVC composite film depends on reaction temperature and the highest conductivity would be obtained at temperature between 0-10 °C.

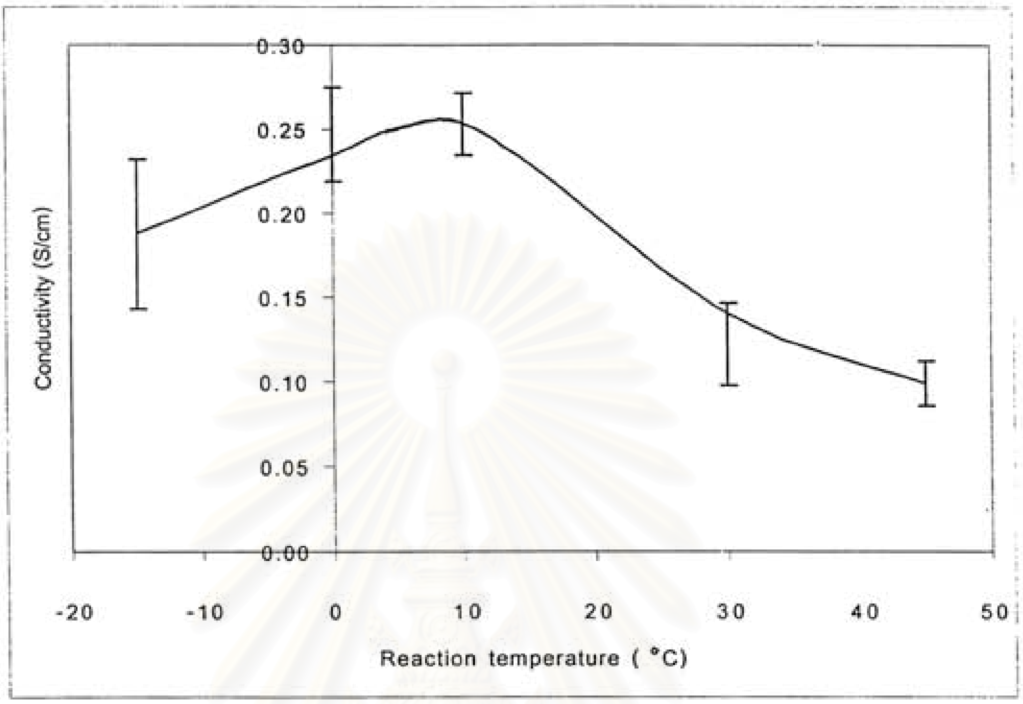


Figure 4.2 Effect of reaction temperature on the conductivity of PPy/PVC composite films prepared by dissolving method using 0.33 M $FeCl_3$ and 2 hours polymerization time.

Similar observations had been marked by several other research groups. For examples, Kaneto et al. [41] had prepared PPy film by electrochemical polymerization in an aqueous medium. They explained that at lower reaction temperature, PPy conductive composite films has higher conductivity owing to the fact that at low temperature structural features of polypyrrole have more extended conjugated double bonds. Besides, Kise et al. [24] prepared polypyrrole/polyethylene composite by vapor polymerization, using 0.50 M $FeCl_3$. They reported that increasing temperature from 0 °C to 10°C resulted in decreasing conductivity from 10 to 10^0 S/cm. PPy formed at lower temperature had much higher intrinsic conductivity compared to

PPy formed at higher temperature and PPy obtained by oxidative polymerization of pyrrole may contain linkage at the 3-position of pyrrole. Furthermore, in some cases carbonyl groups occurred in oxidative polymerization were defected in PPy. These would cause reduction of effective length of conjugated bonds essential for conductivity. In addition, He et al. [30] prepared polypyrrole/polyurethane composite foam by vapor phase polymerization using $FeCl_2/FeCl_3$ at the ratio of 1/3.5 (mol/mol) at reaction temperature 20 °C. They observed that lower polymerization temperature might be indicative of the suppression of undesirable side reaction such as oxidation of pyrrole ring or cross-linking of polymer chain which decreases the length of conjugated double bond.

Furthermore, Yang et al. [25] prepared polypyrrole/polypropylene composite films by chemical polymerization using U-type reactor which consisted of two L-shape tubes and polypropylene film fixed between two tubes. A 0.20 M pyrrole solution was poured into one of L-shaped tube and 0.50 M $FeCl_3$ solution was poured into the other. They found that the conductivity of the composite increased from 0.6 to 6.7 S/cm, with decreasing temperature from 50 °C to 1.5 °C.

However, in this study, at reaction temperature below 0 °C, low conductivity of PPy/PVC composite film is obtained. This may be due to the low rate of exposing of pyrrole onto substrate. It was found that conductivity of PPy/PVC composite film did not change much when polymerization temperature increased from 0 °C to 10 °C. In this research, the conductivities of PPy/PVC composite films when the polymerization temperatures are 10 °C and 0 °C are approximately the same. Thus in this work temperature 10 °C was selected as optimum point of varying reaction temperature.

4.1.1.4 Effect of reaction time

In this work, the reaction time was varied from 1 to 72 hours. Figure 4.3 shows the influence of reaction time on conductivity of PPy/PVC composite films.

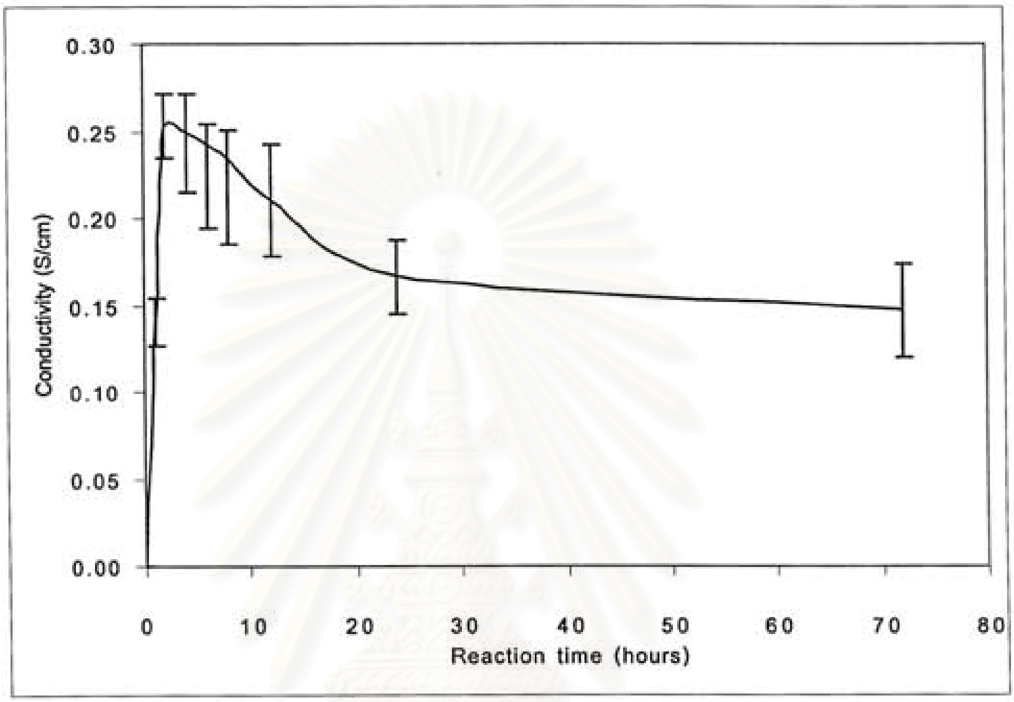


Figure 4.3 Effect of reaction time on the conductivity of PPy/PVC composite films prepared by dissolving method using 0.33 M $FeCl_3$ and 10 °C polymerization temperature.

It clearly exhibits that maximum conductivity of PPy/PVC composite occurs at 2 hours. At reaction time below 2 hours, conductivity of PPy/PVC composite films increases. It suggests that at short reaction time, the polymerization has not been completed which results in the shorter conjugated double bond chain length. Conductivity of PPy/PVC composite films increases rapidly with reaction time in the initial stage and when conductivity approachs closely 2 hours, the conductivity increases slowly. This appearance was similar to the one reported by Yin et al. [42] who prepared polypyrrole/crosslinked poly(styrene-butyl acrylate-hydroxyethyl acrylate) (PSBH) conductive composite film by vapor-phase polymerization of pyrrole within silicon-crosslinked PSBH network at –8 °C using $FeCl_3$ anhydrous 1.20 g as an oxidant. They suggested that the oxidative polymerization of pyrrole by vapor process included the diffusion step and the oxidative polymerization step. If the reaction time was long enough, the conductive PPy network was generated in the neighborhood of the surface of matrix film. The network might form a shield near the matrix surface, which prevented the diffusion of pyrrole and thus prevented the additional oxidative polymerization. The surface of film was well coated by high conductive PPy layers establishing the continuous PPy network on the surface.

However, at reaction time above 2 hours, it is found that the conductivity of PPy/PVC composite film slowly decreases. This phenomenon can be explained by the observation of Machida et al. [43] who prepared PPy by chemical polymerization in $FeCl_3$ solution, using methanol as a solvent. They suggested that the oxidant potential of the solution played an important role in the polymerization process and the conductivity. In the equilibrium state the oxidant potential (E) of the oxidant solution was expressed by Nernst's equation as:

$$E = E_0 + (RT/nF) \ln (A_{ox}/A_{red})$$

Where A_{ox} = the activity of the oxidant ($FeCl_3$)

A_{red} = the activity of reductant ($FeCl_2$)

N = number of moles of electrons that appeared in the half-reaction for the electrode process

F = the Faraday (96,485 Coloumbs)

E_0 = a constant called the standard electrode potential, which was characteristic for each half-reaction

R = the gas constant (8.314 JK^{-1} mol^{-1})

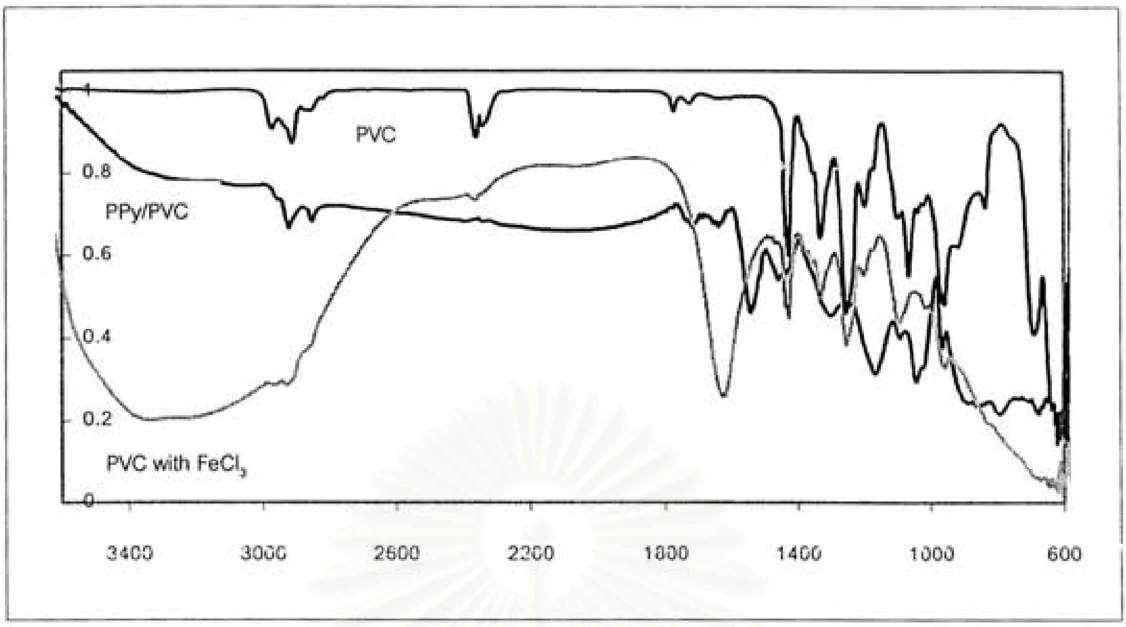
During this reaction, the $FeCl_3$ concentration decreased while the $FeCl_2$ concentration increased. Hence, the oxidation potential would decrease during the process as the reaction time increased. This feature led to low conductivity because of the less oxidized polypyrrole. So that the longer polymerization time is not suitable for the preparation of PPy/PVC composite films.

In this study, it was observed that PPy/PVC composite film of high conductivity with good appearance can be prepared by dissolving PVC in 0.33 M $FeCl_3$ and carrying out the polymerization of pyrrole at 10 °C for 2 hours. Such film exhibited the conductivity is 0.25 S/cm, which was higher than the one, 0.10 S/cm reported by Mano et al. [30]. They prepared PPy/PVC composite films with thickness of 100 μm by dissolving PVC in 0.25 M $FeCl_3$ solution and performing polymerization at 25 °C for 6 hours. This comparison demonstrated that the reaction condition directly influenced on the conductivity of PPy/PVC composite films.

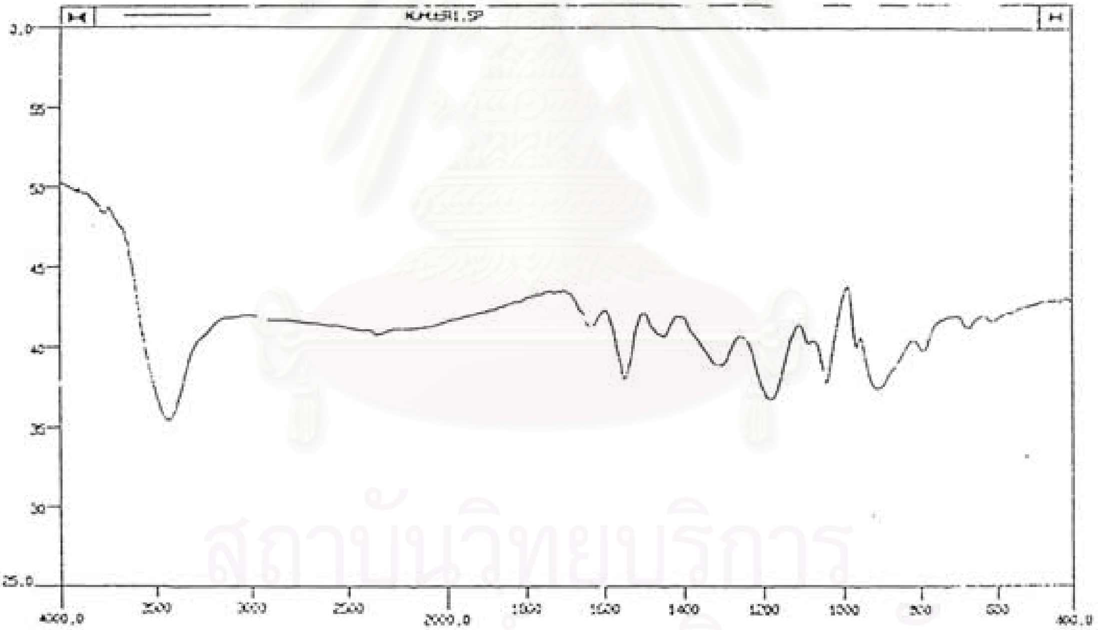
4.1.1.5 Characterization of PPy/PVC composite film

4.1.1.5.1 ATR/FT-IR spectroscopy of PPy/PVC composite film

Figure 4.4 exhibits ATR/FT-IR spectra of PVC, PVC with $FeCl_3$, PPy/PVC composite film and pure polypyrrole.



(a) IR spectra of PVC, PVC with FeCl$_3$ and PPy/PVC composite film prepared by dissolving method



(b) IR spectrum of pure polypyrrole

Figure 4.4 ATR/FT-IR of PVC, PVC with FeCl$_3$, PPy/PVC composite film prepared by dissolving method and pure polypyrrole.

The IR absorption of PPy/PVC composite film is clearly different from PVC matrix. IR spectrum of PPy/PVC composite film shows the characteristic absorption bands of both PVC and PPy. Absorption spectrum of PPy/PVC composite film confirms the incorporation of conductive polymer into PVC. Note that the absorption bands of PPy located at 1540, 1460, 1300, 1040 cm^{-1}, and the absorption bands of PVC located at 2920, 1730, 1430, 1250, 1160, 680 cm^{-1}. However, the absorption spectrum below 1700 cm^{-1} has been dominated by the polypyrrole. It also indicated that there was no chemical bonding between PVC and PPy, PVC acted only as a support.

4.1.1.5.2 TGA of PPy/PVC composite film

Thermal behavior of PPy/PVC composite film was monitored by TGA in order to observe its thermal stability. Figure 4.5 shows TGA curve of PPy/PVC composite film comparing to PVC film and PVC with $FeCl_3$ film.

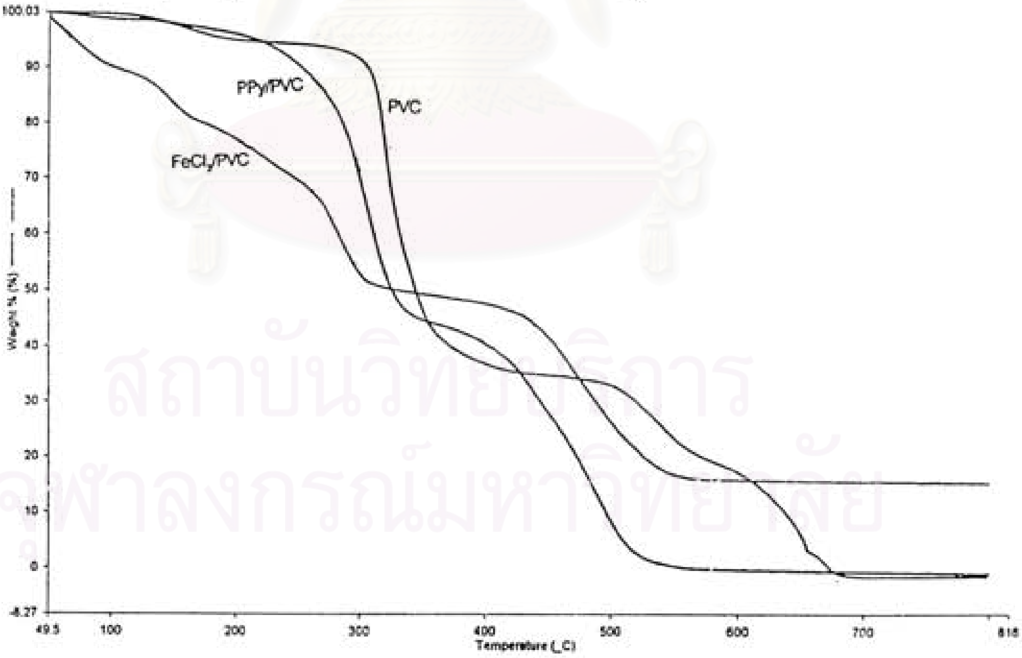


Figure 4.5 TGA of PVC film, PVC with $FeCl_3$ film and PPy/PVC composite film prepared by dissolving method.

It can be seen that all samples begin to lose mass at temperature below 100°C. This initial loss results from residual solvent evaporation and $FeCl_3$ dehydration since films were obtained by casting from THF solution either with or without $FeCl_3$ incorporation. Volatilization of monomers and oligomer adsorbed in the matrix can also be responsible for this initial mass loss.

Both PVC with $FeCl_3$ film and PPy/PVC composite film showed a second mass loss starting at a lower temperature than PVC film, i.e., from 250 °C to 300 °C, while the process occurring from 300 °C to 330 °C for PVC film. This mass loss of all samples can be related to PVC dehydrochlorination. A third mass loss of PVC film occurred at 500 °C can be assigned to cross-linking of the conjugated double bonds generated in the dehydrochlorination process. However, third mass loss of PVC with $FeCl_3$ and PPy/PVC composite film started at 400 °C. TGA curves of these films are shifted to the left. This may be due to the influence of $FeCl_3$ and PPy on PVC decomposition. TGA curve of PVC with $FeCl_3$ has residual. Thermal stability of PPy/PVC composite film is lower than PVC indicating that incorporation of PPy into PVC matrix acts as filler which slightly alters property of PVC.

4.1.2 PPy/PVC composite films prepared by swelling PVC in $FeCl_3$ solution

4.1.2.1 Preliminary investigation

In this study, PVC film, with thickness of 220 μm, was immersed in $FeCl_3$ solution in different solvents i.e., acetonitrile, methanol, chloroform and THF. By observation of the film appearance it was found that THF was the most suitable solvent for swelling PVC film. Therefore PPy/PVC composite film was prepared by firstly immersing PVC films in 1 M $FeCl_3$ in THF for 5 seconds, then solvent evaporated at 50 °C for 15 minutes and the film was subjected to vapor polymerization with pyrrole at 10 °C. After 2 hours of exposing to pyrrole, yellow film was turning black. Its conductivity of polypyrrole showed to be only 1.65 S/cm. To improve its conductivity several factors influenced on its conductivity were studied such as immersion time, $FeCl_3$ concentration, reaction temperature and reaction time.

4.1.2.2 Effect of immersion time

The swelling of PVC film is necessary since it will allow polymerization to proceed inside the film. Therefore PVC films were immersed in 1 M $FeCl_3$ in THF for different periods of time from 1-20 seconds. Figure 4.6 shows the influence of the immersion time of PVC film in $FeCl_3$ solution on the conductivity of PPy/PVC composite films. To determine the conductivity of the composite film, the thickness of PPy was again involved. In the case of PPy/PVC composite films prepared by swelling, it was expected that $FeCl_3$ was deposited mainly on surface of PVC film. Therefore, the conductivity of sample has been calculated by using only the thickness of PPy on top of PVC film.

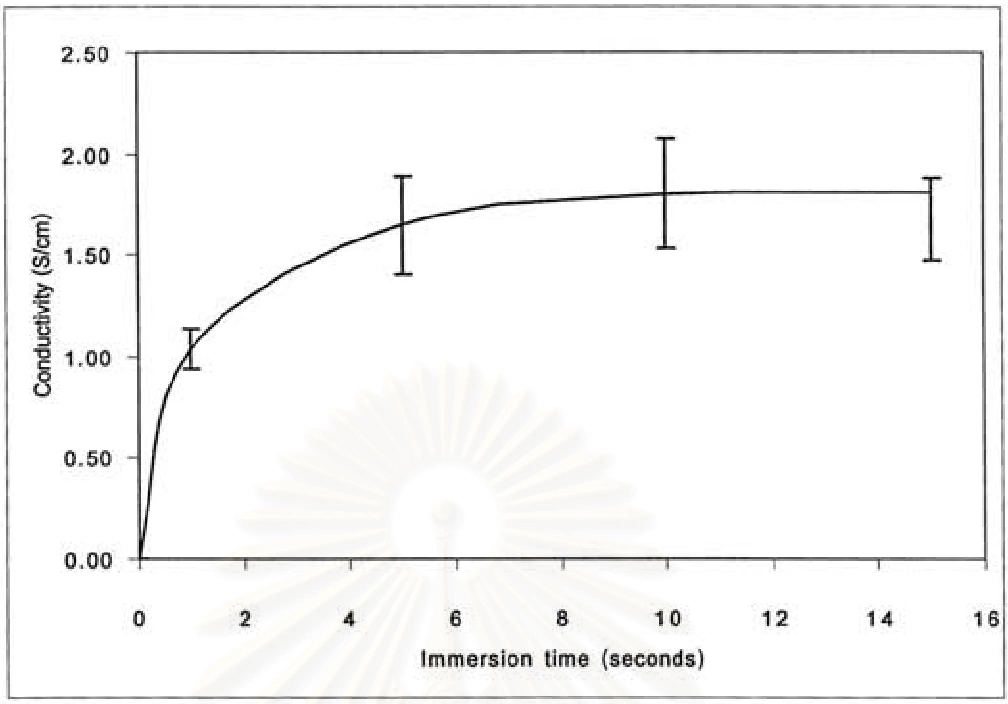


Figure 4.6 Effect of immersion time on the conductivity of PPy/PVC composite films prepared by swelling method using 1 M $FeCl_3$, 10 °C polymerization temperature and 2 hours polymerization time.

At low immersion time, low conductivity of PPy/PVC composite film is obtained while at longer immersion time, the conductivity increases and seems to be constant after 10 seconds of immersion time. It can be explained that at less immersion time $FeCl_3$ is restricted to a surface of PVC film while more amount of $FeCl_3$ can be interpenetrated into PVC film as the immersion time is longer. It should be noted that at immersion time above 15 seconds, PVC films were distorted and started to dissolve in $FeCl_3$ solution. Thus in the following studies PVC film was immersed in $FeCl_3$ solution for 10 seconds.

4.1.2.3 Effect of $FeCl_3$ concentration

According to Section 4.1.1.2, $FeCl_3$ concentration had an influence on conductivity of PPy/PVC composite films prepared by dissolving method, it was also expected the similar result for the swelling method. Thus $FeCl_3$ concentration was varied from 0.10-1.25 M. At $FeCl_3$ concentration greater than 1.25 M, $FeCl_3$ was not completely dissolved in THF due to its solubility limit. Figure 4.7 shows that conductivity of PPy/PVC composite films depend on $FeCl_3$ concentration.

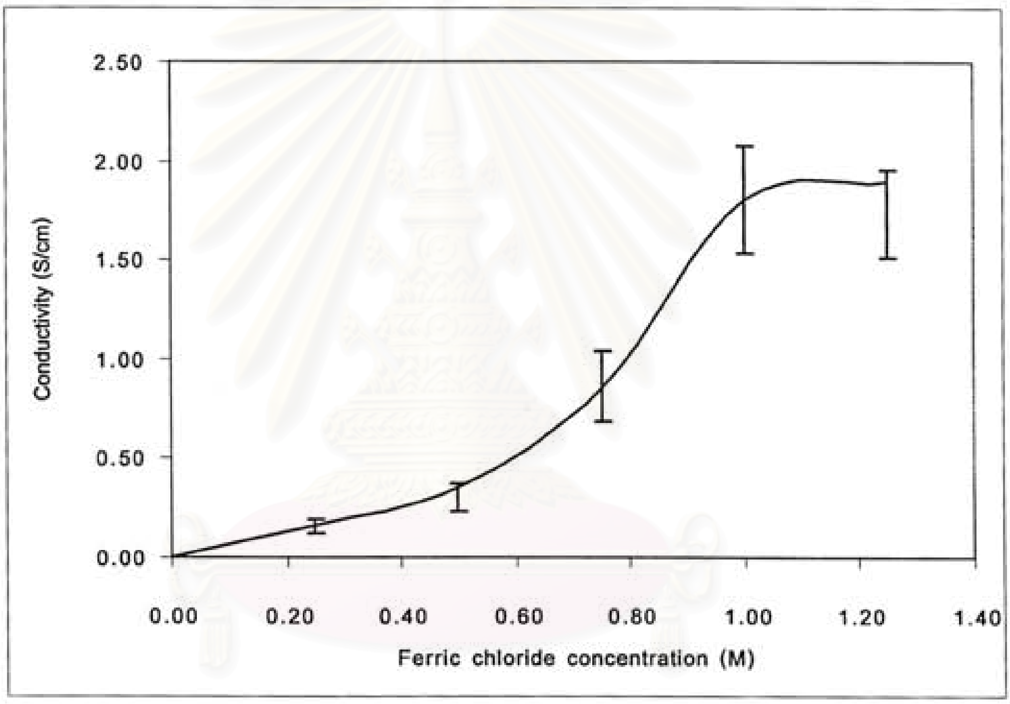


Figure 4.7 Effect of $FeCl_3$ concentration on the conductivity of PPy/PVC composite films prepared by swelling method using at 10 seconds immersion time, 10 °C polymerization temperature and 2 hours polymerization time.

It clearly exhibits that above 1 M $FeCl_3$, conductivity of PPy/PVC composite films approached a constant value. This may be due to constant rate of swelling of PVC. At low $FeCl_3$ concentration, even though high swelling ratio of PVC film was obtained, conductivity of PPy/PVC composite film was low.

Analogous result was observed by Zoppi et al. [5] who prepared polypyrrole/ethylene-propylene-5-ethylidene-2-norbornene rubber, EPDM, composite by swelling of EPDM in $FeCl_3$/THF solution and exposed to pyrrole vapor for 26 hours at room temperature. They explained that the swelling ratio decreased when $FeCl_3$ concentration increased and reached a constant value. This behavior was expected because $FeCl_3$ reduced polymeric matrices solubility in THF. At 1.25 M $FeCl_3$, this was maximum limit for dissolubility of $FeCl_3$ in THF. Therefore, immersed PVC film was not swollen in $FeCl_3$ solution of higher concentration.

Moreover, at above 1 M $FeCl_3$, conductivity of PPy/PVC composite films seemed to be saturated. This observation was similar to one obtained by Kise et al. [27] who prepared PPy film by interphase chemical polymerization between aqueous solution of $Fe_2(SO_4)_3$ and organic solution of pyrrole monomer reactions at 10 °C for 4 hours. They could explain that similar results have been reported for other oxidative polymerization systems of pyrrole. At higher oxidant concentration, the content and bulk density of PPy decrease because the oxidative polymerization of pyrrole occurred rapidly. It seemed that polypyrrole layer which retarded the diffusion of the oxidant solution was formed on surface of matrix film, thus generating of PPy was the non-uniform composite films. Alternatively, excess amount of oxidant led to the loss of regularity in the PPy structure and the overoxidative reaction of PPy, namely, decreasing in the length of conjugation and defecting of structure in the composite films. So that the maximum conductivity of PPy/PVC composite films (1.80 S/cm) was obtained at 1 M $FeCl_3$.

4.1.2.4 Effect of reaction temperature

To investigate the effect of the reaction temperature on conductivity of PPy/PVC composite films prepared by swelling, the reaction temperature was varied from –15 °C to 45 °C. Figure 4.8 shows that reaction temperature influences on conductivity of PPy/PVC composite films. The reaction temperature which provided the highest conductivity was at 10 °C, the same as for preparation of PPy/PVC composite films by dissolving method. The reason for obtaining lower conductivity at the temperature lower or higher than 10 °C was described previously in Section 4.1.1.3.

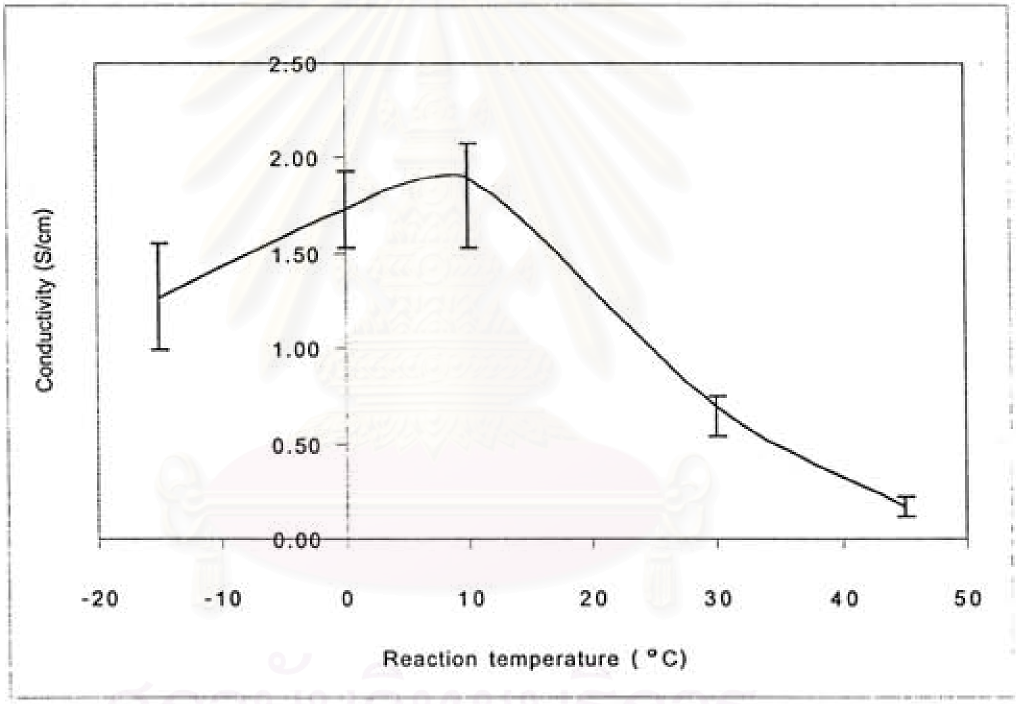


Figure 4.8 Effect of reaction temperature on the conductivity of PPy/PVC composite films prepared by swelling method using 1 M $FeCl_3$, 10 seconds immersion time and 2 hours polymerization time.

4.1.2.5 Effect of reaction time

To investigate effect of reaction time on conductivity of PPy/PVC composite films, reaction time was varied from 1 to 72 hours as shown in Figure 4.9.

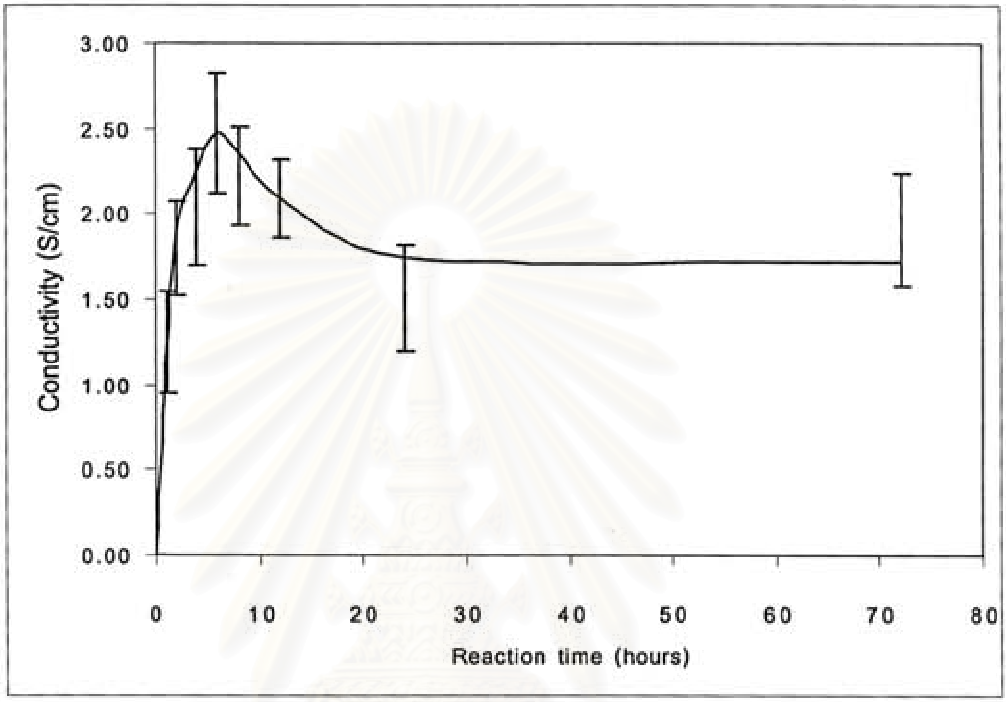


Figure 4.9 Effect of reaction time on the conductivity of PPy/PVC composite films prepared by swelling method using 1 M $FeCl_3$, 10 seconds immersion time and 10 °C polymerization temperature.

It clearly exhibits that the maximum conductivity (2.47 S/cm) of PPy/PVC composite film is obtained at 6 hours polymerization time. The similar explanation on the effect of reaction time on conductivity was previously described in Section 4.1.1.4.

Preparation of PPy/PVC composite film by swelling method closes to preparation of PPy/PVC composite film by Kang et al. [11]. They reported that PVC matrix was immersed in solvent systems of n-hexane, acetone and pyrrole, then immersed in $FeCl_3$ solution of the binary solvent system with acetonitrile and methanol. The mole ratio of 85/15 of acetonitrile/methanol resulted in high electrical conductivity of composite film when polymerized at 0 ° C. The high conductivity of the composite was about 20 S/cm. The result of high conductivity of PPy/PVC composite films obtained by Kang et al. is expected effect of solvent. So that solvent was changed from THF to binary solvent system of acetonitrile and methanol. PVC film was immersed in 1 M $FeCl_3$ in acetonitrile and methanol. It was observed PVC film was not swollen in $FeCl_3$ solution. However, PPy/PVC composite film, with only conductivity of 0.32 S/cm was obtained when PVC film was immersed in 1 M $FeCl_3$ in acetone and 10 ° C polymerization temperature for 6 hours polymerization time. The results in oxidation potential of solvent were not successful. Moreover procedure of preparation of PPy/PVC composite films obtained by Kang et al. was repeated but low conductivity could not be recorded.

In this research it was observed that high conductivity of PPy/PVC composite films prepared by swelling in $FeCl_3$ solution is obtained at 1 M $FeCl_3$ concentration, 10 °C polymerization temperature and 6 hours polymerization time.

4.1.2.6 Characterization of PPy/PVC composite film

4.1.2.6.1 FT-IR spectroscopy of PPy/PVC composite film

Figure 4.10 exhibits FT-IR spectra of PVC film, PVC with $FeCl_3$ film and PPy/PVC composite film.

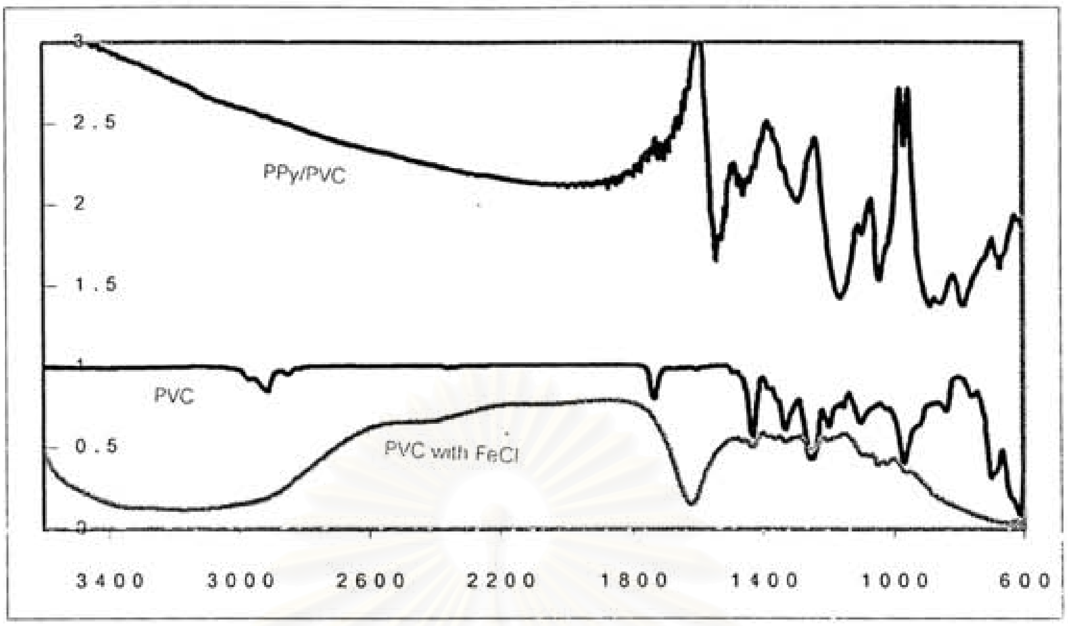


Figure 4.10 FT-IR of PVC, PVC with $FeCl_3$ and PPy/PVC composite film prepared by swelling method.

The IR absorption of PPy/PVC composite film is clearly different from PVC matrix. Absorption bands of PPy/PVC composite film located at 1530, 1435, 1270, 1130, 1030, 880 cm^{-1} while the absorption bands at 2920, 1730, 1410, 1310, 1240, 1170, 950 cm^{-1} belonged to PVC matrix. It is obvious that no absorption band at 2920 cm^{-1} appeared in FT-IR spectrum of PPy/PVC composite film. It indicated that polypyrrole layer covered on the surface of PVC film completely well. This can be confirmed by SEM (Section 4.1.3).

4.1.2.6.2 TGA of PPy/PVC composite film

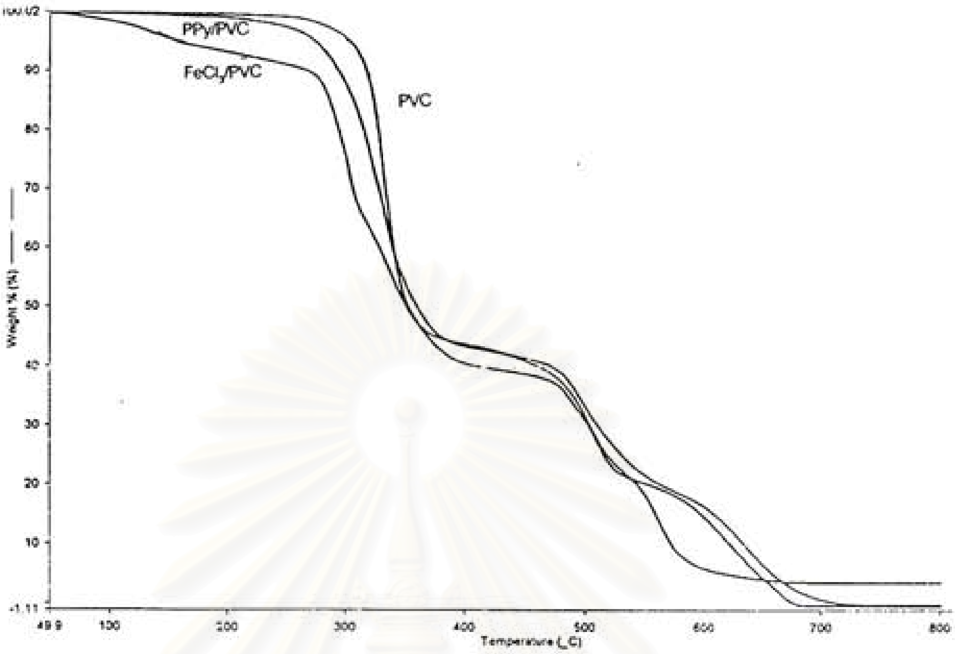


Figure 4.11 TGA of PVC film, PVC with $FeCl_3$ film and PPy/PVC composite film prepared by swelling method.

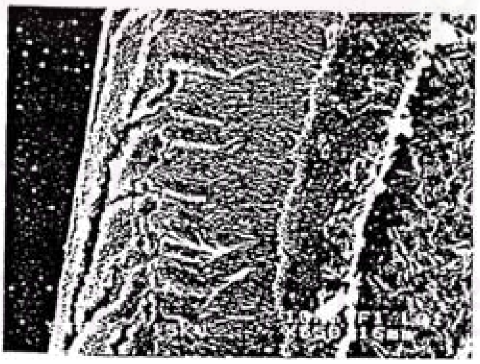
Figure 4.11 shows that the stabilizer or filler which was used in PVC film, volatilization of monomer and oligomer adsorbed in the matrix can be responsible for initial mass loss of all composite films. For PVC with $FeCl_3$ film, initial mass loss may result from solvent evaporation and $FeCl_3$ dehydration. Second mass loss occurring from 280 °C to 350 °C can be related to PVC dehydrochlorination, PVC loses HCl in this step. Third mass loss at 450 °C results from unsaturated carbon-carbon backbone degradation. PVC with $FeCl_3$ film has residual. TGA curve of PPy/PVC composite film resembles to TGA of PVC film. It can be pointed out that the incorporation of PPy into PVC by swelling method seemed not change its thermal stability.

4.1.3 Morphology of PPy/PVC composite film

Figure 4.12 shows that PPy/PVC composite film prepared by swelling method is a sandwich type structure which two layers of PPy were coated on PVC film. The layer of PPy starts to grow while $FeCl_3$ concentration increases and conductivity of PPy/PVC film increases. SEMs of PPy/PVC composite film prepared by swelling method are different from dissolving method (Figure 4.13).

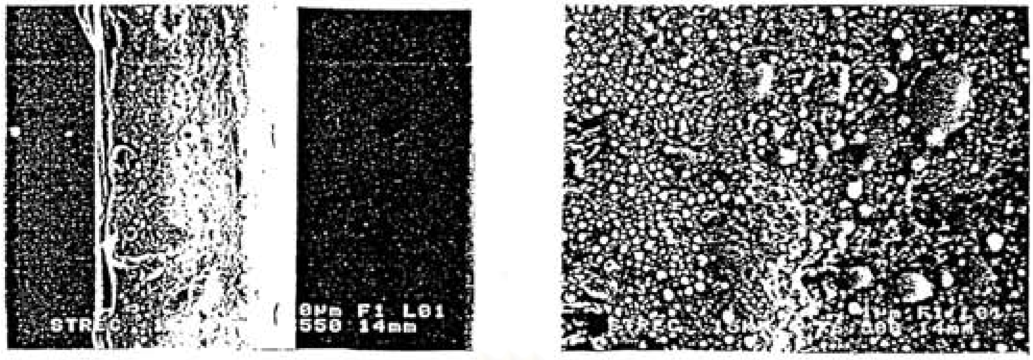
(a) PVC with $FeCl_3$ X 550

(b) PPy/PVC composite film at 0.25 M $FeCl_3$ X 550

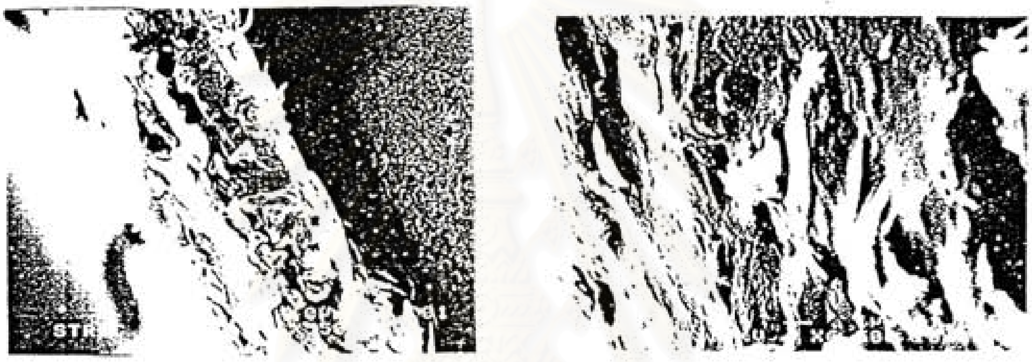


(c) PPy/PVC composite film at 1 M $FeCl_3$ X 550

Figure 4.12 SEMs of PPy/PVC composite films prepared by swelling method.

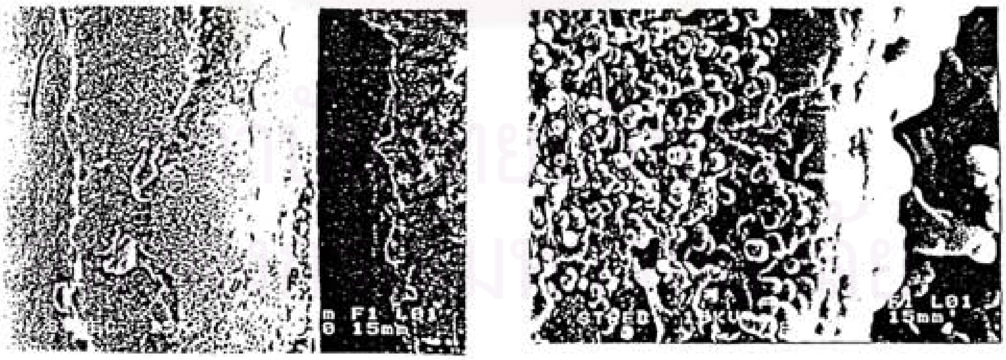


(a) PVC with $FeCl_3$ X 550 (b) PVC with $FeCl_3$ X 6000



(c) PPy/PVC composite film at 0.20 M $FeCl_3$ X 550

(d) PPy/PVC composite film at 0.20 M $FeCl_3$ X 6500

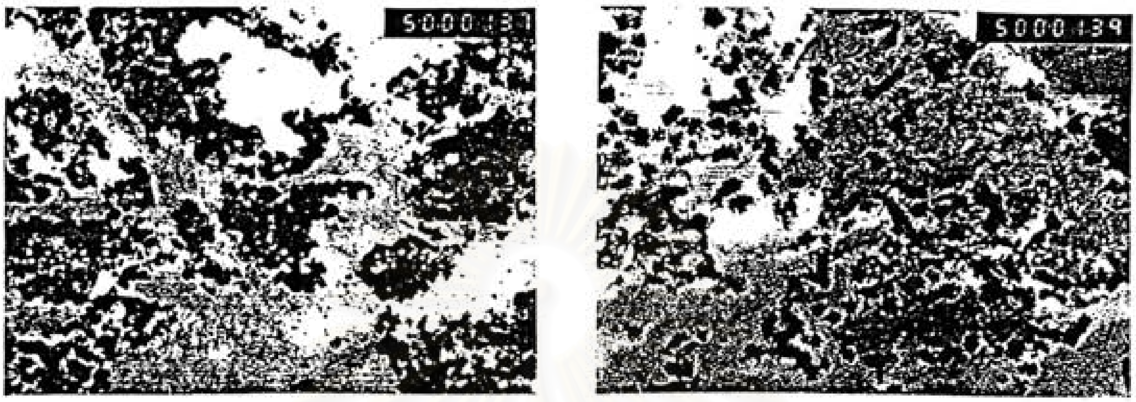


(e) PPy/PVC composite film at 0.33 M $FeCl_3$ X 550

(f) PPy/PVC composite film at 0.33 M $FeCl_3$ X 550

Figure 4.13 SEMs of PPy/PVC composite films prepared by dissolving method.

Figure 4.13 shows that PPy can disperse in PVC matrix. At higher $FeCl_3$ concentration, large amount of globules of PPy particles are obtained. This result led to high conductivity of PPy/PVC composite film.



(a) PPy/PVC composite film prepared by dissolving method

(b) PPy/PVC composite film prepared by swelling method

Figure 4.14 TEMs of PPy/PVC composite film prepared by swelling and dissolving methods.

Figure 4.14 clearly exhibits that PPy in PPy/PVC composite film prepared by dissolving method could disperse into PVC matrix better than by swelling method. For PPy/PVC composite film prepared by swelling, $FeCl_3$ can be dispersed into PVC matrix, however, most of PPy are occurred on surface. This phenomenon explains that during polymerization, pyrrole vapor interpenetrated into PVC film was shielded by PPy network on surface of PVC. After washing composite film in methanol, it was found that $FeCl_3$ was leached out into methanol. SEM and TEM of PPy/PVC composite film prepared by swelling show that less of PPy was interpenetrated into PVC, PPy layer is occurred on surface of PVC film.

4.2 PPy/PS composite films

Many researchers reported on the preparation of PPy/PS composites by chemical polymerization of pyrrole in matrix of host insulating polymer [44-47] and by electrochemical polymerization of pyrrole on electrode coated with PS [48]. The conductivities of composites were as low as 10^{-3} S/cm [48] upto the highest one of 10 S/cm [44,45]. However, very few reports on PPy/PS composites were noted. In this study, preparation of PPy/PS composite films by vapor polymerization of pyrrole on PS films impregnated on oxidant was investigated and compared with PVC and poly (sodium 4-styrene sulfonate) (PSS) films.

4.2.1 PPy/PS composite films prepared by dissolving PS in $FeCl_3$ solution

PS pellet was dissolved in $FeCl_3$ solution in different solvents, i.e. chloroform and THF. It was observed that THF was a suitable solvent for film forming. PPy/PS composite film was thus prepared by firstly dissolving PS pellet in 0.10 M $FeCl_3$ in THF at room temperature, casting into thin film and then subjected to vapor polymerization with pyrrole at 10 °C for 2 hours. Even though the black composite film was obtained, its conductivity could not be measured because less current passed through composite film. Higher $FeCl_3$ concentration was also attempted but the discontinuous film was formed. Therefore PPy/PS composite films prepared by dissolving method could not be successful.

4.2.2 PPy/PS composite films prepared by swelling PS in $FeCl_3$ solution

4.2.2.1 Preliminary investigation

In this study, THF was also the most suitable solvent for preparing PPy/PS composite film. PPy/PS composite film was prepared by immersing PS film, thickness 220 μm, in 1 M $FeCl_3$ solution in THF for 5 seconds, then solvent was evaporated at 50 °C for 15 minutes. After that the film was subjected to vapor polymerization with pyrrole at 10 °C. After 2 hours of exposing to pyrrole vapor, yellow film was turning black. The conductivity of composite film was 0.51 S/cm. To calculate the conductivity the thickness of PPy was a important parameter. In the case of PPy/PS composite films prepared by swelling, it was expected that $FeCl_3$ was deposited mainly on surface of PVC film. Therefore, the conductivity of sample has been calculated by using only the thickness of PPy on PS film. To improve its conductivity several factors were studied such as immersion time, $FeCl_3$ concentration, reaction temperature and reaction time.

4.2.2.2 Effect of immersion time

According to Section 4.1.2.2, immersion time had an influence on conductivity of PPy/PVC composite film prepared by swelling method, it was also expected the similar result for PPy/PS composite films. Immersion time of PS films in 1 M $FeCl_3$ was varied from 1-20 seconds. Figure 4.15 shows that longer immersion time of PS film in $FeCl_3$ solution increases in conductivity of PPy/PS composite films. The conductivity seems to be constant after 10 seconds of immersion time. It should be note that at immersion time above 15 seconds, PS films were dissolved in $FeCl_3$ solution.

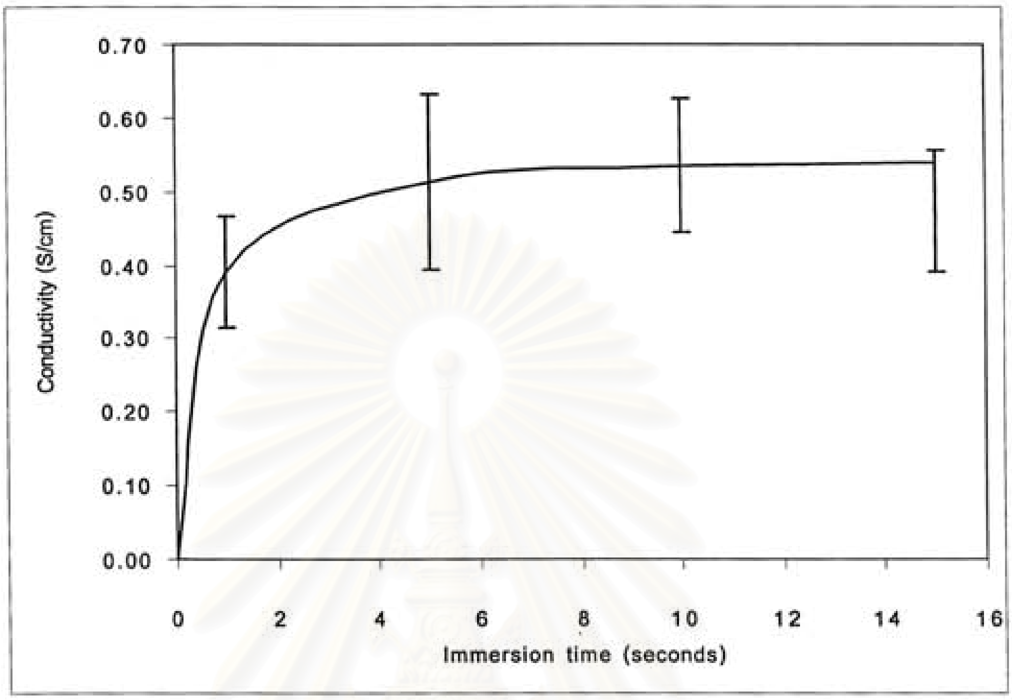


Figure 4.15 The conductivity of PPy/PS composite films prepared by swelling method at various immersion time of PS in 1 M $FeCl_3$ using 10 °C polymerization temperature and 2 hours polymerization time.

The immersion time which provided high conductivity of PPy/PS composite films was at 10 seconds, the same as for PPy/PVC composite films obtained by swelling method. The effect of immersion time on conductivity is the same as was described in Section 4.1.2.2. In this research, 10 seconds was used as the optimum immersion time for preparation of PPy/PS composite films.

4.2.2.3 Effect of $FeCl_3$ concentration

As $FeCl_3$ concentration influenced on conductivity, PPy/PS composite films were prepared at various $FeCl_3$ concentration from 0.10-1.25 M. Figure 4.16 shows that conductivity of PPy/PS composite films depends on $FeCl_3$ concentration. At 1 M $FeCl_3$, the conductivity of PPy/PS composite films reaches 0.53 S/cm. It clearly exhibits that above 1 M $FeCl_3$, conductivity of PPy/PS composite films approached a constant value.

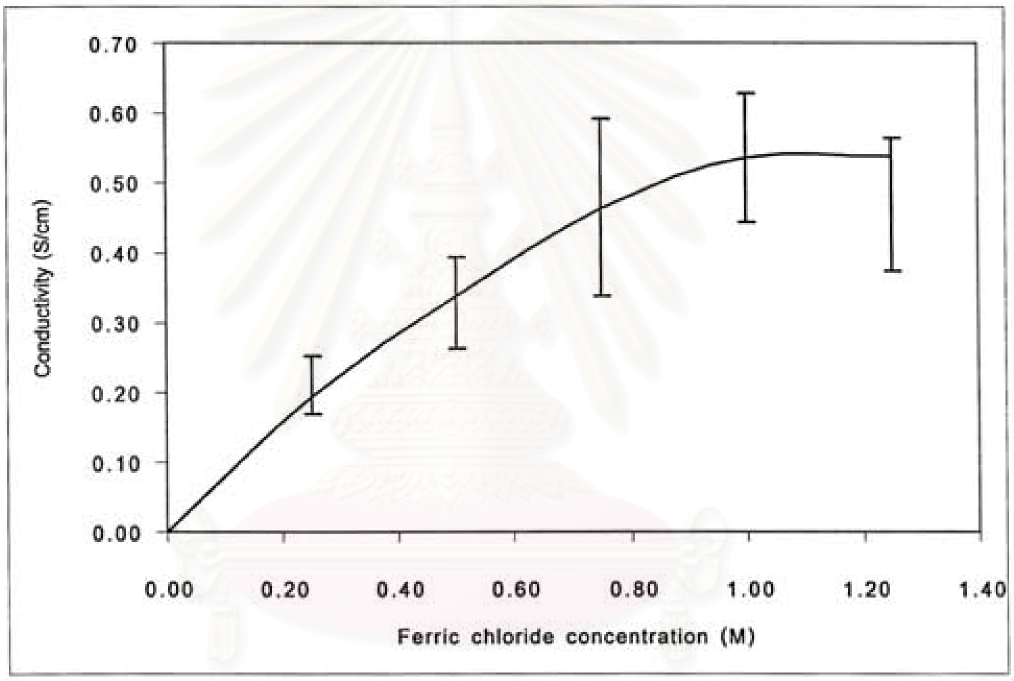


Figure 4.16 Effect of $FeCl_3$ concentration on the conductivity of PPy/PS composite films prepared by swelling method using 10 seconds immersion time, 10 °C polymerization temperature and 2 hours polymerization time.

The same explanation as previously described in section 4.1.2.3, is applied in this case as well, In this work, 1 M $FeCl_3$ was chosen as the optimum concentration for the preparation.

4.2.2.4 Effect of reaction temperature

To investigate effect of reaction temperature on conductivity of PPy/PS composite films prepared by swelling method, reaction temperature was varied from –15 °C to 45 °C. Figure 4.17 shows that reaction temperature affects on conductivity of PPy/PS composite films.

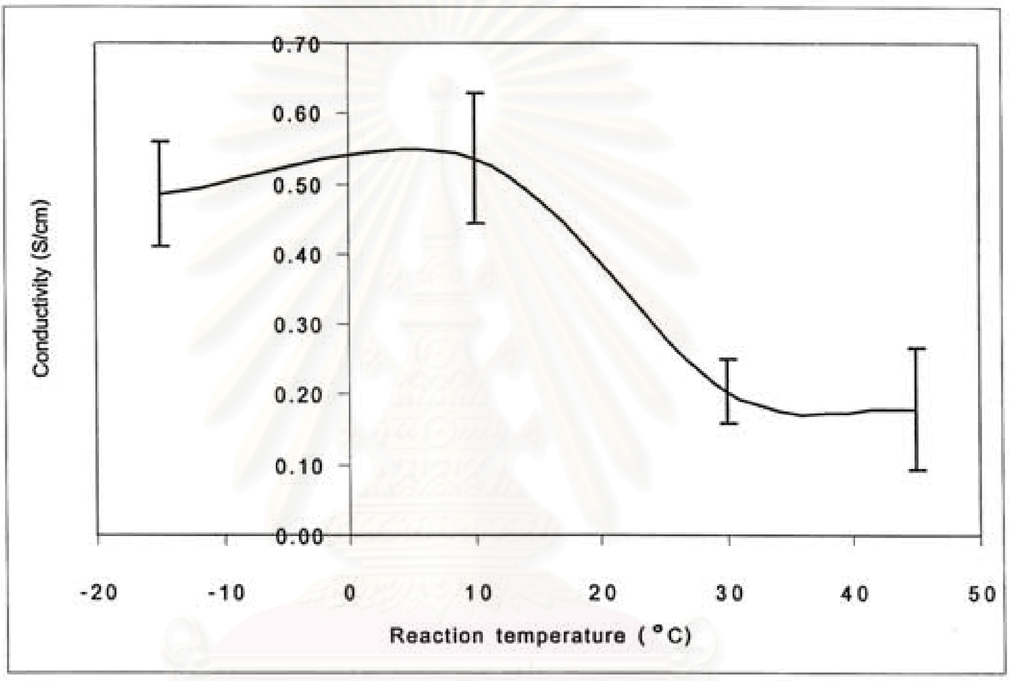


Figure 4.17 Effect of reaction temperature on the conductivity of PPy/PS composite films prepared by swelling method using 1 M $FeCl_3$, 10 seconds immersion time and 2 hours reaction time.

The reaction temperature which provided PPy/PS composite films, high conductivity, was at 10 °C, the same as for preparation of PPy/PVC composite films by swelling method. The result of the reaction temperature influence on conductivity of composite films was previously described in Section 4.1.2.4. The optimum reaction temperature for the preparation of PPy/PS composite films by swelling method was about 10 °C.

4.2.2.5 Effect of reaction time

To investigate the effect of reaction time on conductivity of PPy/PS composite films, reaction time was varied from 1 to 72 hours.

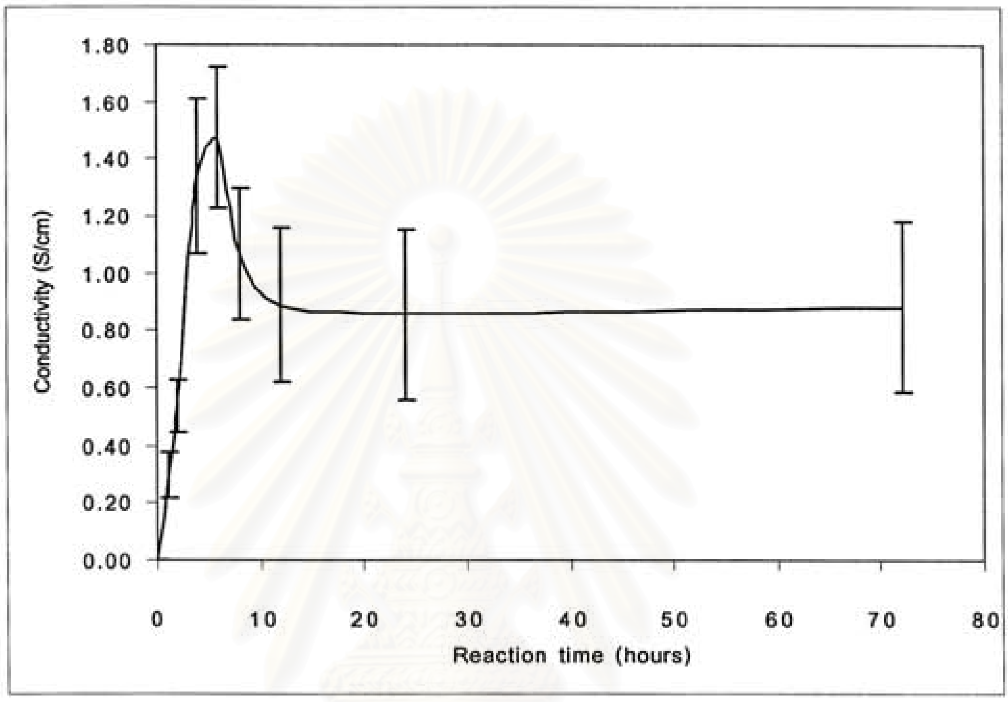
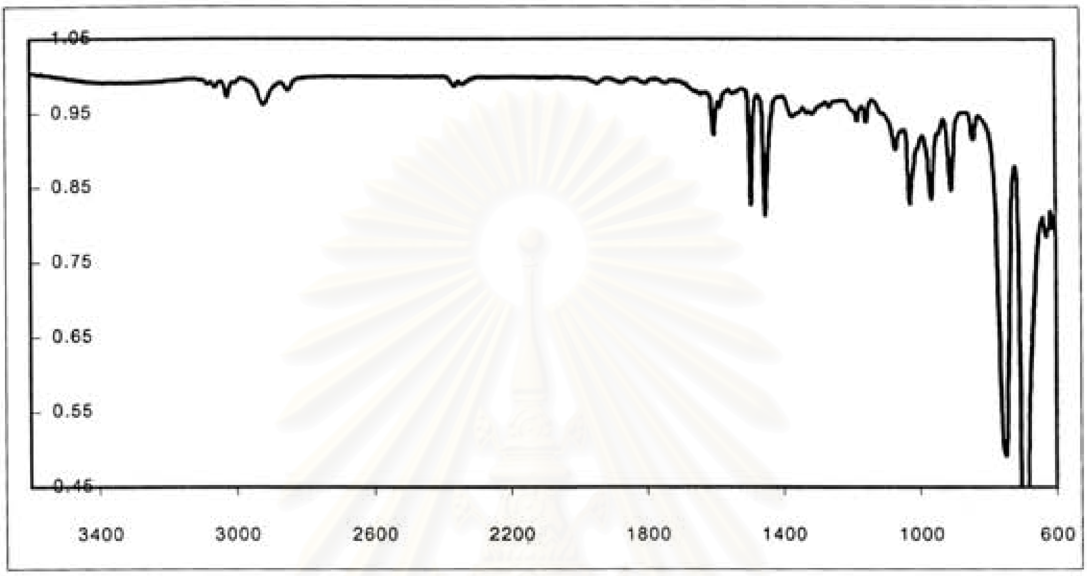


Figure 4.18 Effect of reaction time on the conductivity of PPy/PS composite films prepared by swelling method using 1 M $FeCl_3$, 10 seconds immersion time and reaction temperature 10 °C.

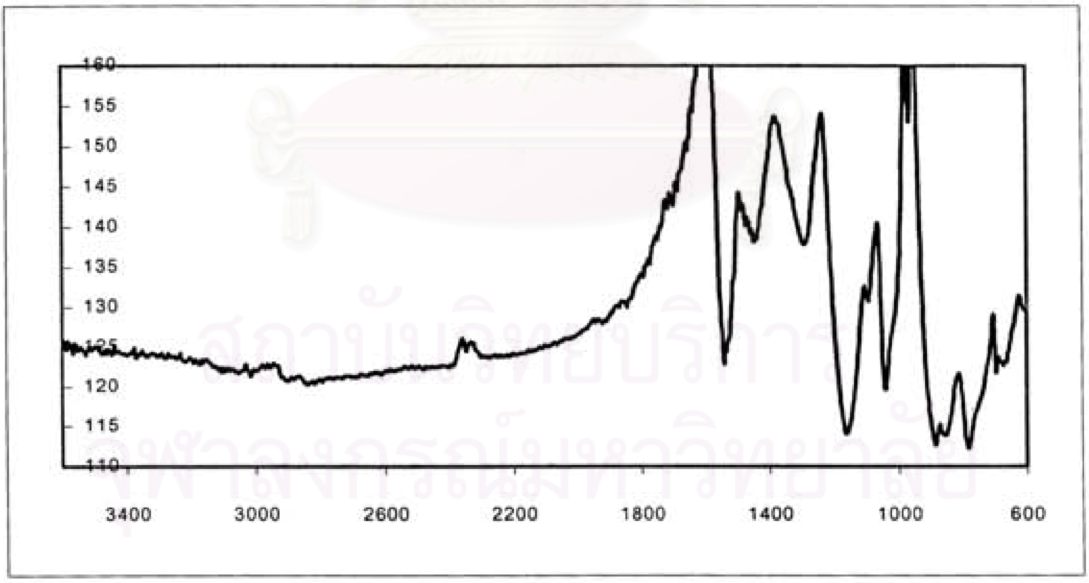
The reaction time influenced on conductivity of composite films was previously described in Section 4.1.1.4. Therefore the highest conductivity of preparation PPy/PS composite films by swelling (1.48 S/cm) is obtained at 10 seconds immersion time of PS film in 1 M $FeCl_3$ at 10 °C polymerization temperature and 6 hours polymerization time.

4.2.2.6 Characterization of PPy/PS composite film

4.2.2.6.1 FT-IR spectroscopy of PPy/PS composite film



(a) FT-IR of PS film



(b) FT-IR of PPy/PS composite film

Figure 4.19 FT-IR of PS film and PPy/PS composite film prepared by swelling method.

IR spectrum of PPy/PS composite film is clearly different from PS matrix. PPy/PS composite film exhibits the absorption bands at 1540, 1450, 1280, 1160, 1030, 880 cm^{-1} while absorption bands of PS matrix appeared at 3000, 2920, 1580, 1490, 1450, 1070, 1030, 970, 760, 690 cm^{-1}. The absorption band at 3000 cm^{-1} characterized as aromatic ring did not appear in the IR spectrum of PPy/PS composite film. It indicated that polypyrrole layer covered on the surface of PS film completely well. This can be confirmed by SEM (Section 4.2.3).

4.2.2.6.2 TGA of PPy/PS composite film

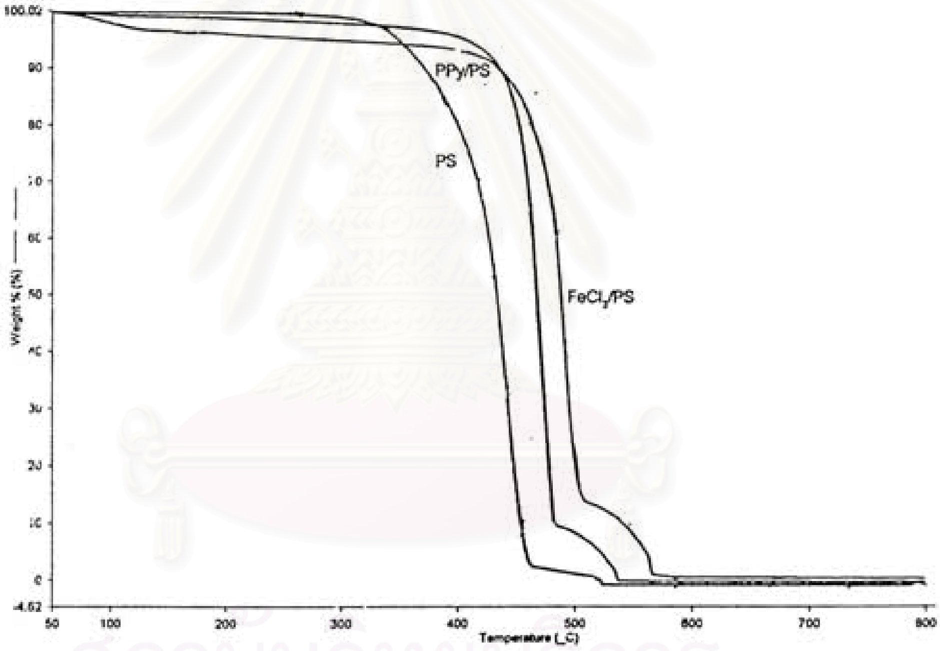
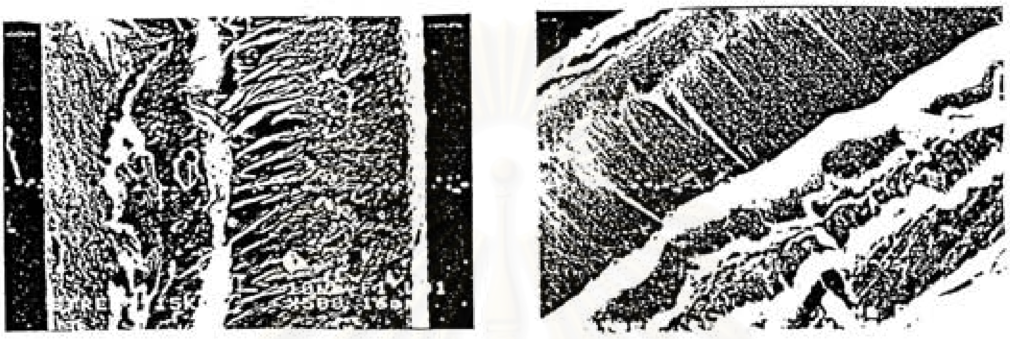


Figure 4.20 TGA of PS film, PS with $FeCl_3$ film and PPy/PS composite film prepared by swelling method.

Figure 4.20 shows that PS underwent only one time of mass loss, probably due to partial depolymerization or evaporation of trapped monomer, starting at 350 °C. In case of PS with $FeCl_3$ film and PPy/PS composite film, mass loss started at

400 °C, higher than mass loss of purely PS film. This indicated that $FeCl_3$ and PPy had some influences on PS decomposition.

4.2.3 Morphology of PPy/PS composite film



(a) SEM of PS with $FeCl_3$ X 550 (b) SEM of PPy/PS at 0.25 M $FeCl_3$ X 550

Figure 4.21 SEMs of PS with $FeCl_3$ film and PPy/PS composite film prepared by swelling method.

(a) TEM of PPy/PVC composite film (b) TEM of PPy/PS composite film

Figure 4.22 TEMs of PPy/PVC and PPy/PS composite films prepared by swelling method.

SEMs indicate that most of PPy formed at surface of PS film which made PPy/PS composite films prepared by swelling method a sandwich type. In comparison, PPy of PPy/PS composite film could less interpenetrated into PS film than PVC as revealed by TEM.

4.3 PPy/PSS composite films

In this study, it was observed that low conductivity of PPy composite films was obtained. This is probable that it is rather difficult for an oxidant agent to diffuse inside the film. This obstacle may be partly avoided by the use of insulating films in which the ionic dopant is already bound to the polymer backbone. The advantage of the ionomer-conducting polymer composite is that the composite preparation is no longer dependent on the diffusion rate of dopant in the film [32]. Recently, polymeric anion has been used as the doping counterion to prepare conducting polymer [49-53]. Advantages reported for this type of polymer include the improvement of mechanical properties and processability [49] and ability for cation exchange [50].

Many researchers have prepared PPy/PSS composite films by electrochemical polymerization of solution of pyrrole and PSS. They reported that PPy was doped with PSS. The conductivity of these composite films were obtained in ranges from 10^{-2} to 10 S/cm [52]. However, Arribas et al. [53] have reported the preparation of conductive PPy/PSS by chemical polymerization, the conductivity of PPy/PSS composite films (4 S/cm) was obtained. So that PSS was expected to improve conductivity of PPy composite films.

4.3.1 PPy/PSS composite films prepared by dissolving PSS in $FeCl_3$ solution

PSS powder was dissolved in $FeCl_3$ solution in different solvents, i.e. chloroform, THF and water. It was observed that H_2O was only solvent for dissolving PSS, but it could not be formed film. So that PPy/PSS composite films prepared by dissolving method was not successful.

4.3.2 PPy/PSS composite films prepared by swelling PSS in $FeCl_3$ solution

4.3.2.1 Preliminary investigation

PSS film, with thickness 380 μm, was prepared by dissolving in H_2O and casted as film, at 50 °C for 48 hours. PSS film could swell very well in THF, thus it was immersed in 1 M $FeCl_3$ solution in THF at room temperature for 1 second, then the solvent was evaporated at 50 °C for 15 minutes and followed by vapor polymerization with pyrrole at 10 °C. After 2 hours of exposing to pyrrole, the yellow film was turning black. Its conductivity showed to be 2.34 S/cm. It should be noted that at immersion time above 1 second, PSS films were easily fractured. The conductivity of sample has been calculated by using only the thickness of PPy on PSS film. To improve its conductivity several factors was studied such as $FeCl_3$ concentration, reaction temperature and reaction time.

4.3.2.2 Effect of $FeCl_3$ concentration

As previously described, $FeCl_3$ concentration has influenced on the conductivity of the prepared film. Therefore, PPy/PSS composite films were prepared at various $FeCl_3$ concentrations from 0.10-1.25 M. When the concentration of $FeCl_3$ is lower than 0.50 M, the immersed PSS films were fractured.

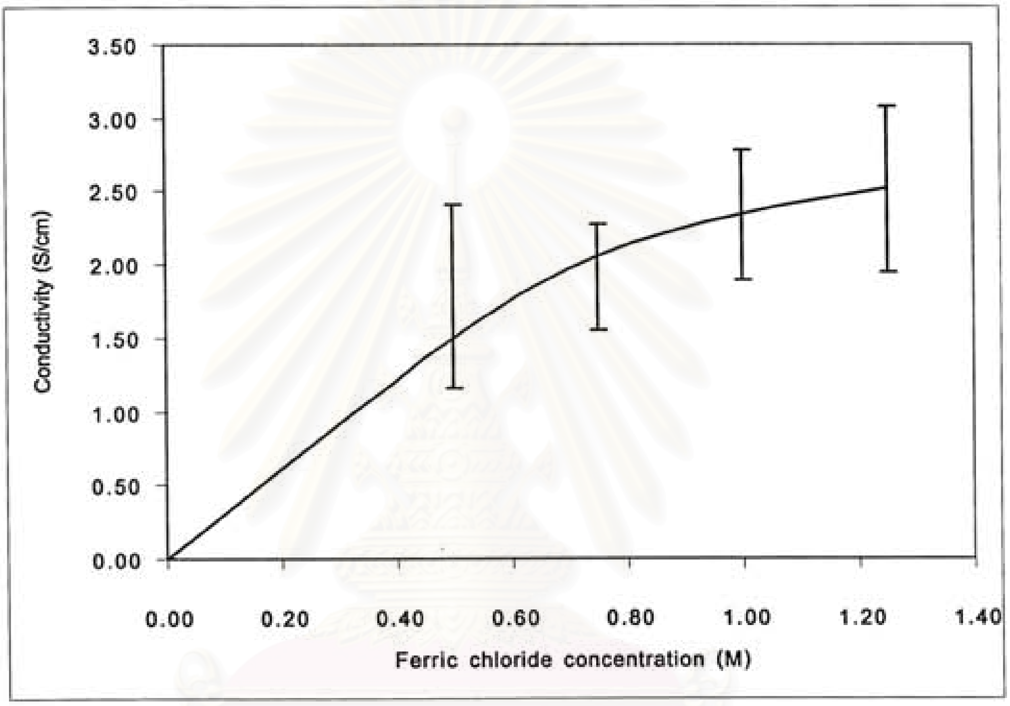


Figure 4.23 Effect of $FeCl_3$ concentration on the conductivity of PPy/PSS composite films prepared by swelling method using at 10 °C polymerization temperature and 2 hours polymerization time.

Figure 4.23 shows that the conductivity of PPy/PSS composite films increases with the $FeCl_3$ concentration. This can be explained that higher concentration of $FeCl_3$ results in higher polymerization rate. The optimum oxidant concentration was 1.25 M.

4.3.2.3 Effect of reaction temperature

To investigate the effect of reaction temperature on conductivity of PPy/PSS composite films prepared by swelling, reaction temperature was varied from –15 °C to 45 °C. Figure 4.24 shows that the reaction temperature affects on conductivity of PPy/PSS composite films.

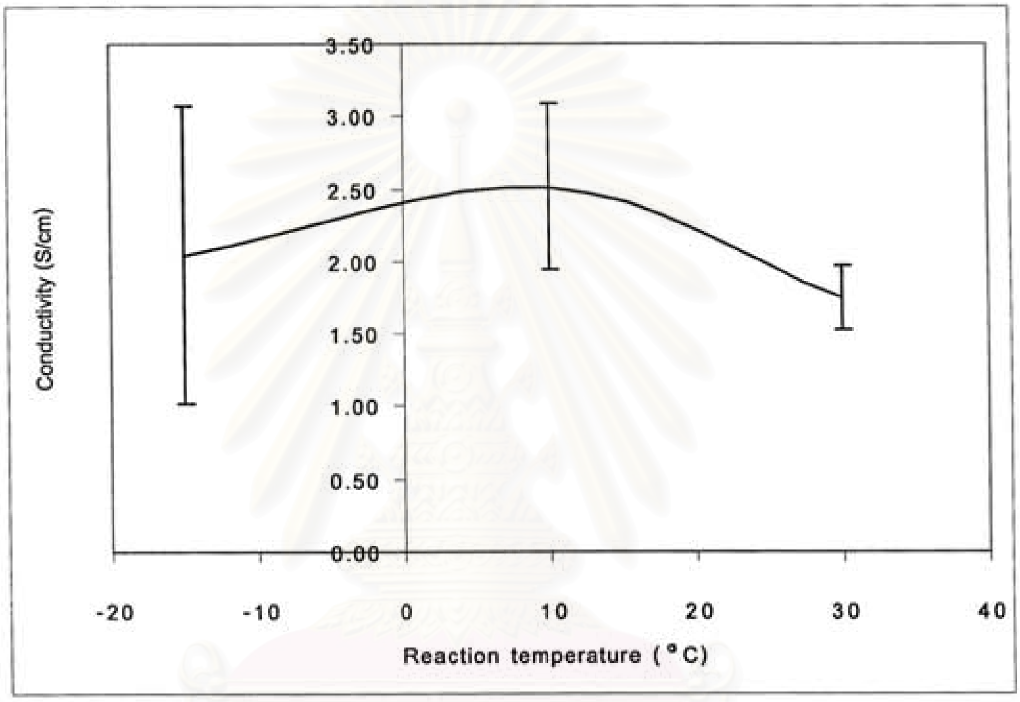


Figure 4.24 Effect of reaction temperature on the conductivity of PPy/PSS composite films prepared by swelling method using 1.25 M $FeCl_3$ and 2 hours polymerization time.

At reaction temperature above 30 °C, it was noticed that PPy/PSS composite film was fractured while polymerization of PPy occurred. The influence of reaction temperature on conductivity of composite films was previously described in Section 4.1.1.3. The optimum reaction temperature of preparation of PPy/PSS composite films by swelling was at 10 °C.

4.3.2.4 Effect of reaction time

The reaction time was varied from 1 to 72 hours.

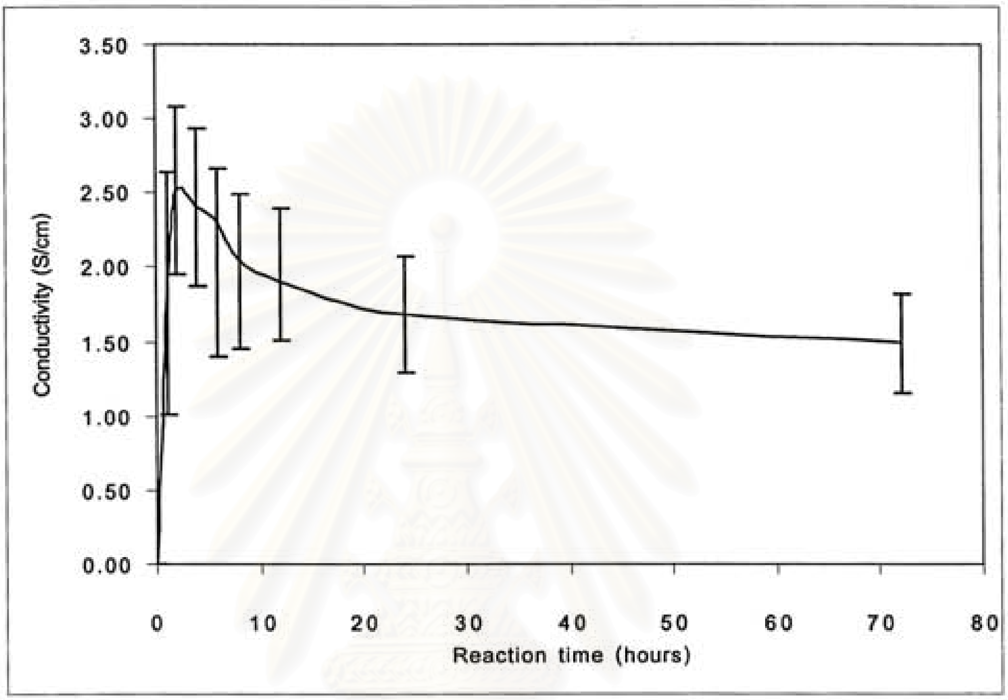


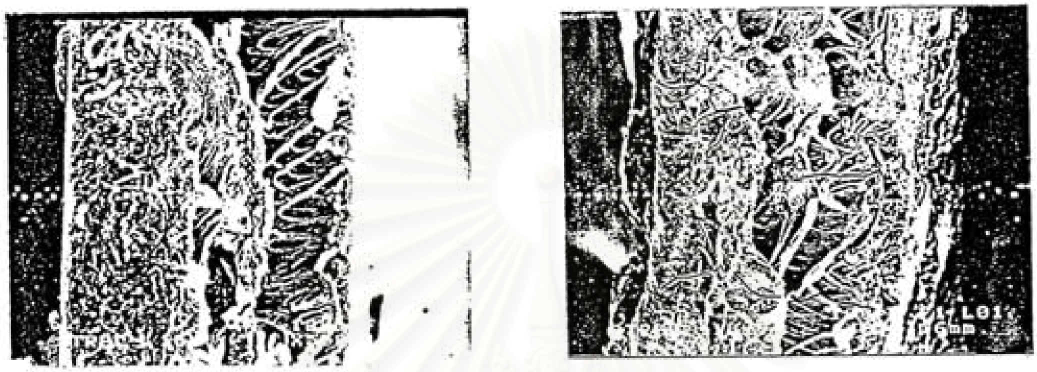
Figure 4.25 Effect of reaction time on the conductivity of PPy/PSS composite films prepared by swelling method using 1.25 M $FeCl_3$ and 10 °C polymerization time.

The result of the reaction time influence on conductivity of composite films was previously described in Section 4.1.1.4. The highest conductivity of PPy/PSS composite films was obtained at reaction time 2 hours.

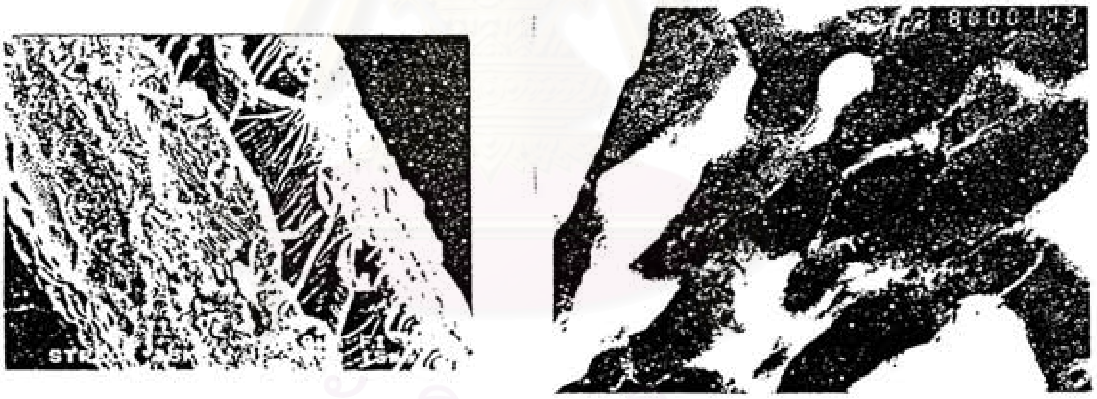
The highest conductivity (2.51 S/cm) PPy/PSS composite films prepared by swelling is obtained at 1.25 M $FeCl_3$, polymerized with pyrrole at 10 °C for 2 hours.

4.3.3 Morphology of PPy/PSS composite film

Morphology of PPy/PSS composite film prepared by swelling are shown in Figure 4.26.



(a) SEM of PSS film X 550 (b) SEM of PSS with $FeCl_3$ film X 550



(c) SEM of PPy/PSS composite film X 550 (d) TEM of PPy/PSS composite film

Figure 4.26 SEMs and TEM of PPy/PSS composite film prepared by swelling method.

SEMs of PPy/PSS composite film show that PPy occurred on surface of PSS film and PSS film is very brittle. TEM explains that PPy can interpenetrate PSS film well.

4.4 Mechanical properties of PPy composite films

Generally, a serious problem in technological application of free-standing PPy films was that these films are hard and brittle. Mechanical properties and processability of PPy films were improved by polymerization of pyrrole into mechanically superior but electrically inert materials. In this study, mechanical properties of PPy composite films were measured by the stress-strain technique and summarized in Appendix B but maximum stress and strain at maximum load of PPy/PSS composite films could not be measured.

Purely casted PVC films behave like brittle, with high maximum stress of 34.10 N/mm^2 and short strain at maximum load of 6.03%. Mechanical properties of PVC was improved from brittle to tough, depending on the addition of $FeCl_3$. It was observed that at lower $FeCl_3$ concentration, PPy/PVC composite film was still obtained high tensile strength of 20.56 N/mm^2 and low elongation at break of 8.15%. Therefore the properties of PPy/PVC composite films prepared by dissolving method were similar to purely casted PVC. When incorporation of $FeCl_3$ increased, these composite films were changed from brittle to soft and tough. At 0.33 M $FeCl_3$, lower maximum stress (6.72 N/mm^2) and longer strain at maximum load (25.86%) of PPy/PVC composite film were obtained. However, at the highest $FeCl_3$ concentration, the amount of PPy in matrix was too much that PPy/PVC composite film began to brittle, with short strain at maximum load (4.15%). Its property likes pure PPy which has high stress at break ca. 64 MPa and short elongation break lower than 5% [26].

The result is similar to observation of Mano et al. [26]. They reported that PVC changed from hard and brittle to soft and tough, depending on the degree of $FeCl_3$ incorporation. In this work, it was found that increasing in reaction time would decrease the toughness of PVC film. When reaction time increased from 2 hours to 12 hours, strain at maximum load decreased from 25.86 to 20.65%.

Maximum stress of PVC film and PS film were 53.57 and 36.44 N/mm^2 and strain at maximum load were 12.06 and 10.33%, respectively. For PPy composite film prepared by swelling method, immersion time of matrices in oxidant solution affected on tensile strength. At longer immersion time, maximum stress (40.23 N/mm^2) of PPy/PVC composite film decreased while strain at maximum load was steady, its property was compared with pure PVC film. It shows that hardness of PPy/PVC composite film was reduced and its toughness retained original property of PVC. Moreover maximum stress (20.53 N/mm^2) and strain at maximum load (6.47%) of PPy/PS composite film decreased from purely PS film.

Stress-strain behavior shows that $FeCl_3$ concentration affects on tensile strength of matrix. At 0.25 M $FeCl_3$, maximum stress (32.38 N/mm^2) of PPy/PVC composite film reduced and strain at maximum load (10.68%) was constant when its property is compared with pure PVC film. Maximum stress (12.26 N/mm^2) and strain at maximum load (5.04%) of PPy/PS composite film reduced when its property is compared with purely PS film. However, at 1.25 M $FeCl_3$, maximum stress of PPy/PVC and PPy/PS composite film increased from 32.38 to 39.56 and 12.26 to 21.83 N/mm^2, respectively. When its property was compared with PPy composite films polymerized at lower $FeCl_3$ concentration.

The effects of reaction time on stress-strain behavior of PPy composite films were studied and shown in Table 4.1.

Table 4.1 Stress-strain behavior of PPy composite films prepared by swelling method at various reaction time

Type of composite film	Reaction time (hours)	Maximum stress (N/mm^2)	Strain at maximum load (%)
PPy/PVC	2	40.23	11.96
	12	34.68	11.98
PPy/PS	2	20.53	6.47
	12	18.36	4.35

Table 4.1 indicated that at 12 hours, maximum stress (34.68 N/mm^2) of PPy/PVC composite film decreased. Maximum stress (18.36 N/mm^2) and strain at maximum load (4.35%) of PPy/PS composite film decreased. Tensile strength and elongation at break of PPy/PVC composite film prepared by swelling method are higher than the one prepared by dissolving method because PVC film was filled plasticizer to improve the hardness for using application. The optimum PPy/PVC composite films prepared by dissolving method with lower maximum stress (6.72 N/mm^2), higher strain at maximum load (25.86%) behave like soft and tough, its mechanical property retains PVC matrix. Moreover mechanical property of PPy/PVC composite film prepared by swelling method retains property of pure PVC film. It can explain that PPy acted as filler into matrices because property of matrices was changed from the original property.

4.5 Time-decay of PPy composite films

It is known that conductive polymer is sensitive to air oxidation. In this study, the conductive stability was explored by measuring the conductivity after storing for 3, 5, 10, 15, 30, 45, 60 and 90 days. Figure 4.27 shows that the conductivities of all the samples prepared by swelling decreases dramatically in the first 10-15 days of storing time.

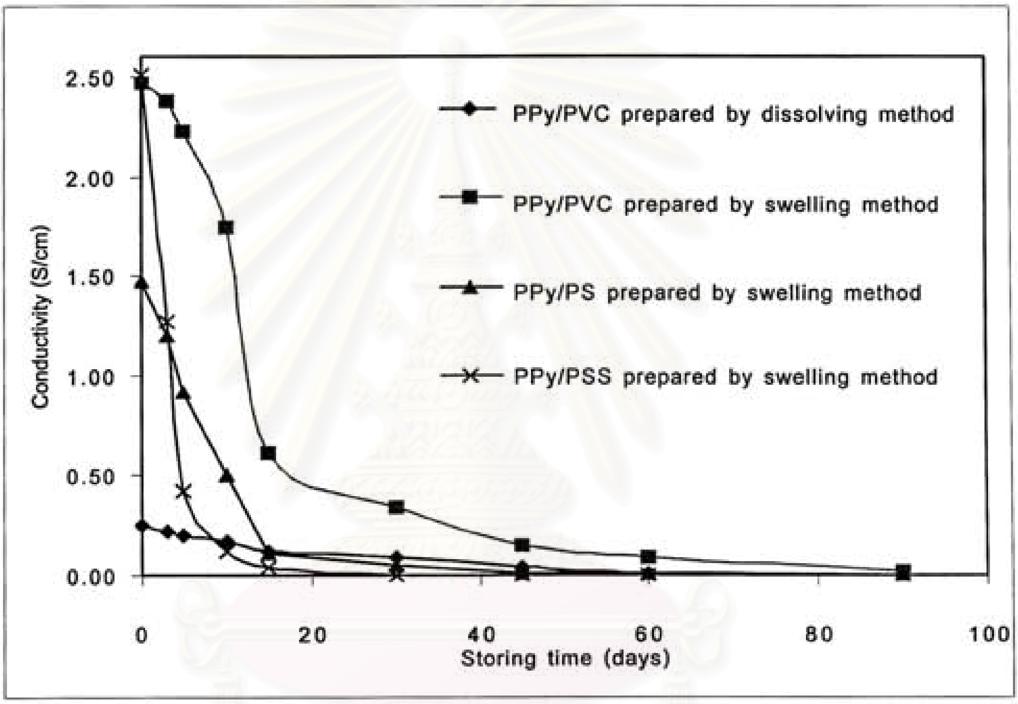


Figure 4.27 Conductivities of PPy composite film after certain storing time.

They slowly decay and finally seem to approach a low value. The conductivity of PPy/PVC composite film prepared by dissolving method decreased slowly until steady at 0.04 S/cm after 45 days. This behavior was suggested by Tanawadee [40] that the possibility of anion on the surface of the polymer matrix was less than anion which hold below the surface because anion on the surface is interfered by moisture or temperature. It was found that conductivity of PPy/PVC, PPy/PS and

PPy/PSS composite films prepared by swelling method, decreased rapidly at the first 10-15 days. The decrease in conductivity of these composites was then, very slow. Conductivities of PPy/PVC, PPy/PS, PPy/PSS composite films prepared by swelling method were steady at 0.10, 0.03, and 0 S/cm after 60, 30 and 30 days, respectively.

4.6 Comparison of PPy/PVC composite films prepared by dissolving and swelling methods

Morphology of PPy/PVC composite film obtained by swelling method was a sandwich type structure. PPy was formed at surface of PVC matrix film. The only layer of PPy was determined conductivity of PPy/PVC composite film. Its mechanical properties such as toughness, retain the same as the property of PVC matrix. Thus PPy acted as filler is less interpenetrated into plastic. Morphology of PPy/PVC composite film obtained by dissolving method shows that no layer was formed. Since PPy was developed where $FeCl_3$ existed as a blend with PVC. Conductivity of one by dissolving method was calculated by using thickness of PPy/PVC composite film. It was found that polymerization time for preparation of PPy/PVC composite films by swelling method is longer than the one by dissolving method. Thermal and air stabilities of PPy/PVC composite film prepared by dissolving method are better than the ones prepared by swelling method.

4.7 Comparison of PPy/PS and PPy/PVC composite film

Conductivity of PPy/PVC composite film is better than one of PPy/PS composite film. It was expected that PVC was polar group polymer and highly flexible. So it could allow interpenetration of polypyrrole into matrix film. The stress-strain behavior shows that PPy/PS composite films were more brittle than PPy/PVC composite film.

4.8 Comparison of PPy/PS and PPy/PSS composite film

In previous purpose, PSS was expected to improve conductivity of PPy composite films. In this study, it was observed that conductivity of PPy/PSS composite film was higher than the one of PPy/PS composite film. However, its conductivity was equal to PPy/PVC composite film obtained by swelling method. Polymerization time of PPy/PSS composite film was shorter than PPy/PS composite film. Even though, high conductivity of PPy/PSS composite film was obtained, other property, such as tensile strength, air stability, were not suitable for its further applications.

CHAPTER V

CONCLUSION

Polypyrrole composite films were obtained by two different methods. The first method, polymeric matrices used such as polyvinyl chloride, polystyrene and polystyrene sulfonate were dissolved in oxidant solution, then casted as films. These samples were exposed to pyrrole vapor. In this case, only PPy/PVC composite film was obtained at 0.33 M $FeCl_3$, 10 °C reaction temperature, 2 hours reaction time. Its conductivity showed to be 0.253 S/cm. An alternative preparation method was investigated in order to obtain final products with higher conductivity. In second method, polymeric matrices films were swollen in oxidant solution, the swollen polymer matrices were exposed to pyrrole vapor. In this case, PPy/PVC composite film was obtained by using 10 seconds immersion time in 1 M $FeCl_3$, 10 °C reaction temperature and 6 hours reaction time. Its conductivity showed to be 2.475 S/cm. PPy/PS composite film was obtained by using 10 seconds immersion time in 1 M $FeCl_3$, 10 °C reaction temperature and 6 hours reaction time. Its conductivity showed to be 1.475 S/cm. PPy/PSS composite film was obtained by using 1 second immersion time in 1.25 M $FeCl_3$, 10 °C reaction temperature and 2 hours reaction time. Its conductivity showed to be 2.541 S/cm.

In former method, polypyrrole could interpenetrate into polymeric matrices well, it was also possible to incorporate some reinforcement polypyrrole that improved the mechanical properties of polymeric matrices. The second method may allow less amount of polypyrrole into polymeric matrices, therefore, polypyrrole composite films retained property of insulating polymer and conductive polymer, except PPy/PSS composite film which is easily fractured. All polypyrrole composite films could be used in electromagnetic interference application with the process developed in this study.

5.2 Suggestion

To improve conductivity polymer composite film for suitable application industry, polymeric matrices should be high polar group polymer such as nylon 6, polyamide and retained mechanical properties of plastic. High polar group polymer can accept incorporation of polypyrrole into it well.

REFERENCES

1. Lewis, T.W., and Wallance, G.G. 1997. The basic for development of intelligent materials. *J. Chem. Educ.* 74: 703-708.
2. Zoppi, R.A.; Fekusberti, M.I.; and De Paoli, M.A. 1994. Chemical preparation of conductive elastomeric blends: Polypyrrole/EPDM-I. Oxidant particle size effect. *J. Polym. Sci. Part A: Polym. Chem.* 32: 1001-1008.
3. Patil, A.O. 1988. Optical properties of conducting polymers. *Chem. Rev.* 88: 183-200.
4. Krohnke, C. *Polymeric Materials Encyclopedia Electrically Conducting Composites*. NW: CRC Press.
5. Zoppi, R.A., and De Paoli M.A. 1996. Chemical preparation of conductive elastomeric blends: Polypyrrole/EPDM-II. Utilization of matrices containing crosslinking agents, reinforcement fillers and stabilizers. *Polymer* 37: 1999-2009.
6. Beadle, P.M.; Rowan, L.; Mykytiuk, J.; Billinghan, N.C.; and Armes, S.P. 1993. Synthesis and characterization of sterically stabilized colloidal dispersions of polypyrrole using novel tailor-made water-soluble block copolymers of narrow molecular weight distribution. *Polymer* 34: 1561-1563.
7. Ruckenstein, E., and Yang, S. 1993. Processable conductive polypyrrole/poly (alkylmethacrylate) composites prepared by an emulsion pathway. *Polymer* 34: 4655-4660.
8. Hearn, M.J.; Fletcher, I.W.; Church, S.P.; and Armes, S.P. 1993. Characterization of polypyrrole fiber composites by time of fight secondary on mass spectrometry and vibrational spectroscopy. *Polymer* 34: 262-266.
9. Kelkar, D.S., and Bhat, N.V. 1993. Composite films of Nylon 6-polypyrrole thermal behavior, mechanical-properties and electrical conduction. *Polymer* 34: 986-989.

10. Martin, C.R.; Liang, W.; Menon, V.; Parthasarathy, R.; and Parthasarathy, A. 1993. Template synthesis of electronically conductive polymers-a new route for achieving higher electronic conductivities. *Synth. Met.* 55-57: 1165-1170.

11. Kang, T.J.; Miyata, S.; and Miyata, Y. 1993. Preparation and morphology of electrically conductive and transparent poly(vinylchloride)-polypyrrole composite films. *Polym. Bull.* 31: 593-599.

12. Sata, T. 1993. Anti-organic fouling properties of composite membranes prepared from anion-exchange membranes and polypyrrole. *J. Chem. Soc. Chem. Commun.* 1122-1124.

13. Sata, T.; Kishimoto, F.; and Oqura, S. 1993. High acid retention properties of composite membranes prepared from anion-exchange membranes and poly(pyrrole). *J. Chem. Soc. Chem. Commun.* 1159-1160.

14. Kathirgamanathan, P. 1993. Novel cable shielding materials based on the impregnation of microporous membranes with inherently conducting polymers. *Adv. Mater.* 5: 281-283.

15. Matencio, T.; Mano, V.; Felesberti, M.I.; and De Paoli, M.A. 1994. Electrochemical study of poly(vinyl chloride)-polypyrrole blends. *Electrochim. Acta.* 39: 1393-1400.

16. Makhlouki, M.; Bernede, J.C.; Morshi, M.; Bonnet, A.; Conan, A.; and Lefrant, S. 1994. XPS study of conducting polypyrrole-poly(vinyl alcohol) composites. *Synth. Met.* 62: 101-108.

17. Atkins, P.W. 1994. *Physical Chemistry.* 5th ed. UK: Oxford University Press.

18. Duke, C.B., and Gibson, H.W. 1982. Polymer conductive. *Encyclopedia of Chemical Technology.* 18: 755-793.

19. Mark, H.F.; Bikales, N.M.; Overberger, G.G.; and Menges, G. 1985. Dielectric heating to embedding. *Encyclopedia of Polymer Science and Engineering*. NY: John Wiley & Son.

20. Harrison, W.A. 1970. *Solid State Theory*. International student edition Mc Graw-Hill Book Company.

21. Puong, V.T. 1997. Conducting polymers: A novel alternative material. *Chemistry in Australia*. 20-22.

22. Chao, T.H., and March, J. 1988. A study of polypyrrole synthesized with oxidative transition metal ion. *J. Polym. Sci. Part A: Polym. Chem.* 26: 743-753.

23. Ojio, T., and Miyata, S. 1986. Highly transparent and conducting polypyrrole-poly (vinyl alcohol) composite films prepared by gas state polymerization. *Polym. J.* 18(1): 95-98.

24. Kurachi, K., and Kise, H. 1994. Preparation of polypyrrole/polyethylene composite films by vapor-phase oxidative polymerization of pyrrole. *Polym. J.* 26: 1325-1331.

25.Yang, J.; Yang, Y.; Hou, J.; Zhang, X.; Zhu, W.; and Xu, M. 1996. Polypyrrole-polypropylene composite films: Preparation and properties. *Polymer* 37: 793-798.

26. Mano, V.; Felisberti, M.I.; Matencio, T.; and De Paoli. M.A. 1996. Thermal, mechanical and electrochemical behaviour of poly(vinyl chloride)/polypyrrole blends (PVC/PPy). *Polymer* 37: 5165-5170.

27. Kise, H.; Nakato, M.; and Taga M. 1992. Synthesis of electrical conductive polypyrrole films by interphase oxidative polymerization-effects of polymerization temperature and oxidizing agents. *Polym.J.* 24: 437-441.

28. Jousse, F.; Hourquebie, P.; Deleuze, C.; and Olmedo, L. 1992. Electrical, optical and magnetic properties of organic. *Mater. Res. Soc. Symp. Proc*. 247: 705-710.

29. Fabianowski, W.; Pron, A.; and Zagorska, M. 1987. Spectroscopic and morphological studies of a polypyrrole-poly(vinyl alcohol) composite. *Polym.Commun.* 28: 193-195.

30. He, F.; Omoto, M.; Yamamoto, T.; and Kise, H. 1995. Preparation of polypyrrole-polyurethane composite foam by vapor phase oxidation polymerization. *J. Appl.Polym.Sci.* 55: 283-287.

31. Tieke, B., and Gabriel W. 1990. Conducting polypyrrole-polyimide composite films. *Polymer* 31: 20-23.

32. Zinger, B., and Kijel, D. 1992. Electrically conducting ionomers. *Polymer* 33: 467-474.

33. De Jesus, M.C.; Weiss, R.A.; and Chen, Y. 1997. The development of conductive composite by a diffusion-limited In situ polymerization of pyrrole in sulfonate polystyrene ionomers. *J. Polym. Sci. Part B: Polym. Phys.* 35: 347-357.

34. De Paoli, M.A.; Waltman, R.J.; Diaz, A.F.; and Bargon, J. 1984. Conductive composites from poly(vinyl chloride) and polypyrrole. *J. Chem. Soc. Chem. Commun.* 1015-1016.

35. Meng, O., and Chi, M.C. 1998. Conductive polymer composites prepared by pyrrole-coated poly(vinyl chloride) powder: Relationship between conductivity and surface morpholgy. *Polymer* 39: 1857-1862.

36. Armes, S.P. et al. 1991. Conducting polymer-colloidal silica composites. *Polymer* 32: 2325-2330.

37. Somchoke Lauhasurayothin *Preparation of Conductive Polypyrrole Composites by Chemical Oxidation*. (Master's thesis, Program of Petrochemistry and Polymer Science, Graduate School, Chulalongkorn University, 1999).

38. Bi, X.; Xu, C.; and Wang, P. 1995. Continuous vapor phase polymerization of pyrrole electrically conductive composite fiber of polypyrrole with poly(*p*-phenylene terepthalamide). *J. Appl. Polym. Sci.* 58: 2155-2159.

39. Mandel, B.M.; Digar, M.L.; and Bhattacharyya, N. 1994. Dispersion polymerization of pyrrole using poly(vinyl methyl ether) as stabilizer. *Polymer* 35: 377-382.

40. Tanawadee Leejarkpai *Synthesis of Electrical Conducting Polymer by Solution Polymerization*. (Master's thesis, Program of Petrochemistry and Polymer Science, Graduate School, Chulalongkorn University, 1993).

41. Kaneto, K.; Satoh, M.; and Yoshino, K. 1986. Dependences of the electrical and mechanical properties of conducting polypyrrole film on conditions of electrochemical polymerization in an aqueous medium. *Synth. Met.* 14: 286-296.

42. Yin, W.; Liu, H.; Li, J.; Li, Y.; and Gu, T. 1997. Conducting based on polypyrrole and crosslinked poly (styrene-butyl acrylate-hydroxyethyl acrylate). *J. Appl. Polym. Sci.* 64: 2293-2298.

43. Machida, S.; Miyata, S.; and Techagumpuch, A. 1989. Chemical synthesis of highly electrically conductive polypyrrole. *Synth. Met.* 31: 311-318.

44. Lacelles, S.F., and Armes, S.P. 1997. Synthesis and characterization of micrometer-sized, polypyrrole-coated polystyrene latexes. *J. Mater. Chem.* 7: 1339-1347.

45. Lacelles, S.F., and Armes, S.P. 1997. Surface characterization of micrometre-sized polypyrrole-coated polystyrene latexes : verification of a 'core-shell' morphology. *J. Mater. Chem.* 7: 1349-1355.

46. Ruckenstein, E., and Park, J.S. New method for the preparation of thick conducting polymer composites. *J. Appl. Polym. Sci.* 42: 925-934.

47. Yassar, A.; Roncali, J.; and Garnier, F. 1987. Aqueous suspension of conducting material from polypyrrole-coated submicronic latex particles. *Polym. Commun.* 28: 103-104.

48. Wang, H.L.; Tappare, L.; and Fernandez, J.E. 1990. Conducting polymer blends: Polythiophene and polypyrrole blend with polystyrene and poly(bis-phenol A carbonate). *Macromolecules* 23: 1053-1059.

49. Bates, N.; Cross, M.; Lines, R.; and Walton, D. 1985. Flexible and heat-processable conductive film of polypyrrole. *J. Chem. Soc. Chem. Commun.* 871-872.

50. Shimidzu, T.; Ohtan, A.; Lyoda, T.; and Honda, K. 1986. A funtionalized polypyrrole film prepared by chemical polymerization at vapour-liquid interface. *J. Chem. Soc. Chem. Commun.* 1414-1415.

51. Hondo, N., and Nakamura, S. 1994. Electrochemical properties of polypyrrole/polystyrene sulfonate composite film and its application to rechargeable lithium battery cathodes. *J. Electrochem. Soc.* 141: 2326-2331.

52. Glatzhofer, D.T.; Ulanski, J.; and Wegher, G. 1987. Controlled conductivity behaviour in poly(*p*-styrenesulphonate) salts of polypyrrole. *Polymer* 28: 449-453.

53. Arribas, C., and Rucda, D. 1996. Preparation of conductive polypyrrole-polystyrene sulfonate by chemical polymerization. *Synth. Met.* 79: 23-26.

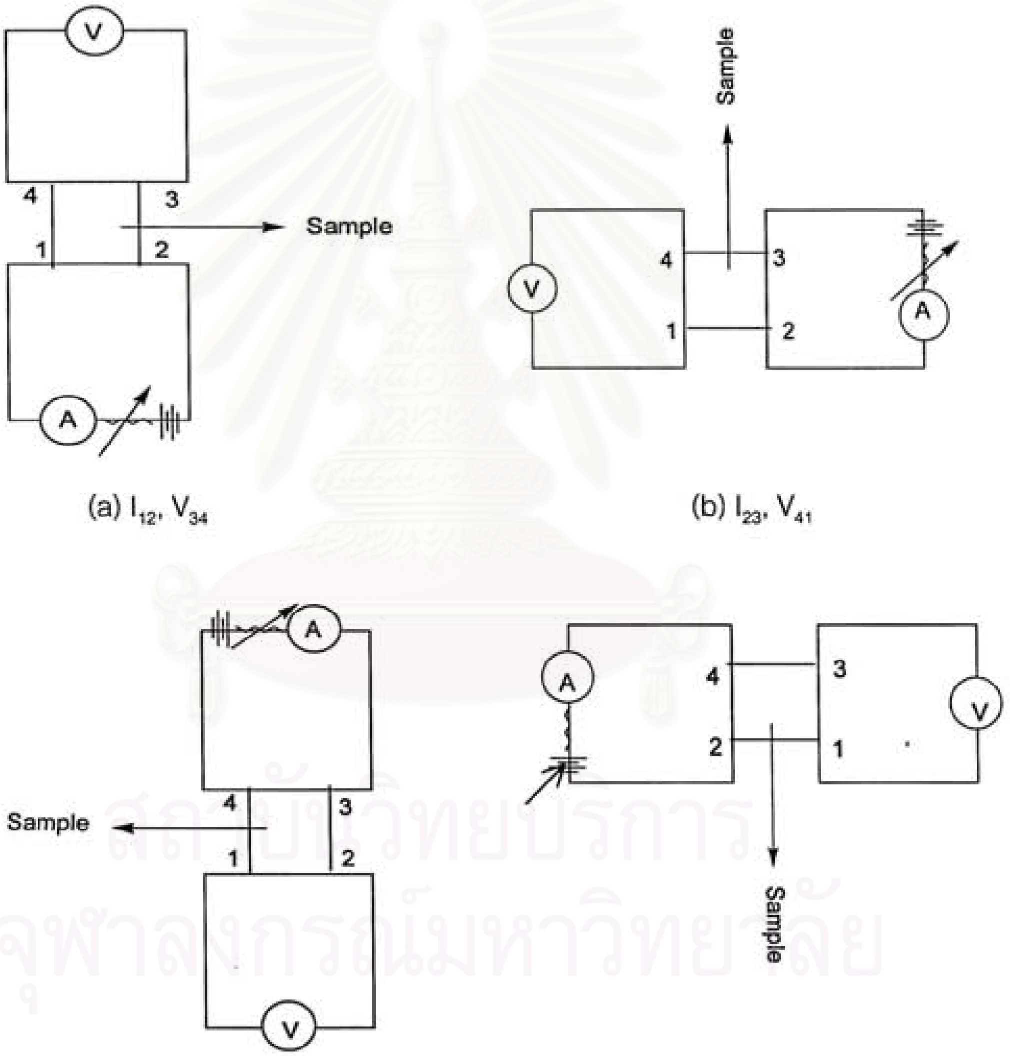
54. Harrick, N.J. 1967. *Internal Reflection Spectroscopy*. NY: John Wiley & Sons.

APPENDICES

APPENDIX A

Electrical conductivity was measured by Van der Pauw method.

Van der Pauw is one technique for measuring conductivity (σ) of sample. Four contacts are put at edge of sample, Figure A-1.



(a) I_{12}, V_{34}

(b) I_{23}, V_{41}

(c) I_{34}, V_{12}

(d) I_{41}, V_{23}

Figure A-1 Van der Pauw method

First, contacts 1 and 2 are applied suitable current (I_{12}) and contacts 3 and 4 are measured voltage potential (V_{34}). Each I_{12} is used the resistance 100 kΩ, 200 kΩ and 300 kΩ, respectively. Table A-1 can show data of I_{12} and V_{34}.

Table A-1 Current and voltage potential data

Resistance	Current (Ampere)	Voltage potential (Volt)
100 kΩ	$I_{12\,I}$	$V_{34\,I}$
200 kΩ	$I_{12\,I}$	$V_{34\,I}$
300 kΩ	$I_{12\,I}$	$V_{34\,I}$

When these data are plotted between I and V, the R_1 is obtained, following equation A-1.

$$V_{34} \quad = \quad R_1 I_{12} \qquad \text{A-1}$$

Second, I_{23} is applied and V_{41} is measured. Data are obtained in the same way. So that R_2 is obtained. Conductivity (σ) can be calculated from R_1 and R_2, following equation A-2.

$$\exp(-\pi R_1 d\sigma_1) + \exp(-\pi R_2 d\sigma_1) = 1 \qquad \text{A-2}$$

Where d is the thickness of the sample.

Third, I_{34} is applied and V_{12} is measured, σ_2 is obtained. Finally, I_{41} is applied and V_{23} is measured , σ_3 and σ_4 are obtained. Table A-2 shows σ_1, σ_2, σ_3 and σ_4 respectively.

Table A-2 Conductivity data

Conductivity	R_1		R_2	
	I	V	I	V
σ_1	I_{12}	V_{34}	I_{23}	V_{41}
σ_2	I_{23}	V_{41}	I_{34}	V_{12}
σ_3	I_{34}	V_{12}	I_{41}	V_{23}
σ_4	I_{41}	V_{23}	I_{12}	V_{34}

Equation A-3 is accuracy conductivity (average conductivity).

$$\sigma = (\sigma_1 + \sigma_2 + \sigma_3 + \sigma_1)/4 \qquad \text{A-3}$$

Contacts resistance is problem of accurate measurement. So that it may be reduced by using carbon paints.

Detail of calculating conductivity

Computer program is constructed following equation A-1 by using program "GW basic" language. The detail of 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 = 1 ; X
Ok
```

Example for calculating conductivity

After Is were applied through 4 contacts, Vs are measured. R can be obtained by least square fit technique.

Sample

1. Thickness d = 0.0035 cm
2. The slope of graph

   I_{12}, V_{34} : (0.88, 0.065); (0.44, 0.033); (0.30, 0.023); $R_1 = 72.49$

   I_{23}, V_{41} : (0.87,0.021); (0.43,0.010); (0.30, 0.007); $R_2 = 24.67$

   I_{34}, V_{12} : (0.88, 0.066); (0.43, 0.033); (0.29, 0.023); $R_3 = 72.99$

   I_{41}, V_{23} : (0.88,0.021); (0.44,0.010); (0.30, 0.007); $R_4 = 24.35$
3. Calculation program

```
Run
Sample Thickness     =     0.0035
Resistance No.1      =     72.49
Resistance No 2      =     24.67
Conductivity         =     1.42
Ok
Run
Sample Thickness     =     0.0035
Resistance No.1      =     24.67
Resistance No 2      =     72.99
Conductivity         =     1.42
```

Run

Sample Thickness = 0.0035

Resistance No.1 = 72.99

Resistance No 2 = 24.35

Conductivity = 1.42

Run

Sample Thickness = 0.0035

Resistance No.1 = 24.35

Resistance No 2 = 72.49

Conductivity = 1.42

σ_1, σ_2, σ_3 and σ_4 can be obtained. These value are averaged to obtain the final value. Conductivity shows to be 1.42 S/cm.

Electrical conductivity value of polypyrrole composite films

Table A-3.1 Effect of reaction time on conductivity value of PPy/PVC composite films prepared by dissolving method

Reaction time (hours)	Conductivity (S/cm)						Thickness (cm)					
	#1	#2	#3	#4	average	SD	#1	#2	#3	#4	average	SD
1	0.1445	0.1515	0.1196	0.1445	0.1400	0.0141	0.0115	0.0110	0.0125	0.0130	0.0120	0.0009
2	0.2762	0.2314	0.2505	0.2550	0.2533	0.0184	0.0120	0.0115	0.0125	0.0120	0.0120	0.0004
4	0.2403	0.2049	0.2572	0.2697	0.2430	0.0281	0.0115	0.0115	0.0115	0.0115	0.0115	0.0000
6	0.1908	0.2310	0.2133	0.2617	0.2242	0.0299	0.0140	0.0100	0.0120	0.0120	0.0120	0.0016
8	0.1896	0.1900	0.2433	0.2495	0.2181	0.0328	0.0135	0.0120	0.0120	0.0105	0.0120	0.0012
12	0.1937	0.1759	0.2215	0.2490	0.2100	0.0320	0.0120	0.0125	0.0115	0.0120	0.0120	0.0004
24	0.1776	0.1777	0.1343	0.1753	0.1662	0.0213	0.0105	0.0115	0.0125	0.0135	0.0120	0.0013
72	0.1277	0.1863	0.1326	0.1405	0.1468	0.0269	0.0150	0.0090	0.0120	0.0100	0.0115	0.0026

Table A-3.2 Effect of $FeCl_3$ concentration on conductivity value of PPy/PVC composite films prepared by dissolving method

$FeCl_3$ Concentration (M)	Conductivity (S/cm)						Thickness (cm)					
	#1	#2	#3	#4	average	SD	#1	#2	#3	#4	average	SD
0.20	0.0280	0.0260	0.0298	0.0279	0.0279	0.0016	0.0090	0.0090	0.0100	0.0100	0.0095	0.0006
0.25	0.0797	0.1045	0.1054	0.1116	0.1003	0.0141	0.0120	0.0110	0.0115	0.0095	0.0110	0.0011
0.33	0.2762	0.2314	0.2505	0.2550	0.2533	0.0184	0.0120	0.0115	0.0125	0.0120	0.0120	0.0004
0.50	0.2936	0.2915	0.2611	0.2362	0.2706	0.0273	0.0125	0.0115	0.0115	0.0125	0.0120	0.0006
1.00	0.3600	0.4008	0.2853	0.2665	0.3282	0.0631	0.0120	0.0120	0.0120	0.0130	0.0123	0.0005

Table A-3.3 Effect of reaction temperature on conductivity value of PPy/PVC composite films prepared by dissolving method

Reaction temperature (°C)	Conductivity (S/cm)						Thickness (cm)					
	#1	#2	#3	#4	average	SD	#1	#2	#3	#4	average	SD
-15	0.1385	0.1680	0.2111	0.2362	0.1885	0.0436	0.0135	0.0125	0.0115	0.0105	0.0120	0.0013
0	0.2603	0.2766	0.2387	0.2113	0.2467	0.0283	0.0125	0.0125	0.0120	0.0120	0.0123	0.0003
10	0.2762	0.2314	0.2505	0.2550	0.2533	0.0184	0.0120	0.0115	0.0125	0.0120	0.0120	0.0004
30	0.1184	0.0904	0.1343	0.1463	0.1224	0.0242	0.0115	0.0130	0.0120	0.0115	0.0120	0.0007
45	0.0998	0.0812	0.1112	0.1037	0.0990	0.0128	0.0110	0.0120	0.0100	0.0110	0.0110	0.0008

Table A-4.1 Effect of $FeCl_3$ concentration on conductivity value of PPy/PVC composite films prepared by swelling method

$FeCl_3$ Concentration (M)	Conductivity (S/cm)						Thickness (cm)					
	#1	#2	#3	#4	average	SD	#1	#2	#3	#4	average	SD
0.25	0.1410	0.1213	0.2030	0.1630	0.1571	0.0350	0.0230	0.0235	0.0230	0.0230	0.0231	0.0002
0.50	0.3990	0.2210	0.2857	0.3030	0.3022	0.0736	0.0240	0.0250	0.0250	0.0240	0.0245	0.0006
0.75	0.7086	0.7038	0.9880	1.0300	0.8576	0.1757	0.0255	0.0260	0.0245	0.0240	0.0250	0.0009
1.00	1.9292	1.8193	1.4160	2.0423	1.8017	0.2728	0.0245	0.0250	0.0255	0.0250	0.0250	0.0004
1.25	1.6280	1.5368	1.7444	2.0460	1.7388	0.2217	0.0245	0.0245	0.0245	0.0240	0.0244	0.0003

Table A-4.2 Effect of immersion time on conductivity value of PPy/PVC composite films prepared by swelling method

Immersion time (seconds)	Conductivity (S/cm)						Thickness (cm)					
	#1	#2	#3	#4	average	SD	#1	#2	#3	#4	average	SD
1	1.0250	0.9633	0.9867	1.1850	1.0400	0.1000	0.0240	0.0250	0.0250	0.0240	0.0245	0.0006
5	1.8680	1.8240	1.5520	1.3480	1.6480	0.2440	0.0245	0.0245	0.0245	0.0245	0.0245	0.0000
10	1.9292	1.8193	1.4160	2.0423	1.8017	0.2728	0.0245	0.0250	0.0255	0.0250	0.0250	0.0004
15	1.6640	1.4114	1.7433	1.8900	1.6772	0.2004	0.0245	0.0255	0.0250	0.0250	0.0250	0.0004

Table A-4.3 Effect of reaction time on conductivity value of PPy/PVC composite films prepared by swelling method

Reaction time (hours)	Conductivity (S/cm)						Thickness (cm)					
	#1	#2	#3	#4	average	SD	#1	#2	#3	#4	average	SD
1	1.1597	1.6605	0.9507	1.2200	1.2477	0.2984	0.0250	0.0240	0.0250	0.0240	0.0245	0.0006
2	1.9292	1.8193	1.4160	2.0423	1.8017	0.2728	0.0245	0.0250	0.0255	0.0250	0.0250	0.0004
4	2.3450	1.6940	1.8109	2.3140	2.0410	0.3368	0.0240	0.0260	0.0255	0.0245	0.0250	0.0009
6	2.9280	2.5600	2.2360	2.1640	2.4720	0.3494	0.0245	0.0245	0.0245	0.0245	0.0245	0.0000
8	2.3156	2.5720	1.9171	2.0640	2.2172	0.2881	0.0245	0.0245	0.0255	0.0245	0.0248	0.0005
12	2.2960	1.8286	2.2700	1.9829	2.0944	0.2270	0.0245	0.0255	0.0240	0.0255	0.0249	0.0007
24	1.0475	1.6233	1.6748	1.6826	1.5070	0.3075	0.0260	0.0250	0.0245	0.0255	0.0253	0.0006
72	1.6436	1.9768	1.6748	2.3556	1.9127	0.3313	0.0245	0.0245	0.0245	0.0245	0.0245	0.0000

Table A-4.4 Effect of reaction temperature on conductivity value of PPy/PVC composite films prepared by swelling method

Reaction temperature (°C)	Conductivity (S/cm)						Thickness (cm)					
	#1	#2	#3	#4	average	SD	#1	#2	#3	#4	average	SD
-15	0.9340	1.4685	1.1388	1.5333	1.2687	0.2822	0.0255	0.0240	0.0245	0.0235	0.0244	0.0009
0	1.5909	1.9305	1.8770	1.5310	1.7324	0.2006	0.0255	0.0245	0.0250	0.0260	0.0253	0.0006
10	1.9292	1.8193	1.4160	2.0423	1.8017	0.2728	0.0245	0.0250	0.0255	0.0250	0.0250	0.0004
30	0.5580	0.6257	0.7143	0.4703	0.5921	0.1034	0.0250	0.0250	0.0250	0.0250	0.0250	0.0000
45	0.1405	0.2280	0.1850	0.1083	0.1655	0.0522	0.0260	0.0250	0.0250	0.0260	0.0255	0.0006

Table A-5.1 Effect of $FeCl_3$ concentration on conductivity value of PPy/PS composite films prepared by swelling method

$FeCl_3$ Concentration (M)	Conductivity (S/cm)						Thickness (cm)					
	#1	#2	#3	#4	average	SD	#1	#2	#3	#4	average	SD
0.25	0.1712	0.2330	0.2608	0.1820	0.2118	0.0420	0.0225	0.0225	0.0225	0.0225	0.0225	0.0000
0.50	0.3558	0.2516	0.3030	0.4056	0.3290	0.0665	0.0225	0.0225	0.0225	0.0225	0.0225	0.0000
0.75	0.4810	0.3870	0.6378	0.3544	0.4651	0.1271	0.0230	0.0230	0.0225	0.0235	0.0230	0.0004
1.00	0.4330	0.4880	0.6368	0.5840	0.5355	0.0920	0.0230	0.0230	0.0230	0.0230	0.0230	0.0000
1.25	0.3810	0.4040	0.5210	0.5840	0.4725	0.0963	0.0230	0.0230	0.0230	0.0230	0.0230	0.0000

Table A-5.2 Effect of immersion time on conductivity value of PPy/PS composite films prepared by swelling method

Immersion time (seconds)	Conductivity (S/cm)						Thickness (cm)					
	#1	#2	#3	#4	average	SD	#1	#2	#3	#4	average	SD
1	0.3180	0.3300	0.4480	0.4620	0.3895	0.0760	0.0225	0.0225	0.0225	0.0225	0.0225	0.0000
5	0.3510	0.5890	0.6120	0.4980	0.5125	0.1184	0.0230	0.0230	0.0230	0.0230	0.0230	0.0000
10	0.4333	0.4880	0.6368	0.5840	0.5355	0.0919	0.0230	0.0230	0.0230	0.0230	0.0230	0.0000
15	0.5230	0.4120	0.3940	0.5620	0.4728	0.0824	0.0230	0.0230	0.0235	0.0230	0.0231	0.0003

Table A-5.3 Effect of reaction temperature on conductivity value of PPy/PS composite films prepared by swelling method

Reaction temperature (°C)	Conductivity (S/cm)						Thickness (cm)					
	#1	#2	#3	#4	average	SD	#1	#2	#3	#4	average	SD
-15	0.4663	0.4639	0.5918	0.4187	0.4852	0.0744	0.0230	0.0230	0.0230	0.0230	0.0230	0.0000
10	0.4333	0.4880	0.6368	0.5840	0.5355	0.0919	0.0230	0.0230	0.0230	0.0230	0.0230	0.0000
30	0.1983	0.2180	0.2560	0.1480	0.2051	0.0450	0.0230	0.0230	0.0230	0.0230	0.0230	0.0000
45	0.1227	0.2220	0.0967	0.2800	0.1803	0.0856	0.0235	0.0225	0.0235	0.0225	0.0230	0.0006

Table A-5.4 Effect of reaction time on conductivity value of PPy/PS composite films prepared by swelling method

Reaction time (hours)	Conductivity (S/cm)						Thickness (cm)					
	#1	#2	#3	#4	average	SD	#1	#2	#3	#4	average	SD
1	0.3190	0.2180	0.3950	0.2430	0.2938	0.0800	0.0230	0.0230	0.0230	0.0230	0.0230	0.0000
2	0.4333	0.4880	0.6368	0.5840	0.5355	0.0919	0.0230	0.0230	0.0230	0.0230	0.0230	0.0000
4	1.4900	1.6320	1.1900	1.0350	1.3368	0.2728	0.0230	0.0230	0.0230	0.0230	0.0230	0.0000
6	1.3700	1.8200	1.4700	1.2400	1.4750	0.2485	0.0230	0.0230	0.0230	0.0230	0.0230	0.0000
8	0.8800	1.3400	0.8751	1.1800	1.0688	0.2303	0.0235	0.0230	0.0230	0.0230	0.0231	0.0002
12	0.8320	0.7500	0.6870	1.2820	0.8878	0.2695	0.0230	0.0230	0.0230	0.0225	0.0229	0.0002
24	1.2840	0.7480	0.6021	0.7900	0.8560	0.2965	0.0225	0.0230	0.0230	0.0230	0.0229	0.0002
72	0.9738	0.6497	0.6410	1.2622	0.8817	0.2972	0.0225	0.0230	0.0230	0.0225	0.0228	0.0003

Table A-6.1 Effect of $FeCl_3$ concentration on conductivity value of PPy/PSS composite films prepared by swelling method

$FeCl_3$ Concentration (M)	Conductivity (S/cm)						Thickness (cm)					
	#1	#2	#3	#4	average	SD	#1	#2	#3	#4	average	SD
0.5	2.4800	2.0933	1.0800	1.4800	1.7833	0.6240	0.0390	0.0395	0.0400	0.0395	0.0395	0.0004
0.75	2.1733	1.3800	1.9750	2.1200	1.9121	0.3645	0.0395	0.0405	0.0400	0.0400	0.0005	0.0004
1	2.4050	2.6400	1.6920	2.6200	2.3393	0.4444	0.0400	0.0395	0.0405	0.0400	0.0005	0.0004
1.25	1.9771	3.3133	2.3840	2.3800	2.5136	0.5663	0.0415	0.0395	0.0405	0.0405	0.0002	0.0008

Table A-6.2 Effect of reaction temperature on conductivity value of PPy/PSS composite films prepared by swelling method

Reaction temperature (°C)	Conductivity (S/cm)						Thickness (cm)					
	#1	#2	#3	#4	average	SD	#1	#2	#3	#4	average	SD
-15	3.4067	1.0143	2.1900	1.5567	2.0419	1.0289	0.0395	0.0415	0.0400	0.0410	0.0405	0.0009
10	1.9771	3.3133	2.3840	2.3800	2.5136	0.5663	0.0415	0.0395	0.0405	0.0405	0.0405	0.0008
30	1.6880	1.5200	1.7600	2.0520	1.7550	0.2221	0.0405	0.0405	0.0405	0.0405	0.0405	0.0000

Table A-6.3 Effect of reaction time on conductivity value of PPy/PSS composite films prepared by swelling method

Reaction time (hours)	Conductivity (S/cm)						Thickness (cm)					
	#1	#2	#3	#4	average	SD	#1	#2	#3	#4	average	SD
1	1.2025	1.3567	2.9900	1.7467	1.8240	0.8140	0.0420	0.0410	0.0400	0.0410	0.0410	0.0008
2	1.9771	3.3133	2.3840	2.3800	2.5136	0.5663	0.0415	0.0395	0.0405	0.0405	0.0405	0.0008
4	2.7720	2.8250	2.3400	1.6771	2.4035	0.5307	0.0405	0.0400	0.0400	0.0415	0.0405	0.0007
6	2.8255	1.3543	2.2260	1.7371	2.0357	0.6360	0.0400	0.0415	0.0410	0.0415	0.0410	0.0007
8	1.7997	2.2370	2.5280	1.3306	1.9738	0.5230	0.0410	0.0410	0.0405	0.0415	0.0410	0.0004
12	1.3657	2.4400	1.9267	2.0594	1.9480	0.4450	0.0415	0.0405	0.0410	0.0415	0.0411	0.0005
24	2.2367	1.6143	1.3109	1.5743	1.6840	0.3922	0.0410	0.0415	0.0435	0.0415	0.0419	0.0011
72	1.2229	1.9680	1.3109	1.4600	1.4904	0.3331	0.0450	0.0430	0.0435	0.0445	0.0440	0.0009

Table A-7 Time-decay of polypyrrole composite films

Type of composite film	Storing time (days)	Conductivity (S/cm)						Thickness (cm)
		#1	#2	#3	#4	average	SD	
PPy/PVC prepared dissolving method	0	0.2762	0.2314	0.2505	0.2550	0.2533	0.0184	0.0120
	3	0.2518	0.2047	0.2211	0.2280	0.2264	0.0195	
	5	0.2094	0.1778	0.2055	0.2048	0.1994	0.0145	
	10	0.1668	0.1516	0.1670	0.1845	0.1675	0.0135	
	15	0.1354	0.1126	0.1234	0.1132	0.1212	0.0107	
	30	0.0947	0.0830	0.0922	0.0823	0.0880	0.0063	
	45	0.0469	0.0416	0.0411	0.0377	0.0419	0.0038	
	60	0.0079	0.0076	0.0075	0.0065	0.0074	0.0060	
	90	0.0021	0.0025	0.0017	0.0021	0.0021	0.0003	
PPy/PVC prepared swelling method	0	2.9280	2.5600	2.2360	2.1640	2.4720	0.3494	0.0250
	3	2.8560	2.4500	2.1300	2.0856	2.3804	0.3562	
	5	2.5956	2.3680	1.9480	1.9800	2.2229	0.3133	
	10	1.4276	1.9040	1.9840	1.6400	1.7389	0.2543	
	15	0.6356	0.5912	0.6296	0.5832	0.6099	0.0265	
	30	0.3941	0.2980	0.3032	0.3693	0.3411	0.0479	
	45	0.1432	0.1742	0.1250	0.1648	0.1518	0.0221	
	60	0.0894	0.0988	0.0849	0.0948	0.0920	0.0061	
	90	0.0219	0.0190	0.0205	0.0215	0.0207	0.0013	

Continue Table A-7

Type of composite film	Storing time (days)	Conductivity (S/cm)						Thickness
		#1	#2	#3	#4	average	SD	(cm)
PPy/PS prepared swelling method	0	1.3700	1.8200	1.4700	1.2400	1.4750	0.2485	0.0230
	3	1.0230	1.4580	1.2390	1.0690	1.1973	0.1971	
	5	0.8475	1.1030	0.9750	0.7560	0.9204	0.1513	
	10	0.4586	0.6024	0.5470	0.4125	0.5051	0.0856	
	15	0.0955	0.1047	0.1058	0.1380	0.1110	0.0186	
	30	0.0564	0.0459	0.0486	0.0659	0.0542	0.0090	
	45	0.0162	0.0127	0.0126	0.0107	0.0131	0.0023	
	60	0.0047	0.0069	0.0064	0.0067	0.0062	0.0010	
	90	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	
PPy/PSS prepared swelling method	0	1.9771	3.3133	2.3840	2.3800	2.5136	0.5663	0.0405
	3	0.9286	1.1893	1.3880	1.5832	1.2723	0.2799	
	5	0.2978	0.5416	0.4140	0.4296	0.4207	0.0998	
	10	0.1423	0.0836	0.1302	0.1262	0.1206	0.0256	
	15	0.0263	0.0463	0.0370	0.0366	0.0365	0.0082	
	30	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	
	45	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	
	60	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	
	90	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	

APPENDIX B

Stress-strain of polypyrrole composite films

Table B-1 Stress-strain of PPy/PVC prepared by dissolving method at various $FeCl_3$ concentrations using 2 hours reaction time and 10 °C reaction temperature

$FeCl_3$ concentration (M)	No. sample	Maximum stress (N/mm)	%Strain at maximum load
0	#1	34.90	6.45
	#2	32.45	5.56
	#3	34.95	6.08
	average	34.10	6.03
	SD	1.43	0.45
0.10	#1	21.36	7.63
	#2	20.74	9.20
	#3	19.58	7.61
	average	20.56	8.15
	SD	0.90	0.91
0.20	#1	11.50	16.14
	#2	9.34	15.45
	#3	9.56	14.27
	average	10.13	15.29
	SD	1.19	0.95
0.25	#1	7.68	20.85
	#2	9.48	20.01
	#3	8.41	19.56
	average	8.52	20.14
	SD	0.91	0.65
0.33	#1	6.68	25.41
	#2	7.23	26.34
	#3	6.26	25.84
	average	6.72	25.86
	SD	0.49	0.47

Continue Table B-1

$FeCl_3$ concentration (M)	No. sample	Maximum stress (N/mm²)	%Strain at maximum load
0.50	#1	5.98	9.45
	#2	6.34	11.25
	#3	5.55	10.40
	average	5.96	10.37
	SD	0.40	0.90
1.00	#1	10.24	4.23
	#2	14.29	3.95
	#3	14.72	4.26
	average	13.08	4.15
	SD	2.47	0.17

Table B-2 Stress-strain of PPy/PVC prepared by dissolving method at various reaction time using 0.33 M $FeCl_3$, 10 °C reaction temperature

Reaction time (hours)	No. sample	Maximum stress (N/mm²)	%Strain at maximum load
2	#1	6.68	25.41
	#2	7.23	26.34
	#3	6.26	25.84
	average	6.72	25.86
	SD	0.49	0.47
6	#1	7.98	20.47
	#2	6.51	21.21
	#3	6.69	20.27
	average	7.06	20.65
	SD	0.80	0.50
12	#1	7.03	21.67
	#2	8.26	20.14
	#3	5.50	20.15
	average	6.93	20.65
	SD	1.38	0.88

Table B-3 Stress-strain of PPy/PVC prepared by swelling method at various $FeCl_3$ concentration using immersion time of 10 seconds, reaction time of 2 hours and reaction temperature of 10 °C

$FeCl_3$ concentration (M)	No. sample	Maximum stress (N/mm^2)	%Strain at maximum load
0	#1	52.41	12.98
	#2	53.98	12.94
	#3	54.32	10.25
	average	53.57	12.06
	SD	1.02	1.56
0.25	#1	30.14	10.47
	#2	33.26	11.69
	#3	33.74	9.89
	average	32.38	10.68
	SD	1.95	0.92
0.5	#1	36.41	11.35
	#2	35.32	11.28
	#3	35.20	10.25
	average	35.64	10.96
	SD	0.67	0.62
0.75	#1	38.45	11.96
	#2	40.27	12.94
	#3	38.69	10.63
	average	39.14	11.84
	SD	0.99	1.16
1	#1	41.03	11.97
	#2	40.29	11.54
	#3	39.38	12.38
	average	40.23	11.96
	SD	0.83	0.42
1.25	#1	40.23	13.22
	#2	38.56	11.96
	#3	39.88	13.39
	average	39.56	12.86
	SD	0.88	0.78

Table B-4 Stress-strain of PPy/PVC prepared by swelling method at various immersion time using 1 M $FeCl_3$, reaction time of 2 hours and reaction temperature of 10 °C

Immersion time (seconds)	No. sample	Maximum stress (N/mm²)	%Strain at maximum load
1	#1	46.23	12.15
	#2	45.87	10.24
	#3	44.98	12.54
	average	45.69	11.64
	SD	0.64	1.23
5	#1	42.42	11.32
	#2	41.39	11.69
	#3	40.46	12.46
	average	41.42	11.82
	SD	0.98	0.58
10	#1	41.03	11.97
	#2	40.29	11.54
	#3	39.38	12.38
	average	40.23	11.96
	SD	0.83	0.42

Table B-5 Stress-strain of PPy/PVC prepared by swelling method at various reaction time using immersion time of 10 seconds,1 M $FeCl_3$ and reaction temperature of 10 °C

Reaction time (hours)	No. sample	Maximum stress (N/mm²)	%Strain at maximum load
2	#1	41.03	11.97
	#2	40.29	11.54
	#3	39.38	12.38
	average	40.23	11.96
	SD	0.83	0.42
6	#1	39.56	13.26
	#2	37.58	12.28
	#3	39.71	12.59
	average	38.95	12.71
	SD	1.19	0.50
12	#1	34.29	11.86
	#2	35.64	11.52
	#3	34.12	12.56
	average	34.68	11.98
	SD	0.83	0.53

Table B-6 Stress-strain of PPy/PS prepared by swelling method at various $FeCl_3$ concentration using immersion time of 10 seconds, reaction time of 2 hours and reaction temperature of 10 °C

$FeCl_3$ concentration (M)	No. sample	Maximum stress (N/mm^2)	%Strain at maximum load
0	#1	36.21	10.23
	#2	37.11	10.45
	#3	36.01	10.31
	average	36.44	10.33
	SD	0.59	0.11
0.25	#1	13.26	5.23
	#2	12.10	4.98
	#3	11.42	4.91
	average	12.26	5.04
	SD	0.93	0.17
0.5	#1	16.47	5.69
	#2	14.69	6.23
	#3	13.99	5.94
	average	15.05	5.95
	SD	1.28	0.27
0.75	#1	21.98	6.25
	#2	19.97	6.21
	#3	18.52	5.51
	average	20.16	5.99
	SD	1.74	0.42
1	#1	20.96	6.58
	#2	20.41	6.31
	#3	20.21	6.53
	average	20.53	6.47
	SD	0.39	0.14
1.25	#1	20.13	6.45
	#2	22.41	5.23
	#3	22.96	7.19
	average	21.83	6.29
	SD	1.50	0.99

Table B-7 Stress-strain of PPy/PS prepared by swelling method at various immersion times using 1 M $FeCl_3$, reaction time of 2 hours and reaction temperature of 10 °C

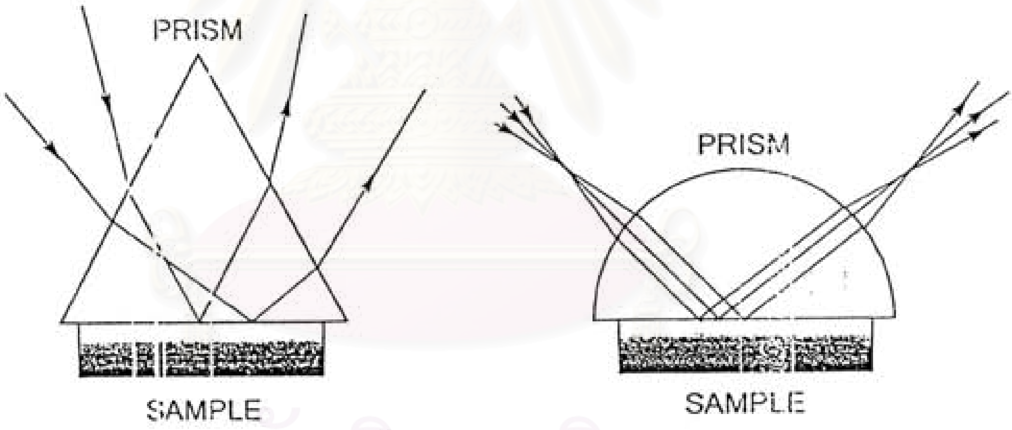
Immersion time (seconds)	No. sample	Maximum stress (N/mm²)	%Strain at maximum load
1	#1	30.21	8.96
	#2	31.25	7.25
	#3	28.65	8.04
	average	30.04	8.08
	SD	1.31	0.86
5	#1	22.36	6.13
	#2	20.13	6.54
	#3	21.08	5.97
	average	21.19	6.21
	SD	1.12	0.29
10	#1	20.96	6.58
	#2	20.41	6.31
	#3	20.21	6.53
	average	20.53	6.47
	SD	0.39	0.14

Table B-8 Stress-strain of PPy/PS prepared by swelling method at various reaction time using immersion time of 10 seconds,1 M $FeCl_3$ and reaction temperature of 10 °C

Reaction time (hours)	No. sample	Maximum stress (N/mm²)	%Strain at maximum load
2	#1	20.96	6.58
	#2	20.41	6.31
	#3	20.21	6.53
	average	20.53	6.47
	SD	0.39	0.14
6	#1	21.48	6.23
	#2	20.33	5.75
	#3	19.96	5.85
	average	20.59	5.94
	SD	0.79	0.25
12	#1	19.02	4.12
	#2	17.89	4.69
	#3	18.16	4.25
	average	18.36	4.35
	SD	0.59	0.30

APPENDIX C

The attenuated total reflectance FT-IR and Kubelka-Munk spectroscopy are sampling techniques based on internal reflection spectroscopy (IRS) and diffusion reflectance, respectively. The ATR technique relies 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 (a), (b). IR radiation was entered the prism at an angle greater than the critical angle and internally reflected within the prism. Its energy was attenuated by absorption of the sample attached to the prism [54]. Spectrum of Kubelka-Munk technique was attenuated by diffusion of sample. Diffuse reflectance accessory is shown in Figure C-2



(a) (b)

Figure C-1 Schematic diagram of internal reflection 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° was employed to observe the outer layer only of polymer composite.

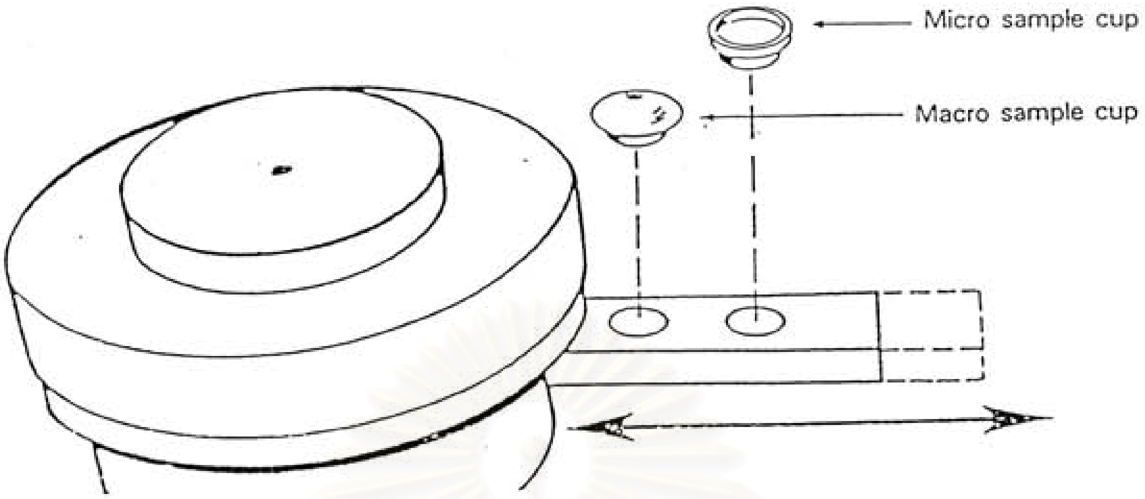


Figure C-2 Diffusion reflectance accessory

VITA

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