

การเตรียมพอลิไพโรลคอมโพสิตที่มีสมบัตินำไฟฟ้าโดยการออกซิเดชันทางเคมี



นาย สมโชค เลาสุริโยธิน

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต

สาขาวิชาปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์

บัณฑิตวิทยาลัย จุฬาลงกรณ์มหาวิทยาลัย

ปีการศึกษา 2542

ISBN 974-333-111-5

ลิขสิทธิ์ของบัณฑิตวิทยาลัย จุฬาลงกรณ์มหาวิทยาลัย

PREPARATION OF CONDUCTIVE POLYPYRROLE COMPOSITES
BY CHEMICAL OXIDATION

Mr. Somchoke Lauhasurayotin

A Thesis Submitted in Partial Fulfillment of the Requirements

for the Degree of Master of Science

Program of Petrochemistry and Polymer science

Graduate School

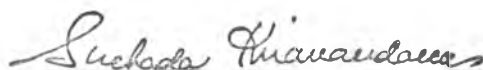
Chulalongkorn University

Academic Year 1999

ISBN 974-333-111-5

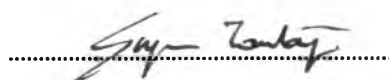
Thesis Title Preparation of conductive polypyrrole composites by
Chemical Oxidation
By Somchoke Lauhasurayotin
Department Petrochemistry and Polymer Science
Thesis Advisor Associate Professor Supawan Tantayanon, Ph.D.
Thesis Co-advisor Associate Professor Anantasin Techagumpuch, Ph.D.


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

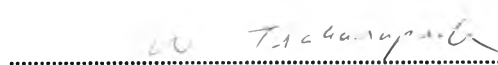
.....Dean of Graduate School
(Associate Professor Suchada Kiranandana, Ph.D.)

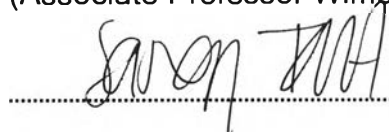
Thesis Committee

.....Chairman
(Professor Pattarapan Prasassarakich, Ph.D.)

.....Thesis Advisor
(Associate Professor Supawan Tantayanon, Ph.D.)

.....Thesis Co-advisor
(Associate Professor Anantasin Techagumpuch, Ph.D.)

.....Member
(Associate Professor Wimongrat Trakarnpruk, Ph.D.)

.....Member
(Sanong Ekgasit, Ph.D.)

สมโชค เลาสุรโยธิน : การเตรียมพอลิไพโรลคอมโพสิตที่มีสมบัตินำไฟฟ้าโดยการออกซิเดชันทางเคมี (PREPARATION OF CONDUCTIVE POLYPYRROLE COMPOSITES BY CHEMICAL OXIDATION) อ.ที่ปรึกษา : รศ.ดร. ศุภวรรณ ตันตยานนท์, อ.ที่ปรึกษาร่วม : รศ.ดร.อนันตสิน เตชะกำพุช ; 115หน้า. ISBN 974-333-111-5

งานวิจัยในครั้งนี้ได้มีการเตรียม พอลิสไตรีน/พอลิไพโรลคอมโพสิต จากพอลิสไตรีน อนุภาคละเอียดซึ่งเตรียมขึ้นจากการนำสไตรีนมาทำปฏิกิริยาพอลิเมอไรเซชันแบบอิมัลชัน หลังจากนั้นจะทำการสังเคราะห์พอลิไพโรลโดยวิธีการออกซิเดชันทางเคมีโดยให้มีพอลิสไตรีน อยู่ในสารละลายเฟอริกคลอไรด์ที่ใช้เป็นตัวออกซิแดนท์ พอลิสไตรีนที่มีพอลิไพโรลเคลือบอยู่ซึ่งมีสีดำจะถูกวิเคราะห์โดย แอทเทนนูเอเต็ดโททอล รีเฟล็กซ์แทนซ์ ฟลูเรียทรานส์ฟอร์ม อินฟราเรด สเปกโตรสโกปี นอกจากนี้ยังได้มีการศึกษาผลกระทบของปัจจัยต่างๆ เช่น ปริมาณของพอลิเมอร์, เวลาในการทำปฏิกิริยา, อุณหภูมิที่ใช้ และ ตัวทำละลาย เพื่อหาภาวะของปฏิกิริยาที่เหมาะสมในการสังเคราะห์คอมโพสิตที่มีค่าการนำไฟฟ้าสูงที่สุด นอกจากนี้แล้วยังมีการใช้ไฮสตรูปโพลิเมอร์ชนิดอื่นๆ เช่น พอลิไวนิลคลอไรด์, พอลิเอทิลีน, และพอลิโพรพิลีนมาทำการทดลองด้วย จากผลการทดลองพบว่า พอลิสไตรีน/พอลิไพโรล และพอลิไวนิลคลอไรด์/พอลิไพโรลคอมโพสิต มีค่าการนำไฟฟ้าสูงถึง 10 ไซเมนต่อเซนติเมตร ซึ่งสูงที่สุดในงานวิจัยด้านนี้เท่าที่มีการรายงานไว้ และยังสามารถศึกษาการลดลงของค่าการนำไฟฟ้าไปกับเวลาของแต่ละคอมโพสิตด้วย

ภาควิชา
สาขาวิชา
ปีการศึกษา 2542

ลายมือชื่อนิสิต
ลายมือชื่ออาจารย์ที่ปรึกษา
ลายมือชื่ออาจารย์ที่ปรึกษาร่วม

3971948323: MAJOR PETROCHEMISTRY AND POLYMER SCIENCE

KEY WORD: POLYSTYRENE / POLYPYRROLE / CONDUCTIVITY / COATING / OXIDATION

SOMCHOKE LAUHASURAYOTIN : PREPARATION OF CONDUCTIVE POLYPYRROLE COMPOSITES BY CHEMICAL OXIDATION. THESIS ADVISOR : ASSOC. PROF. SUPAWAN TANTAYANON, Ph.D. THESIS CO-ADVISOR : ASSOC. PROF. ANANTASIN TECHAGUMPUCH, Ph.D. 115 pp. ISBN 974-333-111-5.

In this research, polystyrene/polypyrrole composite was developed by firstly carrying out the emulsion polymerization of styrene to obtain polystyrene as a fine powder. Then polypyrrole was synthesized by chemical oxidation method in the presence of polystyrene particle using FeCl_3 as the oxidant. The composite appeared as black particle, which was polypyrrole, covered on polystyrene and was analyzed by Attenuated Total Reflectance (ATR) FT-IR spectroscopy. Several factors, i.e. pyrrole volume, reaction time, reaction temperature, and solvent were investigated to optimize the reaction condition for achieving the highest conductivity of this composite. The other host polymers were attempted including poly(vinyl chloride), polyethylene, and polypropylene. The results indicated that polystyrene/polypyrrole and poly(vinyl chloride)/polypyrrole composite could have the conductivity as high as 10 Scm^{-1} which was the highest conductivity for this type of composites ever been reported. The time decay of conductivity of some polypyrrole composite was also explored.

ภาควิชา.....
สาขาวิชา ปิโตร เคมีและวิทยาศาสตร์พอลิเมอร์
ปีการศึกษา 2542

ลายมือชื่อนิสิต Somchoke Lauhasurayotin
ลายมือชื่ออาจารย์ที่ปรึกษา Sr. Subh
ลายมือชื่ออาจารย์ที่ปรึกษาร่วม A. Ch

ACKNOWLEDGEMENT

The author would like to express his sincere thanks to his advisor, Associate Professor Dr. Supawan Tantayanon and co-advisor, Associate Professor Dr. Anantasin Techagumpuch for their valuable advice and encouragement. He wishes to thank Professor Dr. Pattarapan Prasassarakich, Associate Professor Dr. Wimonrat Trakarnpruk, and Dr. Sanong Ekgasit for their comments and suggestions.

He also likes to thank for the allowance of Chemistry Department for the using of necessary equipment and chemicals. Thanks to the staffs of Petrochemistry and Polymer Science program for their helpful and suggestion throughout the course of this research.

Grateful acknowledgement is made to the National Research Council Thailand under the scholarship for the financial support to succeed this research. He also thanks all graduate students in his graduate study program, Petrochemistry and Polymer Science, for assistance and good impressiveness from them during study. Great thank to his girlfriend, Supara Tokunalai, for everything that she has given.

Finally, special gratitude to his family and for their endless love, sympathy, and encouragement.

CONTENTS

	Page
ABSTRACT (IN THAI).....	iv
ABSTRACT (IN ENGLISH).....	v
ACKNOWLEDGEMENT.....	vi
CONTENTS.....	vii
LIST OF TABLES.....	xi
LIST OF FIGURES.....	xii
ABBREVIATIONS.....	xv
CHAPTER I INTRODUCTION	
1.1 Electroactive polymer.....	1
1.2 Conducting polymer composites.....	4
1.3 Objective and scope of research.....	6
CHAPTER II THEORITICAL AND LITERATURE SURVEY	
2.1 Classical theory for electrical conductive materials.....	8
2.1.1 The formation of band.....	8
2.1.1.1 Metal.....	9
2.1.1.2 Insulator and Semiconductor.....	11
2.2 Nature of charge in polymers.....	12
2.2.1 The polymeric solid state.....	12
2.2.1.1 Relaxation.....	13
2.2.1.2 Localization.....	13
2.2.2 Hopping conduction.....	17
2.2.3 Charge carrier in conducting polymer.....	17

2.3 Polypyrrole and general properties.....	19
2.3.1 Synthesis of polypyrrole.....	19
2.3.2 Electrical transport of polypyrrole.....	20
2.4 Polypyrrole coating composites.....	26
2.4.1 Chemical synthesis of polypyrrole coating composites.....	26
2.4.2 Property of conducting particle system.....	27
2.4.2.1 Quality of interparticle contacts.....	27
2.4.2.2 Shape and size of conductive particles.....	28
2.5 Chemical polymerization of dispersion polypyrrole.....	29
2.6 Literature survey.....	30

CHAPTER III EXPERIMENTAL

3.1 Chemicals.....	35
3.2 Glasswares and equipments.....	36
3.3 Instruments.....	36
3.4 Purification and preparation of materials.....	37
3.4.1 Styrene monomer.....	37
3.4.2 Pyrrole monomer.....	37
3.4.3 Methanol.....	37
3.4.4 Oxidant solution.....	37
3.5 Synthesis of micro-particle polystyrene	38
3.6 Synthesis of polypyrrole coating composite.....	38
3.7 Synthesis of dispersion polypyrrole.....	39
3.8 Determination of condition effects.....	40
3.8.1 Polypyrrole coating composites.....	40
3.8.1.1 pyrrole volume.....	40
3.8.1.2 host polymer type.....	40

3.8.1.3 reaction time.....	40
3.8.1.4 solvent.....	40
3.8.1.5 temperature.....	41
3.8.2 Dispersion polypyrrole.....	41
3.8.2.1 pyrrole volume.....	41
3.8.2.2 reaction time.....	42
3.8.2.3 solvent.....	42
3.9 Characterization.....	42
3.9.1 Electrical conductivity measurement.....	42
3.9.2 Conductive stability of polymer composite disc.....	43
3.9.3 Fourier transform infrared spectroscopy.....	43
3.9.4 Scanning electron microscopy.....	43

CHAPTER IV RESULTS AND DISCUSSION

4.1 Preliminary study of polypyrrole coating composite.....	44
4.2 Effects of host polymer on polypyrrole coating composite.....	47
4.2.1 Polystyrene/Polypyrrole composite.....	47
4.2.2 Poly(vinyl chloride)/Polypyrrole composite.....	48
4.2.3 Other insulating polymer/Polypyrrole composite.....	51
4.3 Effect of poly(vinyl pyrrolidone) on dispersion polypyrrole.....	52
4.4 Determination of various effects on Polystyrene/Polypyrrole composite.....	54
4.4.1 Effect of pyrrole	54
4.4.2 Effect of reaction time.....	59
4.4.3 Effect of solvent.....	61
4.5 Conductive stability of Polystyrene/Polypyrrole composites.....	65
4.6 Determination of various effects on Poly(vinyl chloride)/Polypyrrole	

composite.....	67
4.6.1 Effect of pyrrole	67
4.6.2 Effect of reaction time.....	73
4.6.3 Effect of solvent.....	75
4.7 Conductive stability of Poly(vinyl chloride)/Polypyrrole composite.....	79
4.8 Determination of various effects on dispersion polypyrrole.....	81
4.8.1 Effect of pyrrole	81
4.8.2 Effect of solvent.....	83
4.8.3 Effect of reaction time.....	87
4.9 The effect of reaction temperature on the Polystyrene/polypyrrole composite synthesis	89
CHAPTER V CONCLUSION	
Conclusion.....	91
REFERENCES.....	93
APPENDICES.....	98
APPENDIX A.....	99
APPENDIX B.....	104
APPENDIX C.....	109
APPENDIX D.....	111
VITA.....	115

LIST OF TABLES

Table	Page
4.1 Conductivity of PS/PPy composite depends on the pyrrole: PS ratio.....	54
4.2 Conductivity of PS/PPy composite depends on the reaction time.....	59
4.3 Conductivity of PS/PPy composite depends on the solvent.....	63
4.4 Conductivity of PS/PPy composite as storing time.....	65
4.5 Conductivity of PVC/PPy composite depends on the pyrrole: PS ratio.....	68
4.6 Conductivity of PVC/PPy composite depends on the reaction time.....	73
4.7 Conductivity of PVC/PPy composite depends on the solvent.....	76
4.8 Conductivity of PVC/PPy composite as storing time.....	79
4.9 Conductivity of dispersion polypyrrole depends on the pyrrole: PVP ratio.....	81
4.10 Conductivity of dispersion polypyrrole depends on the solvent.....	83
4.11 Conductivity of dispersion polypyrrole depends on the reaction time.....	87
4.12 Conductivity of PS/PPy composite depends on the reaction temperature.....	89
A-1 Current and Potential data measuring as I_{12} and V_{34} , respectively.....	99
B-1 Electrical conductivity of Polystyrene/Polypyrrole composites.....	104
B-2 Electrical conductivity of Poly(vinyl chloride)/Polypyrrole composites.....	105
B-3 Electrical conductivity of Polypyrrole powder prepared by dispersion Polymerization.....	106
B-4 Conductive stability of Polystyrene/Polypyrrole composites.....	107
B-5 Conductive stability of Poly(vinyl chloride)/Polypyrrole composites	108

LIST OF FIGURES

Figure	Page
1.1 The structure of polypyrrole molecular chain.....	2
2.1 The formation of a band on N orbitals.....	9
2.2 The formation of s and p orbital and the band gap.....	10
2.3 The relationship of energy gap in the three type of solids.....	10
2.4 The band diagram for the doping material.....	12
2.5 Schematic indication of the consequences of static diagonal on the localization of one-electron states in a nominally three dimensional undoped polymeric solid.....	16
2.6 Hopping model of electron across an energy barrier.....	17
2.7 Polymerization of pyrrole with FeCl ₃	19
2.8 Evolution of the optical-absorption spectrum of pyrrole as a function of doping level from bottom curve (almost neutral polypyrrole) to top curve (33 mol% doping level).....	21
2.9 Electronic structure diagrams for a polypyrrole chain containing (a) low doping level, polaron formation (b) moderate doping level, bipolaron formation.....	23
2.10 Band structure for highly doping level (33 mol%) polypyrrole, showing the presence of two broad bipolaron bands in the gap.....	24
2.11 The band structure evolution upon (sodium) doping of polypyrrole (a) undoped (b) intermediate doping level: noninteracting bipolarons present.	24
2.12 The coated-formation of polypyrrole on the host polymer.....	27
2.13 Model form of intersphere contacts.....	28
2.14 Preparation of the compressed PVC/PPy composites.....	31
2.15 Polypyrrole-coated PS particle using PVP as stabilizer.....	32

3.1 Polymerization of polypyrrole composite set up	
(A) Three-neck flask (B) Gas inlet tube (C) Drying tube (D) Magnetic stirrer	
(E) Magnetic bar (F) Ice bath (G) Stand and clamp.....	39
4.1 ATR FT-IR spectrum of PS/PPy composite.....	46
4.2 FT-IR spectrum of PVC/PPy composite.....	46
4.3 Scanning electron micrograph of PS/PPy composites.....	47
4.4 Scanning electron micrographs of (a) PVC particle (b) PVC/PPy composite	
surface.....	50
4.5 Scanning electron micrograph of dispersion PPy, using PVP stabilizer.....	53
4.6 The conductivity of PS/PPy composite versus pyrrole: PS ratio.....	55
4.7 Scanning electron micrographs of (a) polystyrene micro-particles (b) PS/PPy	
composite treated with 0.5 pyrrole: PS ratio (c) PS/PPy composite treated with	
1 pyrrole: PS ratio.....	57
4.8 FT-IR spectra of PS/PPy composite as a function of pyrrole: PS ratio (a) PS01	
(b) PS02 (c) PS03 (d) PS04 (e) PS05.....	58
4.9 The conductivity of PS/PPy composite versus reaction time.....	61
4.10 The conductivity of PS/PPy composite versus pyrrole ratio in various	
solvents.....	64
4.11 Scanning electron micrograph of PS/PPy composite using 50% methanol/	
water as solvent.....	64
4.12 The conductive stability of PS/PPy composites versus storing time.....	66
4.13 The conductivity of PVC/PPy composite versus pyrrole: PVP ratio.....	69
4.14 Scanning electron micrographs of (a) PVC/PPy composite treated with	
0.5 pyrrole: PVC ratio (b) PVC/PPy particle surface (treated with 0.5 pyrrole:	
PVC ratio).....	70
4.15 FT-IR spectra of PVC/PPy composites as a function of pyrrole: PVC ratio	
(a) PVC01 (b) PVC02 (c) PVC03 (d) PVC04 (e) PVC05.....	72

4.16 The conductivity of PVC/PPy composite versus reaction time.....	74
4.17 The conductivity of PVC/PPy composite versus pyrrole ratio in various solvent.....	77
4.18 Scanning electron micrographs of PVC/PPy composite 0.1 pyrrole: PVC ratio polymerized in (a) methanol (x950) (b) methanol (x270) (c) 50%methanol/ water (x270).....	78
4.19 The conductive stability of PVC/PPy composite versus storing time.....	80
4.20 The conductivity of dispersion PPy versus pyrrole: PVP ratio.....	82
4.21 The conductivity of dispersion PPy versus pyrrole ratio in various solvents....	85
4.22 Scanning electron micrograph of dispersion PPy polymerized in methanol....	86
4.23 Scanning electron micrograph of dispersion PPy polymerized in 50% methanol/water.....	86
A-1 Conductivity measurement by van der Pauw method.....	100
C-1 Schematic diagram of internal reflection spectroscopy.....	109
C-2 ATR FT-IR study model for polypyrrole coating composite.....	110
D-1 FT-IR spectrum (ATR) of Polystyrene.....	112
D-2 FT-IR spectrum (transmission) of Poly(vinyl chloride).....	113
D-3 FT-IR spectrum (transmission) of pure polypyrrole.....	114

ABBREVIATIONS

°C	degree Celsius
cm	centimetre
d	thickness of sample disc
g	gram
I	current
mA	milliampere
mV	millivolt
mL	millilitre
M	mole per litre
PE	polyethylene
PP	polypropylene
PPy	polypyrrole
PS	polystyrene
PVC	poly(vinyl chloride)
PVP	poly(vinyl pyrrolidone)
Scm ⁻¹	simen per centrimetre
%T	percent transmittance
μm	micrometre
V	potential