

UNIVERSITI PUTRA MALAYSIA

PREPARATION AND CHARACTERIZATION OF POLYPYRROLEPOLYETHYLENE GLYCOL CONDUCTING POLYMER COMPOSITE FILMS

LIM MEI YEE

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PREPARATION AND CHARACTERIZATION OF POLYPYRROLE-POLYETHYLENE GLYCOL CONDUCTING POLYMER COMPOSITE FILMS

By

LIM MEI YEE

Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfilment of the Requirement for the Degree of Master of Science

August 2007



DEDICATION

To my beloved parents Lim Tet Yoong and Lau Mau Ching For their endless love and concern.....

To my beloved Wan Kee Peng

For his romantic love, support, understanding and care.....

To my supervisor Prof. Dr. Anuar bin Kassim, PhD For his guidance, advice, understanding and endless support.....

To my co-supervisors Prof Mohd. Zobir Hussein, PhD and Professor Wan

Mahmood Mat Yunus, PhD

For their kindly advice and indispensable support.....

To my senior H. N. M. Ekramul Mahmud, PhD

For his wonderful encouragement and support.....

To my friends

For their wonderful love and generous moral support.....





Abstract of the thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirement for the degree of Master of Science

PREPARATION AND CHARACTERIZATION OF POLYPYRROLE-POLYETHYLENE GLYCOL CONDUCTING POLYMER COMPOSITE FILMS

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August 2007

Chairman: Professor Anuar Kassim, PhD

Faculty: Science

Polypyrrole-polyethylene glycol (PPy-PEG) conducting polymer composite films were electrochemically prepared on Indium Tin Oxide (ITO) glass electrode from an aqueous solution containing pyrrole monomer, *p*-toluene sulfonate dopant and poly (ethylene glycol) as an insulating polymer. The PPy-PEG composite films prepared from different process conditions were characterized by Fourier Transform infrared (FT-IR) spectroscopy, electrical conductivity measurement, photoacoustic spectroscopy, X-ray diffraction (XRD) analysis and optical microscopy. The FT-IR study of PPy-PEG composite films shows the evidence of the incorporation of PEG in PPy structure forming PPy-PEG composite films.

The highest electrical conductivity of 61 S/cm and thermal diffusivity of 7.88 x 10^{-7} m²s⁻¹ were shown by the PPy-PEG composite film prepared from 0.20 M pyrrole, 0.10 M *p*-toluene sulfonate and 1 x 10^{-3} M PEG at 1.20 volt (vs SCE) at room temperature among all the PPy-PEG composite films produced. The conductivity data of PPy-PEG shows that with the increase in PEG concentration in the pyrrole



solution, the electrical conductivity of the prepared PPy-PEG film increased up to certain level due to the increase in conjugation length and later it decreased with further increase in PEG concentration, which is again linked with the decrease in conjugation length.

The measured values of thermal diffusivity and electrical conductivity for the PPy-PEG composites films showed that there was a correlation between thermal diffusivity and electrical conductivity. Both thermal diffusivity and electrical conductivity showed a similar peak for the same process condition in respective composite films.

The XRD results of PPy-PEG composite films showed that the films were amorphous with very little order. The optical micrographs of PPy-PEG showed the globular surface morphology. The changes in globular surface morphology with the change in process condition of the film preparation indicated that the process parameters used to prepare the composite films had a strong influence over the surface morphology.



Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Master Sains

PENYEDIAAN DAN PENCIRIAN UNTUK POLIPIROL-POLIETILENA GLIKOL FILEM KOMPOSIT POLIMER PENGALIR

Oleh

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Ogos 2007

Pengerusi : Professor Anuar Kassim, PhD

Fakulti : Sains

Filem komposit polimer pengalir bagi pasangan polipirol-polietilena glikol (PPy-PEG) dan telah disediakan melalui kaedah elektrokimia di atas elektrod kaca Indium Stanum oksida (ITO) daripada larutan akueus yang mengandungi monomer pirol, dopan *p*-toluena sulfonat dan polietilena glikol sebagai polimer selulosa penebat. Filem komposit bagi PPy-PEG telah disediakan melalui keadaan proses yang berlainan dan langkah pencirian telah dilakukan melalui penyerapan infra merah (FT-IR), penentukuran kekonduksian elektrik, spektrokopi fotoakustik, pengimbasan analisis sinar-X, dan mikroskopi optikal. Kajian FT-IR ke atas filem komposit PPy-PEG nyata menunjukkan kemasukan PEG ke dalam struktur PPy berkaitan dengan pembentukan filem komposit PPy-PEG.

Filem komposit PPy-PEG yang memberi nilai konduktiviti elektrik tertinggi dan nilai resapan terma iaitu 61 S/cm dan 7.88 x 10^{-7} m²s⁻¹ berbanding dengan yang lain telah disediakan daripada larutan 0.20 M pirol, 0.10 M *p*-toluena sulfonat dan 1 x 10^{-3} M PEG pada keupayaan 1.20 v (melawan SCE) pada suhu bilik. Data



kekonduksian elektrik, PPy-PEG menunjukkan dengan penambahan kepekatan PEG dalam larutan pirol, kekonduksian electrik filem PPy-PEG turut bertambah ke satu paras tertentu disebabkan penambahan panjang konjugatan dan nilai kekonduksian elektrik berkurangan dengan penambahan PEG berlebihan iaitu berkaitan langsung dengan panjang konjugatan yang berkurangan.

Nilai resapan terma dan konduktiviti electrik untuk filem komposit PPy-PEG menunjukkan satu hubungan pertalian secara bersistem di anatra resapan terma dan konduktiviti electrik. Kedua- dua nilai esapan terma dan konduktiviti elektrik esapan terma dan konduktiviti elektrik menyatakan kesamaan puncak daripada keadaan proses yang sama dalam komposit filem masing-masing.

Keputusan XRD menunjukkan bahawa filem komposit PPy-PEG adalah bersifat amorfus dengan mempunyai sedikit sifat ketertiban. Mikrograf optikal PPy-PEG menunjukkan sifat morfologi permukaannya yang berbentuk sfera. Perubahan keadaan penyediaan turut mengubah morfologi permukaan sfera jelas menunjukkan bahawa parameter dalm proses penyediaan mempunyai kesan untuk mempengaruhi sifat permukaannya.

vi



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I certify that an Examination Committee met on 3rd August, 2007 to conduct the final examination of Lim Mei Yee on her Master of Science thesis entitled "Preparation and Characterization Conducting Polymer Composite Films: Polypyrrole-Polyethylene Glycol" in accordance with Universiti Pertanian Malaysia (Higher Degree) Act 1980 and Universiti Pertanian Malaysia (Higher Degree) Regulations 1981. The Committee recommends that the candidate be awarded the relevant degree. Members of the Examination Committee are as follows:

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DECLARATION

I hereby declare that the thesis is based on my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously or concurrently submitted for any other degree at UPM or other institutions.

LIM MEI YEE

Date: 19 December 2007



TABLE OF CONTENTS

DEDICATION	ii
ABSTRACT	iii
ABSTRAK	V
ACKNOWLEDGEMENTS	vii
APPROVAL	ix
DECLARATION	xi
LIST OF TABLES	XV
LIST OF FIGURES	xvi
LIST OF ABBREVIATIONS	xix

CHAPTER

Ι	INTRODUCTION	
	Conducting Polymers	1
	History of Conducting Polymers	6
	Research Objectives	14
II	LITERATURE REVIEW	
	Monomer	15
	Counter ion or Dopant	16
	Insulating Polymer	18
	Solvent	19
	Polypyrrole as a Conducting Polymer	21
	Mechanisms of Pyrrole Electropolymerization- Role	23
	of Doping	
	Mechanisms of Pyrrole Electropolymerization	25
	Applications of Polypyrrole Conducting Polymers	
	Batteries	35
	Polypyrrole Microactuators	36
	Condenser	36
	Transparent Loudspeakers	37
	Electromagnetic Interference (EMI)	38
	Shielding Material	
	Brilliant	38
	Microelectronics	39
тт	ΜΑΤΈΡΙΑΙ Ο ΑΝΌ ΜΕΤΙΙΩΌΟ	
111	MATERIALS AND METHODS	41
	Electrochemical Synthesis	41
	Electione Monomer Electrolyte and Insulating Delymer	41 42
	Proposition of Dry DEC Composite Films	42
	Preparation of PPy-PEG Composite Films	43



	Characterization of the PPy-PEG Composite Films	
	Electrical Conductivity	44
	Fourier Transform Infrared Spectrometry	45
	(FT-IR)	
	X-ray Diffraction (XRD)	46
	Optical Microscopy	46
	Open Photoacoustic Technique	47
IV	RESULTS AND DISCUSSION	
	Electrochemically Prepared Polypyrrole Composite Films	48
	Molecular Structure of PPy-PEG Composite Films	50
	Electrical Conductivity of PPy-PEG Composite Films	54
	Effect of PEG Concentration on the	55
	Electrical Conductivity of PPy-PEG	
	Composite Films	
	Effect of Pyrrole Concentration on the	57
	Electrical Conductivity of PPy-PEG	
	Composite Films	
	Effect of Dopant Concentration on the	58
	Electrical Conductivity of PPy-PEG	
	Composite Films	
	Effect of Applied Voltage on the Electrical	60
	Conductivity of PPy-PEG Composite Films	
	Thermal Diffusivity of PPy-PEG Composite Films	63
	Effect of PEG Concentration on the	64
	Thermal Diffusivity of PPy-PEG Composite	
	Films	
	Effect of Pyrrole Concentration on the	66
	Thermal Diffusivity of PPy-PEG Composite	
	Films	
	Effect of Dopant Concentration on the	68
	Thermal Diffusivity of PPy-PEG Composite	
	Films	
	Effect of Applied Voltage on the Thermal	70
	Diffusivity PPy-PEG composite films	
	The Relation Between Electrical Conductivity and	72
	Thermal Diffusivity of PPy-PEG Composite Films	
	Molecular Order in PPy-PEG Composite Films	79
	Effect of PEG Concentration on the	83
	Molecular Order of PPy-PEG Composite	
	Films	
	Effect of Pyrrole Concentration on the	87
	Molecular Order of PPv-PEG Composite	
	Films	
	Effect of Dopant Concentration on the	89
	Molecular Order of PPv-PEG Composite	
	Films	





	Effect of Applied Voltage on the Molecular	91
	Order PPy-PEG Composite Films	
	Morphological Study of PPy-PEG Composite Films	92
	Effect of PEG Concentration on the	92
	Morphology of PPy-PEG Composite Films	
	Effect of Pyrrole Concentration on the	99
	Morphology of PPy-PEG Composite Films	
	Effect of Dopant Concentration on the	103
	Morphology of PPy-PEG Composite Films	
	Effect of Applied Voltage on the	107
	Morphology PPy-PEG Composite Films	
VI	CONCLUSIONS	110
	Future Studies	111
REFERENCES/BIBLIOGRAPHY		113
APPENDICES		123
BIODATA OF THE AUTHOR		126

LIST OF PUBLICATIONS

127



LIST OF TABLES

Table		Page
1.1	Conducting polymers: preparation methods and conductivities	8
2.1	Examples of copolymer prepared from pyrrole functional polymers	16
2.2	Polypyrrole films with different anoins	18
2.3	Physical properties of polypyrrole with ρ -toulenesulfonate films	20
3.1	The parameter used to synthesize PPy-PEG composite films prepared from various process conditions	43
4.1	Physical observation of PPy-PEG Composite films	48
4.2	Diffraction orders for stretch-aligned polypyrrole (Warren, 2001)	82



LIST OF FIGURES

Figure		Page
1.1	The conductivity of materials (Przyluski, 1991)	4
2.1	Pyrrole is synthesized into polypyrrole with the dopant (A ⁻)	17
2.2	Simple band picture explaining the difference between an insulator, a semiconductor and a metal	24
2.3	First part of the reaction mechanism of polypyrrole film formation	26
2.4	Second part of the reaction mechanism of polypyrrole film formation	30
2.5	Third part of the reaction mechanism of polypyrrole film Formation	33
3.1	The experimental set-up for the electrochemical preparation of PPy-PEG composite films	42
3.2	Circuit used for conductivity measurements	45
4.1	FT-IR spectra of PPy-PEG composite film, PPy film, PEG and <i>p</i> -toluene sulfonate	52
4.2	The formation of PPy-PEG composite film from pyrrole, monomer, <i>p</i> -toluene sulfonate dopant and PEG	53
4.3	Electrical conductivity of PPy-PEG composite films versus PEG concentration used to prepare the PPy-PEG	56
4.4	Electrical conductivity of PPy-PEG composite films against pyrrole concentration	58
4.5	Electrical conductivity of PPy-PEG composite films against different <i>p</i> -toluene sulfonate concentration	60
4.6	Electrical conductivity of PPy-PEG composite films against different applied voltage (vs SCE).	62
4.7	Thermal diffusivity of PPy-PEG composite films versus PEG concentration used to prepare the PPy-PEG composite films	65





4.8	Thermal diffusivity of PPy-PEG composite films versus pyrrole concentration used to prepare the PPy-PEG composite films	67
4.9	Thermal diffusivity of PPy-PEG composite films against different <i>p</i> - toluene sulfonate concentration	69
4.10	Thermal Diffusivity of PPy-PEG composite films against different applied voltage (vs SCE)	71
4.11	The electrical conductivity and thermal diffusivity of PPy- PEG composite films against different PEG concentration	75
4.12	The electrical conductivity and thermal diffusivity of PPy- PEG composite films against different pyrrole concentration	76
4.13	The electrical conductivity and thermal diffusivity of PPy- PEG composite films against different <i>p</i> -toluene sulfonate concentration	77
4.14	The electrical conductivity and thermal diffusivity of PPy- PEG composite films against different applied voltage	78
4.15	Stacked lamellae	80
4.16	Fringed mycelles	80
4.17	XRD diffractograms of PPy-PEG composite films prepared from various concentrations of PEG	84
4.18	The XRD diffractograms of PEG	86
4.19	The XRD diffractograms of PPy	86
4.20	The XRD diffractograms of PPy-PEG composite film	86
4.21	XRD diffractograms of PPy-PEG composite films prepared from various concentrations of pyrrole	88
4.22	XRD diffractograms of PPy-PEG composite films prepared from various concentrations of <i>p</i> -toluene sulfonate	90
4.23	XRD diffractograms of PPy-PEG composite films prepared from various applied voltage	91



xviii

4.24	The optical micrographs of the solution side of PPy-PEG composite films produced from using (a) 5×10^{-4} M, (b) 1 x 10^{-3} M, (c) 3×10^{-3} M, (d) 5×10^{-3} M, (e) 7×10^{-3} M and (f) 9×10^{-3} M PEG in the pyrrole solution (Magnification: 20x)	93
4.25	The optical micrographs of the electrode side of PPy-PEG composite films produced from using (a) 5×10^{-4} M, (b) 1 x 10^{-3} M, (c) 3×10^{-3} M, (d) 5×10^{-3} M, (e) 7×10^{-3} M and (f) 9×10^{-3} M PEG in the pyrrole solution (Magnification: 20x)	95
4.26	The optical micrographs of the solution side of (a) only PPy film and (b) PPy-PEG composite film (magnification: 20x)	97
4.27	The optical micrographs of the electrode side of (a) only PPy film and (b) PPy-PEG composite film (magnification: 20x)	98
4.28	The optical micrographs of the solution side of PPy-PEG composite films produced from using (a) 0.10 M, (b) 0.20 M, (c) 0.30 M and (4) 0.40 M pyrrole (magnification: $20x$)	101
4.29	The optical micrographs of the electrode side of PPy-PEG composite films produced from using (a) 0.10 M, (b) 0.20 M, (c) 0.30 M and (4) 0.40 M pyrrole (magnification: $20x$)	102
4.30	The optical micrographs of the solution side of PPy-PEG composite films produced from using (a) 0.05 M, (b) 0.10 M, (c) 0.20 M and (d) 0.30 M ρ -toluene sulfonate(Magnification: 20x)	104
4.31	The optical micrographs of the electrode side of PPy-PEG composite films produced from using (a) 0.05 M, (b) 0.10 M, (c) 0.20 M and (d) 0.30 M ρ -toluene sulfonate (Magnification: 20x)	106
4.32	The optical micrographs of the solution side of PPy-PEG composite films produced from using (a) 0.80 volt (vx SCE), (b) 1.20 volt (vs SCE) and (c) 1.50 volt (vs SCE) (Magnification: 20x)	108
4.33	The optical micrographs of the electrode side of PPy-PEG composite films produced from using (a) 0.80 volt (vx SCE), (b) 1.20 volt (vs SCE) and (c) 1.50 volt (vs SCE) (Magnification: 20x)	109



LIST OF ABBREVIATIONS

InSb	Indium Antimonide
AsF ₅	Arsenic Pentafluoride.
TTF	Tetrathiafulvalene
TCNQ	Tetracyanoquinodimethane
СН	Methyl
Tc	Glass transition temperature
Ch	Chemical preparation
EP	Electropolymerization
Pt	Platinum
Ру	Pyrrole
PPy	Polypyrrole
PEG	Polyethylene Glycol
FT-IR	Fourier Transform Infrared Spectrometry
XRD	X-ray diffraction analysis
VS	Versus
PMMA	Poly (methyl methacrylate)
PTHF	Polytetrahydrofuran
PCL	Polycaprolactone
PDMS	Poly (dimethyl siloxane)
A	Dopant/ counter-ions
BS	Benzenesulfonate
PTS	sodium ρ -toluenesulfonate



EBS	sodium 4-ethylbenzenesulfonate
MXS	sodium m-xylene-4-sulfonate
MSS	sodium mesitylnesulfonate
OBS	sodium 4-n-noctylbenzenesulfonate
DBS	sodium dodecylbenzenesulfonate
ET ₄ NPTS	tetraethylammonium ρ -toulenesulfonate
mA	Mega ampere
H ₂ O	Hydrogen oxide
CH ₃ CN	Methyl Cyanide
psi	Per square inch
σ	Conductivity
R	Monomer
$R^{+\bullet}$	Cation radical
ITO	Indium-tin-oxide
SCE	Saturated calomel electrode
V	Voltage
dc	Direct current
μm	Micrometre
cm	Centimeter
Hz	Hetze
20	2 Theta
p-TS	<i>p</i> -toluene sulfonate
DMA	Dynamic mechanical analysis
EMI	Electromagnetic interference







xxi

CHAPTER I

INTRODUCTION

Conducting Polymers

Polymers are long chain giant organic molecules assembled from many smaller molecules called monomers. Polymers consist of many repeating monomer units in long chains. The interlinking of many units has given the polymer its name, *poly* meaning 'many' and *mer* meaning 'part' (in Greek) (Gowariker *et al.*, 1987). A polymer is analogous to a necklace made from many small beads (monomers). These monomers react together chemically to give a variety of molecular architectures ranging from linear structures to a three dimensional network of polymer chains.

Another common name for many synthetic polymers is plastic which comes from the Greek word "plastikos", suitable for molding or shaping. Many objects in daily use from packing, wrapping, and building materials include half of all polymers synthesized. Plastics are polymers, molecules that form long chains, repeating themselves like pearls in a necklace. In becoming electrically conductive, a polymer has to imitate a metal, that is, its electrons need to be free to move and not bound to the atoms. The first condition for this is that the polymer consists of alternating single and double bonds, called conjugated double bonds (Said *et al.*, 2000).

Conducting polymer are polymers which can exhibit significant level of electrical conductivity. The electrical conductivity exhibited by conducting polymers is



attributed to the presence of "free electrons" within the body of the specimen. Conducting polymers are usually polyconjugated structures which are insulators in the pure state but when treated with an oxidizing or a reducing agent can be converted into polymer salts with electrical conductivities comparable to metals. Conducting polymeric materials posses great design flexibility together with a number of characteristics that are desirable for a number of specific applications in the fields of catalysis, conversion and storage of energy, chemical and biochemical sensing, microelectronics and optoelectronics (Skotheim, 1998).

Supercapacitors are attracting great attention because of their high capacitance and potential applications in electronic devices. There has been more interest in two types of supercapacitors, the double layer supercapacitors and the redox supercapacitors with different charge storage modes. The redox supercapacitor involves faradic process due to redox reaction. Due to versatility of structure and low cost compared to noble metal oxides, electronically conducting polymers represents a promising class of active materials for electrodes of the redox supercapacitors (Hughes *et al.*, 2002).

For most of the history of polymer technology, one of the most valued properties of synthetic polymers has been their ability to act as excellent electrical insulators both at high voltages and at high frequencies. In spite of this there has been an interest for many years in the possibility of producing electrically conducting polymers. The obvious attraction is to combine in one material the electrical properties and the high added value applications of a semiconductor or a metal with the advantages of a polymer.



Approximately two decades ago, it has been discovered that polyacetylene, which is a type of polymer containing conjugated single and double bonds in its structure, could become highly conductive after carrying out a structural modification process called "doping" (Shirakawa *et al.*, 1977). During the doping process, an organic polymer, either an insulator or a semiconductor having a small conductivity typically in the range of 10^{-10} to 10^{-5} S/cm, is converted to a polymer, which is in the metallic conducting regime (1- 10^{-4} S/cm). Figure 1.1 shows the conductivity range of metals, semiconductors and insulators.

