UNIVERSITI PUTRA MALAYSIA

PREPARATION AND CHARACTERIZATION OF POLYPYRROLEPOLYETHYLENE GLYCOL CONDUCTING POLYMER COMPOSITE FILMS

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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

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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 7.88×10^{-7} m^2s^{-1} were shown by the PPy-PEG composite film prepared from 0.20 M pyrrole, 0.10 M *p*-toluene sulfonate and 1×10^{-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

LIM MEI YEE

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 7.88×10^{-7} m^2s^{-1} berbanding dengan yang lain telah disediakan daripada larutan 0.20 M pirol, 0.10 M *p*-toluena sulfonat dan 1×10^{-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.

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Last but not least, special greetings and thanks to my beloved family for their wonderful love and generous moral support.

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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This thesis submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfilment of the requirement for the degree of Master of Science. The members of the Supervisory 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

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InSb	Indium Antimonide
AsF_5	Arsenic Pentafluoride.
TTF	Tetrathiafulvalene
TCNQ	Tetracyanoquinodimethane
CH	Methyl
Tc	Glass transition temperature
Ch	Chemical preparation
EP	Electropolymerization
Pt	Platinum
Py	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_4NPTS	tetraethylammonium ρ-toulenesulfonate
mA	Mega ampere
H_2O	Hydrogen oxide
CH_3CN	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
2θ	2 Theta
p-TS	*p*-toluene sulfonate
DMA	Dynamic mechanical analysis
EMI	Electromagnetic interference

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.