



UNIVERSITI PUTRA MALAYSIA

**PREPARATION, CHARACTERIZATION AND APPLICATION OF
POLYPYRROLE-CHITOSAN CONDUCTING POLYMER COMPOSITE**

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**PREPARATION, CHARACTERIZATION AND APPLICATION
OF POLYPYRROLE-CHITOSAN CONDUCTING POLYMER
COMPOSITE**

By

Mahnaz M.Abdi

**Thesis submitted to the School of Graduate Studies, Universiti Putra Malaysia, in
Fulfilment of the Requirements for the Degree of Doctor of Philosophy**

December 2009



Special dedication to my beloved family

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirement for the degree of Doctor of Philosophy

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Chairman: Professor Anuar Kassim, PhD

Faculty: Science

Polypyrrole-chitosan (PPy-CHI) conducting polymer composite films were prepared by electropolymerization of pyrrole (Py) in the presence of chitosan (CHI) and *p*-toluenesulfonic acid sodium salt (*P*-TS) at room temperature. The PPy-CHI composite films were synthesized by electrochemical method on the ITO glass surface from different concentrations of pyrrole, CHI, and *P*-TS at different applied voltages. For comparison purposes, film formed from chitosan in acetic acid (CA) by casting method and PPy film without chitosan were prepared.

The electrical conductivity measurements revealed that the composite film prepared from the solution containing 0.3 M pyrrole, 0.1 M *p*-TS and 0.7% (w/v) of CHI at 1.2 volt (against SCE) in 2 hrs, had the highest conductivity of 69.1 Scm⁻¹ measured at room temperature. The electrical conductivity measurement and the DMA results showed the enhanced conductivity and mechanical properties of the prepared conducting polymer composite films were due to the presence of CHI in the composite

films. The enhancement of storage modulus of PPy-CHI composite film compared to PPy indicates that the composite is much stiffer than PPy without CHI. The coexistence of vibrational bands attributable to both benzoic (1546 cm^{-1}) and quinoid forms (1634 cm^{-1}) of PPy in the FT-IR absorption spectra of PPy-CHI film confirmed the presence of two different structures in this composite film. TGA results showed that thermal stability of the PPy increased in the presence of chitosan.

With the increase in CHI content, the band gaps between the valance and conduction bands decreased and subsequently the conductivity of the composite films increased. The band gaps, E_g , estimated from optical absorption data, was between 1.60–2.32 eV, depending on the CHI content. There was a good correlation between the thermal diffusivity and electrical conductivity of composite film. The results indicated that the thermal diffusivity of the PPy-CHI composite films, relates to the electron migration in the conjugation chain length. The surface morphology of PPy showed almost all globular morphology. The agglomeration became more evident when the concentration of CHI increased from 0.5% to 0.9% (w/v).

The potential applications of composite films were found as an electromagnetic shielding material in the microwave frequency range from 8 to 12 GHz and also as an optical sensor characterized by surface plasmon resonance (SPR) technique.

The shielding effectiveness (SE) of the composite films had a strong dependence on chitosan content. The composite films provided shielding efficiencies of 33.9 dB which could be used successfully in some applications which need shielding properties less than 40 dB.

Optical sensor of PPy-CHI was fabricated for detecting trace amount of Hg^{2+} and Pb^{2+} . This optical sensor was used for monitoring of toxic metal ion with and without sensitivity enhancement by chitosan. The refractive indexes of the conducting films were successfully measured by surface plasmon resonance (SPR) technique.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Doktor Falsafah

**PENYEDIAAN, PENCIRIAN DAN PENGAPLIKASIAN POLIMER
KONDUKTOR KOMPOSIT POLIPIROL-KITOSAN**

Oleh

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Polimer pengkonduksian filem komposit polipirol-kitosan (PPy-CHI) telah disediakan melalui kaedah elektropolimeran pirol (Py) dengan kehadiran kitosan (CHI) dan garam sodium asid *p*-toluensulfonik (*P*-TS) pada suhu bilik. Filem komposit PPy-CHI disintesis melalui kaedah elektrokimia pada permukaan kaca ITO dengan pelbagai kepekatan pirol, CHI, *P*-TS pada voltan yang berlainan. Bagi tujuan perbandingan, filem yang dihasilkan menggunakan kitosan dalam asid asetik (CA) menerusi kaedah penyalutan dan filem PPy tanpa kitosan disediakan.

Penentuan kekonduksian elektrik menunjukkan bahawa filem komposit yang disediakan daripada larutan yang mengandungi 0.3 M pirol, 0.1 M *p*-TS dan 0.7% (w/v) CHI pada voltan 1.2 (terhadap SCE) dalam masa 2 jam mempunyai konduktiviti tertinggi, iaitu 69.1 Scm^{-1} , pada suhu bilik. Pengukuran konduktiviti elektrik dan hasil DMA menunjukkan bahawa konduktiviti yang diperkuatkan dan ciri-ciri mekanikal filem komposit polimer kekonduksian yang disediakan adalah disebabkan oleh

kehadiran CHI di dalam filem komposit. Peningkatan modulus simpanan filem komposit PPy-CHI berbanding dengan PPy menunjukkan komposit tersebut lebih keras berbanding tanpa CHI. Kehadiran bersama jalur-jalur getaran hasil daripada kedua-dua bentuk benzoik (1546 cm^{-1}) dan kuinoid (1634 cm^{-1}) PPy dalam spektrum penyerapan FT-IR untuk filem PPy-CHI mengesahkan kehadiran dua struktur yang berbeza di dalam filem komposit ini. Keputusan TGA telah menunjukkan peningkatan kestabilan haba PPy dengan kehadiran kitosan.

Dengan penambahan kandungan CHI, jurang jalur antara jalur valensi dan konduksian menurun dan seterusnya konduktiviti filem komposit meningkat. Jurang jalur, E_g , ditentukan daripada data penyerapan optikal, ialah di antara 1.60-2.32 eV, bergantung kepada kandungan CHI. Terdapat korelasi yang baik antara penyerapan haba dan konduktiviti elektrik filem komposit. Hasil ini menunjukkan bahawa penyerapan haba filem komposit PPy-CHI adalah berkaitan dengan pemindahan elektron dalam rantai panjang konjugasi.

Morfologi permukaan PPy menunjukkan morfologi yang hampir globular. Pengaglomerasian menjadi semakin jelas apabila kepekatan CHI meningkat daripada 0.5% kepada 0.9% (w/v). Ini mungkin diakibatkan oleh peningkatan elektrostatik atau hubungan penyerapan antara CHI dan PPy and oleh itu, pengaglomerasian menjadi lebih ketara.

Applikasi untuk filem komposit PPy-CHI adalah sebagai pengadang gelombang eletromagnetik dalam julat frekuensi mikrogelombang daripada 8 sehingga 12 GHz dan sebagai sensor optikal sensitif yang dicirikan oleh teknik resonans plasmon

permukaan (SPR). Keberkesanan pengadangan (SE) filem komposit sangat bergantung kepada kepekatan kitosan. Filem komposit menghasilkan SE sebanyak 33.9dB yang boleh digunakan secara berkesan dalam aplikasi yang memerlukan ciri pengadangan kurang daripada 40dB.

Sensor optikal PPy-CHI dihasilkan untuk mengesan jumlah surih Hg^{2+} dan Pb^{2+} . Sensor optikal tersebut digunakan untuk mengesan ion logam beracun dengan dan tanpa penguatan sensitiviti oleh kitosan. Indeks refraksi untuk filem konduksian telah berjaya diukur menerusi teknik resonans plasmon permukaan (SPR).

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I certify that an Examination Committee has met on 28 December 2009 to conduct the final examination of Mahnaz M.Abdi on her Doctor of Philosophy thesis entitled “Preparation, Characterization, and Application of Polypyrrole-Chitosan Conducting Polymer Composite” 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.

Mahnaz M.Abdi

Date: 11 January 2010

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