UNIVERSITI PUTRA MALAYSIA

PREPARATION, CHARACTERIZATION AND ELECTROMAGNETIC INTERFERENCE SHIELDING EFFECTIVENESS OF PPY-PVA AND PPY-CMC CONDUCTING POLYMER COMPOSITE FILMS

H. N. M. EKRAMUL MAHMUD.

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By

H. N. M. EKRAMUL MAHMUD

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

January 2006

DEDICATION

I look up the hills,
Where does my help come from?
My help comes from Allah, the Almighty,
The creator of heaven and earth.

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

PREPARATION, CHARACTERIZATION AND ELECTROMAGNETIC INTERFERENCE SHIELDING EFFECTIVENESS OF PPY-PVA AND PPY-CMC CONDUCTING POLYMER COMPOSITE FILMS

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Chairman: **Professor Anuar Kassim, PhD**

Faculty: **Science**

Polypyrrole-poly(vinyl alcohol) (PPy-PVA) and polypyrrole-carboxymethyl cellulose (PPy-CMC) 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(vinyl alcohol)/carboxymethyl cellulose insulating polymer. The PPy-PVA and PPy-CMC composite films prepared from different process conditions were characterized by Fourier Transform infrared (FT-IR) spectroscopy, X-ray diffraction (XRD) analysis, optical microscopy, dynamic mechanical analysis (DMA), and conductivity measurement. The highest conductivity of 64 S/cm measured at room temperature was shown by PPy-PVA composite film prepared from 0.2 M pyrrole, 0.1 M *p*-toluene sulfonate and 12 x 10^{-4} M PVA at 1.2 volt (vs

SCE) among all the PPY-PVA composite films produced. The PPy-CMC composite film prepared from 0.3 M pyrrole, 0.1 M *p*-toluene sulfonate and 0.03 M CMC at 1.2 volt (vs SCE) showed the highest conductivity of 38 S/cm among all the PPy-CMC composite films produced. The FT-IR study of PPy-PVA and PPy-CMC composite films shows the evidence of the incorporation of PVA and CMC in PPy structure forming PPy-PVA and PPy-CMC composite films, respectively.

The conductivity data of PPy-PVA shows that with the increase in PVA concentration in the pyrrole solution, the conductivity of the prepared PPy-PVA film is increasing up to certain level due to the increase in conjugation length and later it is decreasing with further increase in PVA concentration, which is again linked with the conjugation length decrease. This is supported by the FT-IR band intensity of $I_{C=C}/I_{C-N}$. The FT-IR study of PPy-CMC composite films shows that with the increase in CMC concentration from 0.005 M to 0.01 M, the conductivity first decreased and later with further increase in CMC concentration the conductivity showed an increasing trend and finally at 0.04 M CMC, the conductivity dropped.

The DMA results of PPy-PVA and PPy-CMC composite films show the enhanced mechanical properties of both the composite films over PPy films without PVA or CMC. The storage moduli of both the composite films were found much higher than the PPy film prepared without PVA or CMC indicating that PPy-PVA and PPy-CMC composite films are much stiffer than PPy films. The gradual decrease of storage moduli of both the composite films with the increase in temperature

ranging from 25 °C to 250 °C suggests that the composite films have got flexibility in their chains and thus the chains are soft. On the other hand, the storage modulus of PPy film only without PVA or CMC shows no decreasing tendency with the increase in temperature ranging from 25 °C to 250 °C indicating that the PPy film is very hard and have got no flexibility in its backbone chain.

The XRD results of both PPy-CMC and PPy-PVA composite films show that the films are amorphous and have got very little order. The optical micrographs of PPy-CMC and PPy-PVA show the globular surface morphology. The changes in globular surface morphology with the change in process condition of the film preparation indicates that the process parameters used to prepare the composite films have got a good influence over the surface morphology. The intense polymerization reaction has been evidenced from the surface morphology of the films.

The results of electromagnetic interference (EMI) shielding effectiveness in the microwave range of 8-12 GHz show that the highest shielding effectiveness of 45.67 dB measured in the microwave range of 8-12 GHz corresponds to the total attenuation of 99.4 % of microwave energy has been exhibited by the PPy-PVA composite film prepared from 0.2 M pyrrole, 0.1 M *p*-toluene sulfonate and 12 x 10^{-4} M PVA at 1.2 volt (vs SCE) among all the PPy-PVA composite films prepared. The highest shielding effectiveness of 35.7 dB measured in the microwave range corresponds to the total attenuation of 98.32 % of microwave energy has been exhibited by the PPy-CMC composite film prepared from 0.3 M

pyrrole, 0.1 M *p*-toluene sulfonate and 0.03 M CMC at 1.2 volt (vs SCE) among all the PPy-CMC composite films prepared. Thus, the promise of finding any electromagnetic interference (EMI) shielding applications in the microwave frequency range lies in PPy-PVA and PPy-CMC conducting polymer composite films.

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

PENYEDIAAN, PENCIRIAN DAN KEBERKESANAN LINDUNGAN INTERFERENS ELEKTROMAGNETIK FILEM KOMPOSIT POLIMER PENGALIR PPY-PVA DAN PPY-CMC

Oleh

H. N. M. EKRAMUL MAHMUD

Januari 2006

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Fakulti : Sains

Filem komposit polimer pengalir bagi pasangan polipirol-poli(vinil alkohol) dan polipirol-karboksimetil selulosa 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 sebatian polimer selulosa penebat poli(vinil alkohol)/karbosimetil selulosa. Filem komposit bagi PPy-PVA dan PPy-CMC telah disediakan melalui keadaan proses yang berlainan dan langkah pencirian telah dilakukan melalui penyerapan infra merah (FT-IR), pengimbasan analisis sinar-X, mikroskopi optikal, analisis mekanikal dinamik (DMA) dan penentukuran kekonduksian. Filem komposit PPy-PVA memberi nilai konduktiviti tertinggi iaitu 64 S/cm berbanding dengan yang lain. Filem tersebut disediakan daripada larutan pirol 0.2 M, 0.1 M *p*-toluena sulfonat dan 12 x 10^{-4} M PVA pada keupayaan 1.2 v (melawan SCE). Sebaliknya, filem komposit PPy-CMC

yang disediakan dengan 0.3 M pirol, 0.1 M *p*-toluena sulfonat dan 0.03 M CMC pada keupayaan 1.2 v (melawan SCE) menunjukkan nilai kekonduksian tertinggi 38 S/cm berbanding dengan yang lain. Kajian FT-IR ke atas filem komposit PPy-PVA dan PPy-CMC nyata menunjukkan kemasukan PVA dan CMC ke dalam struktur PPy berkaitan dengan pembentukan filem komposit PPy-PVA and PPy-CMC masing-masing.

Data kekonduksian, PPy-PVA menunjukkan dengan penambahan kepekatan PVA dalam larutan pirol, kekonduksian filem PPy-PVA turut bertambah ke satu paras tertentu disebabkan penambahan panjang konjugatan dan nilai kekonduksian berkurangan dengan penambahan PVA berlebihan iaitu berkaitan langsung dengan panjang konjugatan yang berkurangan. Keadaan ini disokong oleh nisbah keamatan jalur FT-IR ikatan $I_{C=C}/I_{C-N.}$ Menurut kajian FT-IR bagi filem komposit menunjukkan bacaan kekonduksiannya berkurangan dengan penambahan kepekatan CMC dari 0.005 M ke 0.01 M. Dengan penambahan kepekatan CMC yang berlebihan, kekonduksian semakin bertambah sehingga mencapai 0.04 M dan seterusnya berkurang.

Keputusan DMA berkaitan dengan filem-filem komposit PPy-PVA dan PPy-CMC menunjukkan sifat mekanikal yang lebih baik berbanding dengan filem-filem tanpa komposisi PVA mahupun CMC. Moduli "pulih" bagi kedua-dua jenis filem komposit didapati jauh lebih tinggi sekiranya dibandingkan dengan filem PPy yang disediakan tanpa PVA dan CMC. Ini jelas menunjukkan bahawa filem-filem komposit PPy-PVA dan PPy-CMC adalah jauh lebih kental atau kuat berbanding

dengan filem-filem PPy. Nilai moduli "pulih" berkurangan secara beransur-ansur dengan kenaikan suhu dari 25 °C ke 250 °C bagi kedua-dua jenis komposit mencadangkan bahawa rantai filem komposit tersebut memiliki sifat fleksibiliti dan ini menyebabkan rantai tersebut lembut. Sebaliknya, nilai modulus "pulih" bagi filem PPy tanpa komposisi PVA atau CMC tidak menunjukkan sifat kecenderungan kekurangan dengan kenaikan suhu dari 25 °C ke 250 °C menunjukan sifat keras dan tidak fleksibiliti pada pembentukan rantai utama ikatan.

Keputusan XRD menunjukkan bahawa kedua-dua filem komposit PPy-CMC dan PPy-PVA adalah bersifat amorfus dan mempunyai sedikit sifat ketertiban. Mikrografi optikal PPy-CMC dan PPy-PVA menunjukkan sifat morfologi permukaannya yang berbentuk sfera. Perubahan keadaan penyediaan turut mengubah morfologi permukaan sfera jelas menunjukkan bahawa parameter proses kajian yang digunakan mempunyai kesan untuk mempengaruhi sifat permukaannya. Jelasnya, tindak balas pempolimeran telah mempengaruhi morfologi permukaan filem-filem tersebut.

Interferen keelektromagnetan lindungan berkesan (EMI) pada julat mikrogelombang 8-12 GHz menunjukkan nilai pelindungan berkesan tertinggi pada 45.67 dB telah dihasilkan oleh filem komposit menerusi 0.2 pirol, 0.1 M *p*-toluena sulfonat dan 12 x 10^{-4} M PVA pada keupayaan 1.2 volt (melawan SCE) berbanding filem-filem komposit PPy-PVA yang disediakan. Nilai tertinggi bagi pelindungan berkesan (EMI) 35.7 dB ukuran pada julat mikrogelombang telah dihasilkan oleh filem komposit PPy-CMC yang disediakan daripada 0.3 M pirol,

0.1 M *p*-toluena sulfonat and 0.03 M CMC pada keupayaan 1.2 volt (melawan SCE) berbanding filem komposit PPy-CMC lain yang disediakan. Maka, sebarangan aplikasi interferen keelektromagnetan lindungan berkesan boleh ditemui dalam julat frekuensi mikrogelombang filem-filem polimer komposit berkonduksian jenis PPy-PVA dan PPy-CMC.

ACKNOWLEDGMENTS

In The Name of ALLAH, The Most Merciful And Most Beneficent

All praises goes to Allah, the Lord of the universe. Only by His grace and mercy this thesis has been completed.

First and foremost, I am extra-ordinarily grateful to my supervisor Professor Anuar Kassim, PhD for his strong support, guidance and patience for the very enriching and thought provoking discussions and lectures, which helped shape the thesis. He was always there to provide everything I needed in the laboratory. I would also like to express my sincere thanks to my co-supervisors Professor Zulkarnain Zainal, PhD and Professor Wan Mahmood Mat Yunus, PhD for their guidance, support, and encouragement throughout my study period.

I am also indebted to the staff of the Department of Chemistry, Universiti Putra Malaysia, for their help and cooperation.

Special thanks are extended to my lab members Miss Masnizaayu, Mrs. Rozita Yahya, and Mr. Fariz Adzmi who helped me in every possible way providing a congenial and enthusiastic atmosphere in the laboratory. Special thanks are also extended to Mr. Mainul Hassan, Mr. Lim Chee Siong, Mr. Zahid Rezwan, Mr. Yusouf Hossain, Mr. Hamzah Haroon and Mr. Shahril Hussin for their encouragement, help and support in every aspect of my thesis. A deep

acknowledgment is also extended to Mrs Yusmawati Wan Yusof, Mrs Rusnani, Miss Yusnita Osman, and Mr. Lee Kim Yee for their assistance in analyzing the samples. I owe to Mr. Mohammad Alghoul, the PhD candidate in the department of Physics for providing the colour printing of the micrographs and some XRD spectra. Mr. Abdullah Al Mamun and Dr. Lutfor Rahman will be remembered with deep appreciation for helping me find this research project in UPM. The great help from Dr. Dedy Suhendra is highly acknowledged and will remain ever fresh in the memory.

I wish to express my deepest gratitude to my parents, brother, sisters and sister-in-law for their prayers, continuous moral support and unending encouragement. Finally, I wish to express my sincere gratitude to my beloved wife Kazi Jebunnesa Eti and my dearest and only son Shakir Mahmud for extending their moral support, encouragement, patience and understanding.

I certify that an Examination Committee met on 5th January, 2005 to conduct the final examination of H. N. M. Ekramul Mahmud on his Doctor of Philosophy thesis entitled "Preparation, Characterization and Electromagnetic Interference Shielding Effectiveness of PPY-PVA and PPY-CMC Conducting Polymer Composite Films" 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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Date: 27 MAR 2006

This thesis submitted to the Senate of Universiti Putra Malaysia has been accepted as fulfilment of the requirement for the degree of Doctor of Philosophy. The members of the Supervisory Committee are as follows:

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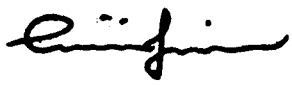

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Date: 13 APR 2006

DECLARATION

I do 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.

Ekramul Mahmud

H. N. M. EKRAMUL MAHMUD

Date: March 6, 2006.

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