UNIVERSITI PUTRA MALAYSIA

ELECTRICAL PROPERTIES OF CHEMICALLY SYNTHESIZED POLYPYRROLE PELLETS AND GAMMA-RAY INDUCED POLYPYRROLE COMPOSITE FILMS

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By

MOHD HAMZAH BIN HARUN

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

June 2007

Dedication

To my family, relatives, colleagues, friends and lecturers aka supervisors,

who have given me all supports, love, patience and responsibility.

Thank you.

Abstract of 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 Elias bin Saion, PhD**

Faculty: **Science**

The polypyrrole, PPy conducting polymer pellets and PVA-PPy-$FeCl_3$ composite polymer films have been prepared by using pyrrole, Py monomer, polyvinyl alcohol as polymer binder for polypyrrole composite, and iron (III) chloride, $FeCl_3$ as oxidizing and doping agent by conventional technique; chemical polymerization method. Further, PVA-PPy-CH and PVA-PPy-TCA composite films have been prepared by utilizing Py monomer and doping agents of chloral hydrate, CH and trichloroacetic acid, TCA respectively via gamma irradiation technique. The influence of composition of doping agent was investigated by using x-ray diffraction (XRD) for the structural analysis and by using an impedance analyzer (LCR meter) for the electrical conductivity and dielectric properties in frequency range from 20 Hz to 1 MHz. The temperature effect of PVA-PPy-$FeCl_3$ of composites and the radiation effect of PVA-PPy-CH and PVA-PPy-TCA composites on electrical conductivity and dielectric properties were also investigated.

The XRD analysis for the samples at different composition of the dopants indicated that the redox mechanism had been taken placed particularly for polypyrrole pellets as it clearly showed that the peak presence of the dopant. On the other hand, for PVA-PPy-$FeCl_3$ composite films, it was observed that the broad peak of PVA was diminished as a result of the competition between insulating PVA and PPy formation, in which PPy yield becomes higher at higher concentration of the dopant. The gamma ray induced PVA-PPy-TCA and PVA-PPy-CH composite films gave the same trends for both of the samples. The broad peak of PVA was present for all samples. New peak was observed upon irradiation particularly for higher composition of the dopant. It was attributed to the radiation scission of TCA and CH molecules, which do not involve in PPy polymerization as all of the Py monomers were already consumed.

The electrical conductivity, σ for all samples increased with the increase of dopant composition, temperature and irradiation dose. Polypyrrole pellets contained highest conductivity among the others, as they do not contain insulating polymer binder in which could reduce the magnitude of conductivity. Among PPy composite films, PVA-PPy-$FeCl_3$ gave better conductivity as compared to PVA-PPy-TCA and PVA-PPy-CH due to factor of $FeCl_3$ in which it is known that iron (III) chloride is reactive electron acceptor and the reason that it is genuinely oxidation agent in which TCA and CH do not own. Therefore, gamma-rays were used to induce the electrical properties of TCA and CH doped polypyrrole composites. The gradual increase of the conductivity as increase the dopant concentration and irradiation dose can be attributed to more free charges (i.e.

polarons) available in the composite system whereas for temperature dependent study, the conductivity increased as the temperature increased, was due to the high mobility of free charges interact in composite system.

Dielectric properties in respect of relative permittivity (dielectric constant), ε' and loss permittivity (dielectric loss), ε" showed that the value increased as the dopant composition, temperature and irradiation dose were increased. The number of dipoles available became prominent as the dopant and irradiation dose were increased thus increase the value of dielectric properties. On the other hand, the value for relative permittivity and loss became higher as the temperature was increased, attributed to the higher mobility of dipoles in the composite system. The trend for all samples; PPy pellets and composites films, were almost similar as at the lower frequency region (~ 20 Hz to 1 kHz), sharp decrease were observed due to the dipoles orientation along applied electric field and reaching almost a constant value at higher frequency (~ 1 kHz to 1 MHz) region. It was due to the difficulty of the dipoles to orient themselves as the applied frequency became higher. The relaxation time, $\tau(\omega)$ in which represents dielectric relaxation obtained for all samples, almost reduced with the dopant composition, irradiation dose and temperature. Such an inconsistent value of $\tau(\omega)$ might be due to the uncertain value of the angular frequency peak, ω_p and irregularity of the electrical displacement.

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

SIFAT-SiFAT ELEKTRIK BAGI PELET POLIPIRROL YANG DISEDIAKAN SECARA KIMIA DAN FILEM KOMPOSIT POLIPIRROL YANG DIRANGSANGKAN DENGAN SINARAN GAMA

Oleh

MOHD HAMZAH BIN HARUN

Jun 2007

Pengerusi: **Profesor Elias bin Saion, PhD**

Fakulti: **Sains**

Polipirrol, polimer pelet pengalir elektrik, PPy dan filem komposit polipirrol PVA-PPy-$FeCl_3$ telah disediakan dengan kaedah konvensional; teknik pempolimeran kimia, menggunakan pirrol, Py sebagai monomer, polivinil alkohol sebagai polimer pengikat dan ferum (III) klorida, $FeCl_3$ sebagai agen dopan dan pengoksidaan. Selanjutnya, filem komposit PVA-PPy-CH dan PVA-PPy-TCA disediakan menggunakan Py sebagai monomer, asid trikloroasetik dan kloral hidrat sebagai agen dopan menggunakan kaedah penyinaran sinar gama. Pengaruh komposisi agen dopan pengoksidaan telah dicirikan dengan menggunakan pembelauan sinar-x (XRD) untuk menganalisis struktur sampel dan alat penganalisa impedans (meter LCR) untuk mencirikan parameter kekonduksian elektrik dan sifat-sifat dielektrik dari julat frekuensi 20 Hz hingga 1 MHz. Kesan penambahan suhu bagi filem komposit PVA-PPy-$FeCl_3$ dan kesan penambahan dos

untuk PVA-PPy-CH dan PVA-PPy-TCA terhadap sifat-sifat kekondusian elektrik dan dielektrik telah dikaji.

Daripada analisis XRD untuk sampel-sampel yang mempunyai komposisi dopan berbeza telah menunjukkan yang mekanisma redoks wujud terutamanya bagi pellet polipirrol dimana ia dengan jelasnya menunjukkan puncak yang mewakili dopan. Selain itu, untuk filem komposit PVA-PPy-$FeCl_3$, ia menunjukkan puncak yang agak mendatar mewakili PVA semakin menghilang disebabkan wujudnya persaingan diantara PVA dan penghasilan PPy, dimana penghasilan PPy semakin meningkat pada komposisi dopan yang semakin tinggi. Bagi filem komposit PVA-PPy-TCA dan PVA-PPy-CH yang dirangsangkan dengan sinaran gama, telah memberikan keputusan yang sama bagi kedua-dua jenis sampel. Puncak yang agak mendatar mewakili PVA wujud bagi kesemua sampel. Puncak yang baru telah wujud hasil proses penyinaran dimana ia agak jelas pada komposisi dopan yang agak tinggi. Ia disebabkan oleh proses pemutusan ikatan bagi molekul-molekul TCA dan CH daripada tindakbalas sinaran, dimana ia tidak melibatkan pempolimeran PPy kerana monomer Py sebelum itu telah digunakan kesemuanya ketika proses pempolimeran.

Kekondusian elektrik, σ bagi keseluruhan sampel meningkat dengan pertambahan komposisi dopan, suhu dan dos penyinaran. Pelet polipirrol mempunyai kekonduksian tertinggi jika dibandingkan dengan sampel yang lain kerana ia tidak mempunyai polimer pengikat yang bersifat penebat yang akan menurunkan nilai kekonduksian. Diantara

filem komposit PPy, PVA-PPy-$FeCl_3$ telah memberikan nilai kekonduksian yang lebih baik jika dibandingkan dengan filem komposit PVA-PPy-TCA dan PVA-PPy-CH disebabkan faktor Fe(III) klorida adalah penerima elektron yang reaktif dan ia adalah agen pengoksidaan semulajadi dimana ciri-ciri ini tidak terdapat pada TCA dan CH. Justeru, bagi sampel komposit didopkan dengan TCA dan CH, sinaran gama telah digunakan bagi meningkatkan sifat keelektrikannya. Peningkatan kekonduksian yang seragam apabila komposisi dopan dan dos penyinaran ditambah adalah disebabkan oleh bertambahnya cas-cas bebas (i.e. polarons) di dalam sistem komposit. Bagi kekonduksian elektrik bagi suhu berbeza, nilai kekonduksian meningkat apabila suhu ditambah adalah disebabkan oleh pergerakan cas yang semakin meningkat di dalam sistem komposit.

Ciri-ciri dielektrik bagi pemalar dielektrik, ε' dan lesapan dielektrik, ε" telah menunjukkan yang nilainya meningkat dengan pertambahan komposisi dopan, suhu dan dos penyinaran. Bilangan dwikutub terhasil semakin meningkat dengan dopan dan dos penyinaran lalu meningkatkan nilai dielektrik. Selain itu, nilai pemalar dielektrik dan lesapan dielektrik meningkat dengan peningkatan suhu disebabkan pergerakan dwikutub bertambah di dalam sistem komposit. Pemerhatian bagi kesemua sampel hampir sama dimana pada julat frekuensi rendah (~ 20 Hz ke 1 kHz), graf menurun kerana orientasi dwikutub disepanjang medan elektrik dan agak mendatar kemudiannya pada julat frekuensi tinggi (~ 1 kHz ke 1 MHz). Ia disebabkan oleh orientasi dwikutub berkurang kerana terhalang dengan nilai frekuensi medan elektrik yang semakin meningkat. Masa santaian, $\tau(\omega)$ yang mewakili relaksasi dielektrik hampir berkurang dengan pertambahan

komposisi dopan, dos penyinaran dan suhu. Nilainya yang tidak konsisten mungkin disebabkan oleh nilai puncak frekuensi angular, ω_p yang tidak tetap dan ketidakseimbangan nilai penyingkiran elektrik.

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In the name of Allah, the most Gracious and the most Merciful

Praise is to Allah the Almighty, for thee (alone) we worship and thee (alone) we ask for help. Praise also is upon Muhammad S.A.W. who is guidance and has led us to the path that God has favored.

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I certify that an Examination Committee has met on 18th June 2007 to conduct the final examination of Mohd Hamzah bin Harun on his Master of Science thesis entitled "Electrical Properties of Chemically Synthesized Polypyrrole Pellets and Gamma-Ray Induced Polypyrrole Composite Films" in accordance with Universiti Pertanian Malaysia (Higher Degree) Act 1980 and Universiti Pertanian Malaysia (Higher Degree) Regulation 1981. The committee recommends that the candidate be awarded the relevant degree. Members of the Examination 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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Date: 13 September 2007

DECLARATION

I hereby declare that the thesis is based on my original work except for quotation 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.

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MOHD HAMZAH BIN HARUN

Date: 10 August 2007

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