



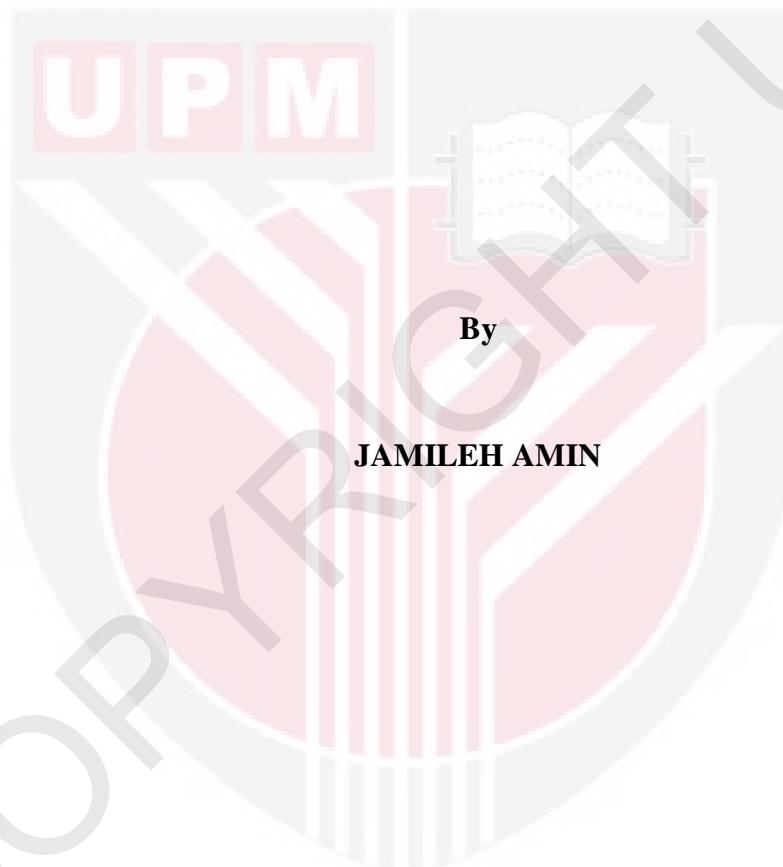
UNIVERSITI PUTRA MALAYSIA

**PREPARATION, AND ELECTRICAL, MAGNETIC AND THERMAL
INVESTIGATION OF POLYPYRROLE-CHITOSAN COMPOSITE AND
POLYPYRROLE-CHITOSAN-IRON OXIDE POLYMER NANOCOMPOSITE**

JAMILEH AMIN

FS 2013 37

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INVESTIGATION OF POLYPYRROLE-CHITOSAN COMPOSITE AND
POLYPYRROLE-CHITOSAN-IRON OXIDE POLYMER
NANOCOMPOSITE**



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

June 2013

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Dedicated to my beloved mother, father, my sister Jelveh and her family

Without their understanding and support, I would never have completed this

project.



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

PREPARATION, AND ELECTRICAL, MAGNETIC AND THERMAL INVESTIGATION OF POLYPYRROLE- CHITOSAN COMPOSITE AND POLYPYRROLE-CHITOSAN-IRON OXIDE POLYMER NANOCOMPOSITE

By

JAMILEH AMIN

June 2012

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Faculty: Science

Conducting polymer composite based on Polypyrrole-Chitosan (PPy-CHI) and Polypyrrole-Chitosan-Iron oxide nanoparticles (PPy-CHI- Fe_3O_4) nanocomposite were prepared by using in-situ chemical polymerization method. (PPy-CHI) composites and (PPy-CHI- Fe_3O_4) nanocomposite were prepared with various percentages of CHI and Fe_3O_4 ranging from 0.0% (w/v) to 0.9% (w/v) and 0 wt% to 15wt% respectively. Results from conductivity experiments revealed that the highest conductivity was obtained from PPy-CHI- Fe_3O_4 nanocomposite prepared from 0.1 % (w/v) CHI, 3 Molar PPy and 3wt% Fe_3O_4 in 30 minutes at room temperature

The X-ray diffractogram of PPy and CHI illustrated a broad scattering peak for PPy and two scattering peaks of almost equal intensity for CHI which is due to

their highly amorphous and semi-crystallinity structure respectively. The XRD spectra for PPy–CHI composite was almost similar to those of PPy with a broad scattering at around 25°–26° indicating an amorphous structure. The XRD spectrum of PPy–CHI–Fe₃O₄ nanocomposite demonstrated similar to those observed from PPy and PPy–CHI composite matrix especially in the lower weight percentage of Fe₃O₄. However, as the nanoparticle loading increased, the characteristic peaks of Fe₃O₄ begun to dominate the nanocomposite spectra indicating to some uncoated Iron oxide nanoparticle which was confirmed by Energy-Dispersive X-ray (EDX) and transmission electron microscopy (TEM). The Fourier transform infrared spectroscopy (FT-IR) spectra of PPy–CHI and PPy–CHI–Fe₃O₄ illustrated almost the same characteristic positions of IR absorption bands similar to those of PPy. The small shift of PPy in the PPy–CHI composites is due to the identical peaks of PPy and CHI while in the PPy–CHI–Fe₃O₄ nanocomposites, the matrix layer of polypyrrole which covered the surface of iron oxide has absorbed most of the IR radiation. The results of Scanning Electron microscopy (SEM) and transmission electron microscopy (TEM) confirmed that the Fe₃O₄ nanoparticles have been coated with the layers of polymeric matrix. A distribution of discrete globular nanoparticles with almost uniform size and dimensions was exhibited in all PPy–CHI–Fe₃O₄ nanocomposite samples. The reduced size of PPy–CHI and PPy–CHI–Fe₃O₄ particles was explained by the effect of Chitosan and iron oxide, the steric stabilization effect of CHI and a core-shell structure for PPy–CHI–Fe₃O₄ nanocomposite which was confirmed by SEM and TEM.

The results of Vibrating Sample Magnetometer (VSM) revealed the magnetic properties for various PPy–CHI–Fe₃O₄ nanocomposites strongly depended on the

concentration loading of Fe_3O_4 . The hysteresis loops of VSM illustrated superparamagnetic behavior for all the nanocomposite of PPy–CHI– Fe_3O_4 with different loading Fe_3O_4 percentage. The M_s (saturation magnetization) and H_c (coercivity) were monitored for samples with percentage loaded of Fe_3O_4 from 0.1 wt% to 15 wt%. M_s increased from 0.874 emu/g to 5.97 emu/g while H_c decreased from 241.4 Oe to 194.48 Oe.

The results of electron spin resonance (ESR) spectroscopy revealed a reduction in the Peak-to-peak line-width (ΔH_{pp}) value between PPy and PPy–CHI. The adding of Fe_3O_4 have resulted in (ΔH_{pp}) values increased in the order PPy–CHI <PPy–CHI– Fe_3O_4 (1wt%) < PPy–CHI– Fe_3O_4 (3wt%) > PPy–CHI– Fe_3O_4 (5wt %) < PPy–CHI– Fe_3O_4 (7wt %) < PPy–CHI– Fe_3O_4 (10wt %) < PPy–CHI– Fe_3O_4 (15wt %) at room temperature. The spin concentration (N_s) measurement of PPy–CHI– Fe_3O_4 with the various Fe_3O_4 content revealed to be larger than PPy–CHI (8×10^6 , 1.59×10^7 , 3×10^7 , 2.29×10^7 , 2.43×10^7 and 2.49×10^7 spin g-1 for PPy–CHI and 1wt%, 3wt%, 5wt%, 7wt% and 10wt%, of Fe_3O_4 respectively). The increase in percentage loading of iron oxide also resulted in better thermal stability of the nanocomposites.

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

**PENYIASATAN DAN PENYEDIAAN, ELEKTRIKAL, MAGNETIK DAN
TERMAL BAGI POLIPYRROLE-KITOSAN KOMPOSIT
POLIPYRROLE-KITOSAN OKSIDA POLIMER KOMPOSIT NANO**

Oleh

JAMILEH AMIN

Jun 2012

Pengerusi : Profesor Zainal Abidin Talib, PhD

Fakulti: Sains

Penyediaan komposit polimer berdasarkan ke atas Polipyrrole-Kitosan (PPy-CHI) dan partikel nano Polipyrrole-Kitosan-Besi oksida ($\text{PPy-CHI-Fe}_3\text{O}_4$) komposit nano telah disediakan menggunakan kaedah pempolimeran kimia setempat. Komposit (PPy-CHI) dan komposit nano ($\text{PPy-CHI-Fe}_3\text{O}_4$) telah disediakan menggunakan pelbagai peratusan CHI dan Fe_3O_4 masing-masing dari 0.0% (w/v) sehingga 0.9% (w/v) dan 0 wt% kepada 15wt%. Dapatan daripada eksperimen kekonduksian mendapati bahawa konduksi tertinggi diperolehi daripada komposit nano PPy-CHI- Fe_3O_4 disediakan daripada 0.1 % (w/v) CHI, 3 Molar PPy dan 3wt% Fe_3O_4 dalam 30 minit pada suhu bilik.

X-ray difraktogram bagi PPy dan CHI ditunjukkan pada puncak tertinggi serakan terluar bagi PPy dan dua puncak serakan bagi hampir sama keamatannya bagi

CHI yang mana disebabkan masing-masing oleh struktur amorphous yang tinggi dan semi-habur mereka yang tinggi masing-masing. Spektra XRD bagi komposit PPy-CHI adalah hampir sama dengan PPy yang serakan luasnya adalah pada 25° - 26° menunjukkan struktur amorfus. Spektrum XRD spectrum bagi komposit nano PPy-CHI- Fe_3O_4 menunjukkan hasil sama dengan yang telah diperhatikan daripada matrik komposit PPy dan PPy-CHI khasnya dalam peratusan berat yang lebih rendah bagi Fe_3O_4 . Walaubagaimanapun, semakin bebanan partikel nano bertambah, karekter puncak bagi Fe_3O_4 mula mendominasi spektrum komposit nano menunjukkan yang beberapa partikel nano Besi oksida tidak diselaputi yang telah disahkan oleh Energy-Dispersive X-ray (EDX) dan transmisi mikroskopi elektron (TEM). Fourier merubah spektrum infra merah spektroskopi (FTIR) bagi PPy-CHI dan PPy-CHI- Fe_3O_4 menunjukkan hampir sama karekter kedudukannya bagi penyerapan jalur IR adalah sama dengan PPy. Perubahan kecil PPy dalam komposit PPy-CHI adalah disebabkan kepada puncak yang sama bagi PPy dan CHI sementara dalam komposit nano PPy-CHI- Fe_3O_4 , lapisan matrik bagi polipyrrole yang telah diselaputi dengan permukaan besi oksida telah menyerap kebanyakannya radiasi IR. Hasil daripada mikroskopi Scanning Electron (SEM) dan transmisi mikroskopi elektron (TEM) mengesahkan yang partikel nano Fe_3O_4 telah dilaputi dengan lapisan matrik polimerik. Taburan bagi partikel nano diskret globular dengan hampir saiz uniform dan dimensi yang sama telah ditunjukkan dalam semua sampel komposit nano PPy-CHI- Fe_3O_4 . Pengurangan saiz bagi PPy-CHI dan partikel PPy-CHI- Fe_3O_4 telah diterangkan dengan kesan oksida Kitosan dan besi , kesan penstabilan sterik bagiCHI dan struktur teras-luaran bagi komposit nano PPy-CHI- Fe_3O_4 telah disahkan dengan SEM dan TEM.

Dapatan bagi Vibrating Sample Magnetometer (VSM) menunjukkan yang sifat magnetik bagi pelbagai komposit nano PPy–CHI–Fe₃O₄ secara kuatnya bergantung kepada bebanan tumpuan bagi Fe₃O₄. Histeresis lilitan bagi VSM berasaskan tingkah laku superparamagnetik bagi kesemua komposit nano PPy–CHI–Fe₃O₄ dengan peratusan berbeza bebanan Fe₃O₄. M_s (penepuan pemagnetan) dan H_c (koektiviti) telah diperhatikan kepada sampel dengan peratusan yang mengandungi Fe₃O₄ daripada 0.1 wt% kepada 15 wt%. M_s meningkat daripada 0.874 emu/g kepada 5.97 emu/g sementara Hc berkurangan daripada 241.4Oe kepada 194.48 Oe.

Dapatan dari putaran resonan elektron (ESR) spektroskopi menunjukkan pengurangan dalam nilai Peak-to-peak line-width (ΔH_{pp}) antara PPy dan PPy–CHI. Penambahan Fe₃O₄ telah menyebabkan dalam nilai (ΔH_{pp}) meningkat dalam turutan PPy–CHI <PPy–CHI–Fe₃O₄ (1wt%) < PPy–CHI–Fe₃O₄ (3wt%) > PPy–CHI–Fe₃O₄ (5wt %) < PPy–CHI–Fe₃O₄ (7wt %) < PPy–CHI–Fe₃O₄ (10wt %) < PPy–CHI–Fe₃O₄ (15wt %) pada suhu bilik. Pengukuran putaran tumpuan (N_s) bagi PPy–CHI–Fe₃O₄ dengan pelbagai kandungan Fe₃O₄ menunjukkan iaanya lebih besar daripada PPy–CHI (8×10^6 , 1.59×10^7 , 3×10^7 , 2.29×10^7 , 2.43×10^7 dan 2.49×10^7 spin g-1 kepada PPy–CHI dan 1wt%, 3wt%, 5wt%, 7wt% dan 10wt%, of Fe₃O₄ masing-masing). Peningkatan dalam peratusan bebanan oksida besi turut menyebabkan kestabilan terma bagi komposit nano yang lebih baik .

ACKNOWLEDGMENTS

Pursuing a Ph.D. project like climbing a mountain is painful and enjoyable, step by step, accompanied with bitterness, hardships, frustration, experience, encouragement and trust also with help of many people. I realized that it was teamwork that it would not have been possible to write a doctoral thesis without the help and support of the kind people around. Though it will be very hard to express my gratitude to all those people in words, I would like to appreciate of all their helps.

First of all, I am grateful to the Almighty Allah for all happiness, strength and patience offered me during the undertaking of this project. This thesis would not have been possible without the help, support and patience of my honorific supervisor, Professor Zainal Abidin Talib, PhD. I'd like to give him my sincere thanks for giving me the opportunity to be his student and for his kind advice and encouragement throughout this entire project. I would like to express my deepest appreciation and special to Professor Anuar Kassim PhD, and my committee members, Professor Mohammad Zaki AB. Rahman and Doctor H.N.M. Ekramul Mahmud for their good advice, suggestions, support and friendship.

I am very grateful for my very supportive parents who always were beside me to give me love. Their understanding and love encourage me to continue and pursuing a Ph.D project abroad. I would like to give my sincere thanks to my

parents, my sister and her family for giving me their unequivocal support throughout, as always, for which my mere expression of thanks likewise does not suffice.

I am grateful to all the staff of the Faculty of Science for helping me feel home here at UPM. Special thanks go to the XRD, Mrs Rusnani Amirudin, Mr Mohd Zain Mohd Yusof, Mrs Zaidina and other science officers whose names are not mentioned in this section for their assistance in analyzing the samples and their valuable effort and time.

It is a pleasure to acknowledge my colleagues Dr. Mahnaz, Dr. Kamyar, Majid Afain, Kasra, Masoud, Mohammad Reza, Rahima, Sabri, who have been helpful and willing to share their knowledge, skills and experience.

Last but not least, without the love, support, guidance, and encouragement of my family, this moment would never have been realized. I would like to express my deepest gratitude to all my family members. I love you and thank you so much.

I certify that an Examination Committee has met on 4 June 2013 to conduct the final examination of Jamileh Amin on her Doctor of Philosophy thesis entitled “Preparation, and Electrical, Magnetic and Thermal Investigation of Polypyrrole–Chitosan Composite and Polypyrrole– Chitosan–Iron Oxide Polymer Nanocomposite” in accordance with the Universities and University Colleges Act 1971 and the Constitution of the Universiti Putra Malaysia [P.U.(A) 106] 15 March 1998. The Committee recommends that the student be awarded the Doctor of Philosophy.

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DECLARATION

I declare that the thesis is 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 University Putra Malaysia or other institutions.

2013/8/14

JAMILEH AMIN

Date: 4 June 2013



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