RADIATION SYNTHESIS AND CHARACTERIZATION OF CONDUCTING POLYANILINE AND POLYANILINE/SILVER NANOPARTICLES

MOHAMMED AHMED ALI OMER

FS 2007 63
RADIATION SYNTHESIS AND CHARACTERIZATION OF CONDUCTING POLYANILINE AND POLYANILINE/SILVER NANOPARTICLES

By

MOHAMMED AHMED ALI OMER

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

September 2007
Dan mereka bertanya kepadamu tentang roh. Katakkan: “Roh itu dari perkara urusan tuhanku dan kamu tidak diberikan ilmu pengetahuan melainkan sedikit sahaja”
(Al-Israa – 85)
DEDICATION

To the Soule of my parent mum Maddeina M.O. and Ahmed Ali O. who were sincerely encourage and foster me through out my study-hood, I dedicate the benefits of this humble work. To the Soule of Uncle Abdelrahman Ali O., Omer Awad O. and my brother Alfatih Shaikh Alddin Ali, Allah rewards them with paradise.

To my friend as well as my Uncle Salahualdinn Ali O, whose generous help and sincere encouragement motivated me to go ahead for further study, to my patientful wife Omsalam Mohamed Ismail, our son Ahmed Mohammed Ahmed and those who are sincerely pray for my success.
RADIATION SYNTHESIS AND CHARACTERIZATION OF CONDUCTING POLYANILINE AND POLYANILINE/SILVER NANOPARTICELS

By

MOHAMMED AHMED ALI OMER

September 2007

Chairman: Professor Elias Saion, PhD

Faculty: Science

The conducting polymer PANI nanoparticles were synthesized from polyvinyl alcohol PVA and aniline hydrochloride (AniHCl) blend films at different AniHCl monomer concentrations (0.5, 1.0, 1.5 and 2.0 g or as 9.0, 16.7, 23.1, and 28.6 wt %) and irradiated with gamma radiation at different doses (0, 10, 20, 30, 40, and 50 kGy) at ambient conditions. Upon irradiation AniHCl undergoes dechlorination by the loss of Cl\(^-\) that acts as an oxidant and ‘in situ’ polymerizing aniline into conducting PANI nanoparticles. The formation of conducting PANI has been observed by the change of colour from colourless to dark green due to the formation of polaron species characterized by the defect in molecular structure of the polymer and was confirmed by Raman scattering at 1637 cm\(^{-1}\) Raman shift assigned for C=N stretching of imines group. The SEM morphology of PVA/PANI composites reveals the spherical structure of nanoparticles, 50 – 100 nm in diameter which then
transformed into globular clusters of conducting PANI with good environmental stability.

The optical properties of PANI nanoparticles were measured by means of UV-visible spectrophotometry and found that the absorbance at 790 nm band of conducting PANI increased exponentially with the increase of dose and fitted the expression of the form: \( y = y_0 \exp\left(\frac{D}{D_0}\right) \), where \( D \) is the absorbed dose and \( D_0 \) is the dose sensitivity. The results reveal that the optical parameters such as absorption edge, activation energy, and band gap energy decreased with the increase of dose and AniHCl concentration. When the dose increased from 10 kGy to 50 kGy the absorption edge decreased from 1.0 to 0.91 eV for 9.0% AniHCl and from 0.82 to 0.44 eV for 28.6% AniHCl, the activation energy decreased from 2.25 to 1.5 eV for 9.0% AniHCl and from 0.8 to 0.69 eV for 28.6% AniHCl, and the band gap energy decreased from 1.36 to 1.18 eV for 9.0% AniHCl and from 1.12 to 1.00 eV for 28.6 wt% AniHCl. The electrical conductivity was determined by an impedance analyzer and found the conductivity increased with the increase of dose and AniHCl concentration. The conductivity is mainly the direct current (dc) component attributed to the creation of polarons in the PANI structure and they are the charge carriers of conducting PANI which are set in motion in a form of electron hopping within the backbone of the composites. The dc conductivity increased from \( \times 10^{-6} \) S/m to \( \times 10^{-3} \) S/m for 9.0 wt% and from \( 7.76 \times 10^{-5} \) S/m to \( 1.17 \times 10^{-1} \) S/m for 28.6 wt% AniHCl when the dose was increased from 10 kGy to 50 kGy. The dc conductivity is therefore governed by the exponential relation of the form: \( \sigma_{dc} = \sigma_0 \exp\left(\frac{D}{D_0}\right) \), where \( \sigma_0 \) and \( D_0 \) were found varied with different AniHCl concentration.
The silver nanoparticles were synthesized from PVA/silver nitrate (AgNO$_3$) blend films at different AgNO$_3$ dopant concentration of 0.01 wt % and irradiated with gamma radiation at different doses (0, 10, 20, 30, 40, and 50 kGy) at ambient conditions. Upon gamma irradiation, the released electrons interact with silver ions Ag$^+$ which reduce to silver nanoparticles Ag$^0$. The formation of Ag$^0$ nanoparticles has been observed by the colour change from colourless to golden yellow due to the presence of Ag$^0$ nanoparticles and was confirmed by XRD analysis. Further, the presence of metal nanoparticles was verified with the UV-visible absorption measurement that reveals the absorption peak at 425 nm due to surface plasmon resonant phenomenon at the conduction band of Ag$^0$ nanoparticles where the absorbance increased with the increase of dose and fitted the expression of the form:

$$y = y_0 \exp\left(\frac{D}{D_o}\right).$$

The composites of PVA/PANI/Ag$^0$ nanoparticles were radio-synthesized with the concentration of AniHCl at 28.6 wt%. The concentrations of AgNO$_3$ dopant are different (0.01, 0.03, 0.05, and 0.07 wt %) and different radiation doses (0, 10, 20, 30, 40, and 50 kGy). The results from optical absorption measurement reveal two absorption bands at 415 nm due to surface plasmons of Ag$^0$ nanoparticles and at 600 nm due to polarons of low conducting PANI. The absorption band shifted from 425 nm to 415 nm correspond to decreasing diameter of Ag$^0$ nanoparticles in the presence of PANI in the composites. The band gap increased with the increase of AgNO$_3$ dopant, from 1.72 eV for 0.01 wt% to 2.58 eV for 0.07 wt% dopant irradiated at 50 kGy. The dc conductivity increased with the increase of dose and decreased with the increase of dopant concentration Ag$^+$. The dc conductivity for 0.01 wt% dopant increased from $9.77 \times 10^{-6}$ S/m at 10 kGy to $8.51 \times 10^{-4}$ S/m at 50 kGy. For dopant
concentration at 0.07 wt%, however, the dc conductivity increased from $1.07 \times 10^{-7}$ S/m at 10 kGy to $1.23 \times 10^{-5}$ S/m at 50 kGy. The dc conductivity of PVA/PANI/Ag\textsuperscript{0} nanocomposites was found to have an exponential expression of the form: $\sigma_{dc} = \sigma_0 \exp(D / D_0)$. 
Zarah nano bagi polimer konduktor PANI telah disintesiskan daripada film adunan PVA/aniline hidroklorida (AniHCl) pada kepekatan monomer AniHCl berbeza (9.0, 16.7, 23.1, and 28.6 wt%) dan disinarkan dengan sinaran gama pada dos berbeza (0, 10, 20, 30, 40, and 50 kGy) dalam keadaan ambien. Setelah disinarkan AniHCl mengalami nyahklorin dengan kehilangan Cl\(^{-}\) yang bertindak sebagai pengoksidan dan secara ‘in situ’ mengpolimerkan anilina kepada zarah nano PANI konduktor. Pembentukan PANI konduktor telah diperhatikan sebagai perubahan warna daripada tak berwarna kepada hijau gelap kerana pembentukan spesis polaron yang dikaitkan sebagai kecacatan struktur molekul polimer dan telah disahkan oleh pengukuran serakan Raman pada anjakan Raman 1637 cm\(^{-1}\) yang dipadankan kepada rengangan ikatan C=N dalam kumpulan amina. Morpologi SEM bagi komposit PVA/PANI menunjukkan struktur zarah nano berbentuk sfera berdiameter 50 – 100 nm dan
kemudian struktur zarah nano PANI bertukar kepada kulster PANI dengan mempunyai kestabilan alam sekitar yang baik.

Ciri optik zarah nano PANI telah diukur dengan menggunakan kaedah spektrofotometri UV-tampak dan didapati penyerapan pada 790 nm bertambah secara eksponen dengan pertambahan dos berpadanan dengan bentuk: 

\[ y = y_0 \exp(D / D_0) \]

yang mana \( D \) ialah dos terserap dan \( D_0 \) ialah kepekaan dos.

Keputusan menunjukkan parameter optik seperti penyerapan pinggir, tenaga pengaktifan dan tenaga jalur celah didapati berkurangan dengan pertambahan dos dan kepekatan AniHCl. Apabila dos ditingkatkan daripada 10 kGy kepada 50 kGy didapati penyerapan pinggir berkurangan daripada 1.0 kepada 0.91 eV untuk 9.0% AniHCl dan daripada 0.82 kepada 0.44 eV untuk 28.6% AniHCl, tenaga pengaktifan berkurangan daripada 2.25 kepada 1.5 eV untuk 9.0% AniHCl dan daripada 0.8 kepada 0.69 eV untuk 28.6% AniHCl, serta tenaga jalur celah berkurangan daripada 1.36 kepada 1.18 eV untuk 9.0% AniHCl dan daripada 1.12 kepada 1.00 eV untuk 28.6% AniHCl. Kekonduksina elektrik telah ditentukan secara analisis impedans dan didapati kekonduksian bertambah dengan pertambahan dos dan kepekatan AniHCl. Kekonduksian dipengaruhi oleh komponen arus terus (dc) kerana kewujudan polaron dalam struktur PANI dan ia adalah pembawa cas bagi PANI. Kekonduksian arus terus dc bertambah daripada \( 5.75 \times 10^{-6} \) S/m kepada \( 1.32 \times 10^{-3} \) S/m untuk 9.0% dan daripada \( 7.76 \times 10^{-5} \) S/m kepada \( 1.17 \times 10^{-1} \) S/m untuk 28.6% AniHCl dimana dos ditingkatkan daripada 10 kGy kepada 50 kGy. Kekonduksian dc dipengaruhi oleh hubungan eksponen dalam bentuk \( \sigma_{dc} = \sigma_0 \exp(D / D_0) \), dimana \( \sigma_0 \) dan \( D_0 \) didapati berubah dengan kepekatan AniHCl.
Zarah argentum nano telah disentisis daripada film adunan PVA/argentum nitrat (AgNO₃) pada kepekatan dopan AgNO₃ ialah 0.01 wt % dan disinarkan dengan sinar gama pada dos berbeza (0, 10, 20, 30, 40, and 50 kGy) dalam keadaan ambient. Semasa penyinaran gama electron yang dihasilkan bersaling tindak dengan ion argentum Ag⁺ lalu menghasilkan zarah argentum nano Ag⁰. Pembentukan zarah argentum nano Ag⁰ telah diperhatikan sebagai perubahan warna daripada tak berwarna kepada kuning emas kerana kehadiran zarah argentum nano Ag⁰ dan telah disahkan secara analisis XRD. Seterusnya kehadiran zarah argentum nano Ag⁰ telah ditentusahkan secara kaedah penyerapan UV-tampak yang menghasilkan puncak penyerapan pada 425 nm kerana kehadiran plasmon pada jalur konduksi zarah nano argentum Ag⁰. Penyerapan bertambah dengan pertambahan dos dan berpadanan dengan hubungan eksponen dalam bentuk \( y = y_o \exp(D / D_o) \).

Komposit zarah nano PVA/PANI/Ag⁰ telah disentisis dengan kepekatan AniHCl 28.6 wt%. Kepekatan dopan AgNO₃ berbeza (0.01, 0.03, 0.05, and 0.07 wt %) dan berbeza dos sinar gama (0, 10, 20, 30, 40, and 50 kGy). Keputusan daripada pengukuran penyerapan optik menunjukkan dua jalur penyerapan pada 415 nm bersumber daripada plasmon dipermukaan zarah argentum nano Ag⁰ dan pada 600 nm disebabkan oleh polaron pada PANI konduksi rendah. Jalur penyerapan beranjak daripada 425 nm kepada 415 nm yang menunjukkan bahawa diameter zarah argentum nano Ag⁰ telah berkurangan kerana kehadiran PANI dalam komposit. Tenaga jalur celah bertambah dengan pertambahan dopan AgNO₃ daripada 1.72 eV untuk 0.01 wt% kepada 2.58 eV untuk 0.07 wt% pada dos 50 kGy. Kekonduksian dc bertambah dengan pertambahan dos dan berkurangan dengan pertambahan kepekatan dopan. Kekonduksian dc untuk dopan 0.01 wt% bertambah daripada \( 9.77 \times 10^{-6} \) S/m
pada 10 kGy kepada $8.51 \times 10^{-4}$ S/m pada 50 kGy. Untuk dopan 0.07 wt% kekonduksian dc bertambah daripada $1.07 \times 10^{-7}$ S/m pada 10 kGy kepada $1.23 \times 10^{-5}$ S/m pada 50 kGy. Kekonduksian dc komposit nano PVA/PANI/Ag$^0$ didapati mempunyai hubungan eksponen dalam bentuk $\sigma_{dc} = \sigma_0 \exp(D/D_0)$. 
ACKNOWLEDGEMENTS

I would like to express my utmost gratitude to Prof. Dr. Elias Saion, Chairman of the Supervisory Committee whose fingerprint illuminates the pages of this thesis and moreover the academic and even social experiences that he taught us during the period of my study, as well as to my cosupervisor Dr. Khairulzaman Hj Mohamad Dahlan from Nuclear Agency Malaysia and Associate Prof. Dr. Noorhana Yahaya and Prof. Dr. Anuar Kassim who are sincere and hones in helping me through my work to compolete this humble thesis.

I Also feel so indebted with thanks and warm appreciation to Prof. Dr. Abdul Halim Shahri whose ideas directed and quidet me to have wider knowledge in the field of material characterizations. Also I have to acknoeledge and to show my specially thanks and considerations to my friends and lab-mates Mr. Khalid Ahmed M. from Jordon (UPM), Mr. Awad Ahmed A. from Saudi Arabia (UPM), Mr. Iskander H. (UPM) and Mr. Hamzah Mohd.H. (MNA).

Also sincere thanks and acknowledge to Mr. Mohammad Zain, Mr. Mohammad Shah, Miss. Usnita Osman, and Miss. Azian Osman for their assistance and encouragement.

Thanks are expressed to the Nuclear Agency of Malaysian for allowing me to irradiate my research samples, especially the department of high dose rate represented by Mr. Shahri bin Hashim and Mr. Taiman Kadni at SDDL department.
I certify that an Examination Committee has met on September 18, 2007 to conduct the final examination of Mohammed Ahmed Ali Omer on his Doctor of Philosophy thesis entitled “Radiation Synthesis and Characterization of Conducting Polyaniline and Polyaniline/Silver Nanoparticles” in accordance with Universiti Pertanian Malaysia (Higher Degree) Act 1980 and Universiti Pertanian Malaysia (Higher Degree) Regulations 1981. The Committee recommends that the student be awarded the relevant degree.

Members of the Examination Committee are as follows:

**Hj. Wan Mahmood Mat yunus, PhD**  
Associate Professor  
Faculty of Science  
Universiti Putra Malaysia  
(Chairman)

**Mohamad Maarof H. A. Moksin, PhD**  
Professor  
Faculty of Science  
Universiti Putra Malaysia  
(Internal Examiner)

**Zainal Abidin Talib, PhD**  
Associate Professor  
Faculty of Science  
Universiti Putra Malaysia  
(Internal Examiner)

**Ibrahim Talib, PhD**  
Professor  
School of Physics  
Universiti Kebangsaan Malaysia  
(External Examiner)

__________________________________  
HASSANA MOHD. GHAZALI, ph D  
Professor / Deputy Dean  
School of Graduate Studies  
Universiti Putra Malaysia

Date: 24 October 2007
This thesis was submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfilment of the requirement for the degree of Doctor of Philosophy. The members of the Supervisory Committee are as follows:

**Elias Saion, PhD**  
Professor  
Faculty of Science  
Universiti Putra Malaysia  
(Chairman)

**Khairulzaman Hj. Moh. Dahlan, PhD**  
Associate Professor  
Nuclear Energy Agency Malaysia-Bangi (NEAM)  
(Member)

**Anuar Kassim, PhD**  
Professor  
Faculty of Science  
Universiti Putra Malaysia  
(Member)

**Noorhana Yahaya, PhD**  
Associate Professor  
Faculty of Science  
Universiti Putra Malaysia  
(Member)

**AINI IDERIS, ph D**  
Professor and Dean  
School of Graduate Studies  
Universiti Putra Malaysia

Date:15 November 2007
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>iii</td>
</tr>
<tr>
<td>iv</td>
</tr>
<tr>
<td>vii</td>
</tr>
<tr>
<td>xii</td>
</tr>
<tr>
<td>xiii</td>
</tr>
<tr>
<td>xiv</td>
</tr>
<tr>
<td>xx</td>
</tr>
<tr>
<td>xxi</td>
</tr>
<tr>
<td>xxii</td>
</tr>
<tr>
<td>xxxi</td>
</tr>
</tbody>
</table>

## CHAPTER

### 1 INTRODUCTION

1.1 Background of the Study  
1.2 Conducting Polyaniline Nanoparticles  
1.3 Polyaniline/Silver Nanoparticles  
1.4 Statement of the Problems  
1.5 Significant of the Study  
1.6 Scope of the Present Study  
1.7 Objectives of the Study.  
1.8 Thesis Outline  

### 2 LITERATURE REVIEW

2.1 Background of conducting polymers.  
2.1.1 History of conducting polymers.  
2.1.2 Conjugated polymer.  
2.1.3 Concepts of solitons, polarons, and bipolarons.  
2.1.4 Types of conducting polymers.  
2.1.5 Conducting polyaniline.  
2.1.6 Polyvinyl Alcohol  
2.2 Synthesis of PANI and its composites  
2.2.1 Chemically polymerization.  
2.2.2 Electrochemically polymerization of PANI.  
2.2.3 Polymerization of PANI by UV photo-doping.  
2.2.4 Polymerization of PANI by γ-irradiation doping.  
2.3 Characterization of PANI and PANI composites  
2.3.1 Chemical structure and oxidation state of PANI.  
2.3.2 Optical properties of PANI.  
2.3.3 Electrical properties of PANI.  
2.3.4 Morphological structure of PANI anocomposites  
2.4 Applications of conducting polymers  
2.4.1 Sheilding of electromagnetic radiation and electrostatics.  

2.4.2 Electrode materials for ion batteries
2.4.3 Supercapacitors
2.4.4 Electrocatalystics and biosensors
2.4.5 Photoconductivity and solar energy conversion
2.4.6 Biological sensors

2.5 Metal Nanoparticles
2.5.1 Fundamental of metallic nanoparticles.
2.5.2 History of metal nanoparticles.
2.5.3 Classes of metal nanoparticles.

2.6 Synthesis of composite polymer/metal nanoparticles.
2.6.1 Liquid metals atomization by electrospraying
2.6.2 Gas phase spattering condensation method
2.6.3 Solution phase chemical reduction method
2.6.4 Solution phase electrochemical method
2.6.5 Ultrasound irradiation method
2.6.6 Photo-reduction by UV-irradiation method
2.6.7 Ionizing radiation reduction method

2.7 Characterization of metal nanoparticles
2.7.1 Electrical conduction
2.7.2 Electron spin resonance
2.7.3 Linear optical properties
2.7.4 X-ray diffraction
2.7.5 SEM and TEM nanoparticles morphology

2.8 Applications of metal nanoparticles and their composites
2.8.1 Surface enhanced Raman scattering (SERS)
2.8.2 Surface enhanced fluorescence
2.8.3 Surface plasmon resonant absorption
2.8.4 Electrocatalysts
2.8.5 Metallic nanoparticles for nanobiotechnology

3 THEORETICAL STUDIES
3.1 Ionizing radiation.
3.1.1 Radiation sources
3.1.2 γ-radiation source

3.2 γ-radiation interaction with matter
3.2.1 Photo-electric absorption
3.2.2 Compton scattering
3.2.3 Pair production
3.2.4 Releagh scattering
3.2.5 γ-ray attenuation coefficients

3.3 γ-radiation interaction with molecules
3.3.1 Polymerization
3.3.2 Crosslinking
3.3.3 Radiation grafting

3.4 Interaction of electron with specimen
3.4.1 Elastic scattering
3.4.2 Inelastic scattering
3.4.3 Scanning electron microscopy (SEM) principle

3.5 X-ray diffraction spectroscopy XRD
3.6 Interaction of light with molecules
  3.6.1 Molecular bonding transition
  3.6.2 The spinning transition
  3.6.3 Translational motion
  3.6.4 Rotational transition
  3.6.5 Molecular vibration
  3.6.6 Electronic transition in molecules
  3.6.7 Transition involving nucleus

3.7 Absorption of light and UV-visible spectrophotometry
  3.7.1 Optical absorption
  3.7.2 Mechanism of absorption process
  3.7.3 Absorption edge
  3.7.4 Optical band gap
  3.7.5 UV-visible absorption spectrophotoscopy
  3.7.6 Light interaction with nanoparticles

3.8 Scattering of light and Raman Spectroscopy

3.9 Interaction of electric field with dielectric materials
  3.9.1 Dielectric Constant and Dielectric Loss
  3.9.2 Electrical Conduction in Dielectrics

4 MATERIALS AND METHOD
  4.1 Materials
  4.2 Preparation of composite of PVA/AniHCl film samples
  4.3 Preparation of composite of PVA/AniHCl/AgNO₃ film
  4.4 Irradiation of film samples
  4.5 Scanning Electron Microscopy (SEM) and morphological study
  4.6 X-ray diffraction (XRD) and crystallinity measurement
  4.7 UV-visible spectroscopy and absorbance measurement
  4.8 Raman spectroscopy and chemical structure identification
  4.9 Impedance analyzer and conductivity measurement

5 RESULTS AND DISCUSSION
  5.1 Oxidation and reduction process by radiation.
  5.1.1 The formation of PANI nanoparticles.
  5.1.2 The formation of Ag⁰ nanoparticles.
  5.1.3 The formation of nanocomposites of PANI/Ag⁰ nanoparticles.
  5.2 Scanning electron microscope (SEM) morphology.
  5.2.1 The SEM morphology of PANI nanoparticles.
  5.2.2 The SEM morphology of solid phase HCl.
  5.2.3 The SEM morphology of Ag⁰ nanoparticles.
  5.2.4 The SEM morphology of PANI/Ag⁰ nanoparticles.
  5.3 X-ray diffraction (XRD) analysis.
  5.3.1 XRD spectra of PVA/PANI nanocomposites.
  5.3.2 XRD spectra of PVA/PANI/Ag⁰ nanocomposites
  5.4 Raman scattering analysis of PANI nanoparticles
5.5 Color change of irradiated PVA/PANI and PVA/AgNO₃ nanocomposites.
5.5.1 Color change of PANI nanoparticles. 176
5.5.2 Color change of Ag⁰ nanoparticles. 178
5.6 Optical characteristics of PANI nanoparticles 180
5.6.1 UV-visible spectra 180
5.6.2 Quantitative analysis formation of PANI nanoparticles. 184
5.6.3 Quantitative analysis of HCl formation 187
5.6.4 Absorption edge of PANI nanoparticles 189
5.6.5 Activation energy ($\Delta E$) of PANI nanoparticles. 194
5.6.6 Band gap of PANI nanoparticles 197
5.7 Optical characteristics of PANI/Ag⁰ nanoparticles 202
5.7.1 UV-visible spectra of Ag⁰ nanoparticles 202
5.7.2 Band gap of Ag⁰ nanoparticles 204
5.7.3 UV-visible spectra of PANI/Ag⁰ nanoparticles. 206
5.7.4 Absorption edge of PANI/Ag⁰ nanoparticles. 211
5.7.5 Band gap of PANI/Ag⁰ nanoparticles. 215
5.8 Electrical conductivity of composites of PVA/PANI nanoparticles. 219
5.8.1 Conductivity of PVA irradiated at various doses. 220
5.8.1.1 The dc conductivity of irradiated PVA. 222
5.8.1.2 The ac conductivity of irradiated PVA. 226
5.8.2 Conductivity of PVA/AniHCl composites at various concentrations. 228
5.8.3 Conductivity of PANI nanoparticles at various doses. 231
5.8.4 The dc conductivity of PANI nanoparticles determine from direct extrapolation method. 234
5.8.5 The dc conductivity of PANI nanoparticles determine from Cole-Cole plot. 236
5.9 Electrical conductivity of composite of PVA/PANI/Ag⁰ nanoparticles. 249
5.9.1 Conductivity of PANI/Ag⁰ nanoparticles at various Ag⁺ concentration and doses. 249
5.9.2 The ac conductivity of PANI/Ag⁰ nanoparticles determined from direct extrapolation. 252
5.9.3 The ac conductivity of PANI/Ag⁰ nanoparticles determined from Cole-Cole plots. 255
5.9.4 Analysis of the ac conductivity of PANI/Ag⁰ nanoparticles 264

6 CONCLUSION AND FUTURE WORKS 270
6.1 Conclusion 270
6.2 Future Works 273

REFERENCES 275
BIODATA OF THE AUTHOR 311
## LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.1</td>
<td>The properties of different ionizing radiation. (Smith F. A. 2000)</td>
<td>79</td>
</tr>
<tr>
<td>3.2</td>
<td>The common sources of ionizing radiation. (Smith F. A. 2000)</td>
<td>81</td>
</tr>
<tr>
<td>3.3</td>
<td>The different types of γ-radiation interactions with mater. (Siegahn K. 1965)</td>
<td>93</td>
</tr>
<tr>
<td>5.1</td>
<td>The relation between monomer concentration and dose sensitivity $D_0$.</td>
<td>247</td>
</tr>
<tr>
<td>5.2</td>
<td>The dependant of dose sensitivity $D_0$ of the PVA/PANI/AgNO$_3$ composite on variation of AgNO$_3$ concentration</td>
<td>262</td>
</tr>
</tbody>
</table>
# LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>Selection of common conjugated polymers</td>
<td>12</td>
</tr>
<tr>
<td>2.2</td>
<td>Schematic energy levels diagrams of emeraldine salt, after modification. (Huang and McDiarmid, 1993)</td>
<td>14</td>
</tr>
<tr>
<td>2.3</td>
<td>Molecular structures of different types of conducting polymers</td>
<td>16</td>
</tr>
<tr>
<td>2.4</td>
<td>Theoretical representation of the different polyaniline forms (Bernard et al., 2006)</td>
<td>20</td>
</tr>
<tr>
<td>2.5</td>
<td>Chemical structure of poly(vinyl alcohol) (PVA) monomer.</td>
<td>21</td>
</tr>
<tr>
<td>2.6</td>
<td>Two mechanisms of electropolymerization, (a) deposition of monomers on the electrode surface and (b) the growth of polymer chains on the surface. (Donald et al., 1998)</td>
<td>25</td>
</tr>
<tr>
<td>2.7</td>
<td>Radiation induced conducting PANI/PVC and PVDC blends. (After Hatice et al., 2005)</td>
<td>28</td>
</tr>
<tr>
<td>2.8</td>
<td>The different oxidation states of polyaniline. (After MacDiarmid, 2002)</td>
<td>30</td>
</tr>
<tr>
<td>2.9</td>
<td>Tracing of imine group C=N at Raman shift 1639 cm⁻¹ in amine and carbonyl group of ketone (Chloroform) media. (After Moonkwon et al., 2003)</td>
<td>31</td>
</tr>
<tr>
<td>2.10</td>
<td>Raman spectra of PANI film polymerized by electrochemical cycling implies the formation of polaron traced by imines group C=N. (After Bernard et al., 2006)</td>
<td>31</td>
</tr>
<tr>
<td>2.11</td>
<td>Colour of PANI, (a) doped PANI, (b) de-doped PANI, (c) the de-doped PANI turns green after exposed to L-phenylalanine and (d) the de-doped PANI stay blue after exposed to D-phenylalanine. (After Jiaxing et al., 2003)</td>
<td>33</td>
</tr>
<tr>
<td>2.12</td>
<td>UV–visible spectra of PANI peaking at 617 nm, prepared by chemical method. (After Liangchao et al., 2006)</td>
<td>34</td>
</tr>
<tr>
<td>2.13</td>
<td>UV–visible spectra of (a) conductive PVA/PANI films (b) before polymerization (chemical method). (After Kun et al., 2002)</td>
<td>34</td>
</tr>
</tbody>
</table>
2.14 Optical absorption spectra of PANI films synthesized electrochemically under cyclic voltammetric conditions in aqueous solutions of (a) H$_2$SO$_4$ and in the presence of organic salts, (b) K-acetate, (c) Na-acetate and (d) Mg-acetate. (After Borole et al., 2003)

37

2.15 Optical absorption spectra of PANI/PVA dispersions at pH 4, 7 and 9. (After Dispenza et al., 2006)

37

2.16 The UV-visible spectrum of PANI base (nonconductive) and PANI salt (conductive) prepared by chemical method. (After Daming et al., 2005)

38

2.17 The variation of electrical conductivity of PANI by increasing the dopant concentration.

39

2.18 The specific conductivity of PANI blends films as a function of HCl concentration. (After Tuspon et al., 2006)

41

2.19 Effect of different dopant concentration of Te on the conductivity of PANI at 350 K. (After Samrana et al., 2007)

41

2.20 Conductivities of PANI/PVC blends with respect to blend composition at 200, 500, 800 kGy doses. (After Hatice and Guven, 2005)

43

2.21 The conductivity of pure PANI base as a function of radiation doses. (After Hatice and Guven, 2005)

43

2.22 Effect of dose rate of the gamma and electron on PPCI/PANI blends. (After Sevil et al., 2003)

44

2.23 Shows the PANI micrograph image (SEM) prepared by different oxidation method (After Jia et al., 2007).

46

2.24 The micrograph (SEM) of PANI prepared by sonochemical method shows nanofibres of PANI structure (After Wang and Jing (2007)

47

2.25 SEM morphology of PMMA/PANI composite with the PANI nanoparticles shown (After Wang and Jing (2007)

47

2.26 The chemical structure of the silver nitrate compound

56

2.27 UV-Vis spectra of (a) the Ag nanoparticles colloid and (b) the Ag/PANI composite. (After Jing et al., 2006)

65

2.28 UV–Vis absorption spectra of Ag/PANI nanocomposites prepared by photolysis at 254 nm illumination (a–c; 0.5,
1.5 and 2M silver nitrate solution used for reaction. (After Khanna et al., 2005)

2.29 The UV–visible spectra of a few samples of solution irradiated with 6 MeV electrons at different fluences in the range $2 \times 10^{13} - 3 \times 10^{15}$ cm$^{-2}$. (After Bogle et al., 2006)

2.30 XRD patterns of the PVA and PVA/Ag nanocomposite films. (After Yu et al., 2006)

2.31 XRD patterns of the Ag/thiophere nanocomposites. (After Lee et al., 2007)

2.32 XRD patterns of the Ag/PANI nanocomposites. (After Jing et al., 2006)

2.33 SEM image of silver nanoparticles synthesized by irradiating a mixture of AgNO$_3$ and PVA solutions with 6 MeV electrons at a fluence of $2 \times 10^{13}$ e cm$^{-2}$. (After Bogle et al., 2006)

2.34 Morphology structures of (a) SEM and (b) TEM images of the Ag/PANI nanocomposites. (After Jing et al., 2006)

2.35 SERS, emission and Raman inelastic scattering spectra for various dye molecules adsorbed on Ag nanoparticles (a) rhodamine (3 molecules/particle), (b) rhodamine (30 molecules/particles), (c) crystal violet (30 molecules/particle), and (d) malachite green (300 molecules/particle). (After Maruyama and Futamata, 2005)

2.36 The lanthanide-coated silver colloids showing lanthanide luminescence increased over 10-fold and the lifetime reduced by 10-fold. (After Aslan et al., 2005)

2.37 Electroluminescence enhancement of surface plasmon-enhanced Si light-emitting diode, before and after the deposition of of Ag islands and ZnS over-coating. (After Catchpole and Pillai, 2006)

3.1 Decay scheme of $^{60}$Co radioisotope which ends by Nicle-60 stable. Another frequently used $\gamma$-ray source is cesium-137, a fission product from nuclear reactors. The energy of the emitted photon is 662 keV and the half-life is 30.17 years. Nuclear reactors themselves are potential sources of $\gamma$-rays.

3.2 Schematic diagram of photoelectric absorption of $\gamma$-radiation resulting in ejection of orbital electron from L shell leading to ionization process of an atom.
3.3 Schematic diagram of Compton scattering for γ-radiation resulting in ionization and scattering of the incident photon with less energy.

3.4 Schematic diagram of Pair Production process for γ-radiation being interfered in the nucleus field and orbital electron to produce triplet particles.

3.5 The expected irradiation results of the organic molecules, where R, and S, are free radicals and M and N are molecular products.


3.7 Schemes for electron beam interaction with sample and the subsequent scattering types.

3.8 Steps of electron beam production, interaction with sample and the detection of the scattered secondary electron.

3.9 Scheme for light photon interaction with matter, giving its energy to electron which set in excitation state.

3.10 The possible electronic transition for the electrons at π,σ and n bonds.

3.11 Schematically illustrates the sequence of direct electronic transitions from the initial state i to the final state f, or by an indirect process in which the intermediate state k is populated by scattering and relaxation of “hot” electrons, which are photo-excited in the substrate.

3.12 Schemes for UV-visible spectroscopy principle and steps of taking the spectra.

3.13 The different possibilities of visual light scattering: Rayleigh scattering (no Raman effect), Stokes scattering (molecule absorbs energy) and anti-Stokes scattering (molecule loses energy).

3.14 The principle of Raman spectroscopy sample process (Fadini, 1989).


3.16 The resultant Cole-Cole plot of really impedance Z’ versus imaginary impedance Z’.
4.1 \( \gamma \)-irradiation system model (J. L. Sherperd) at the Malaysian Nuclear Agency, Bangi

4.2 The change of colour of the irradiated (a) PVA/AniHCl composites and (b) PVA/AniHCl/AgNO\(_3\) composites after irradiating with different doses at 30 kGy and 50 kGy.

4.3 The sample set up and the XRD system model 7602EA, Philips. Faculty of Science, Department of Physics-UPM

4.4 The UV-visible spectrophotometer model Camspec M530. Faculty of Science, Department of Physics-UPM.

4.5 Raman system and its accessories for sample set up and characterization, Faculty of Science, department of Physics - UPM

4.6 The LCR-meter model HP 4284A with the sample set up for conductivity measurement. Faculty of Science, department of Physics - UPM

5.1 Conducting PANI in polyemeraldine (EB) structure represents the polaron species induced by radiation doping showing N\(^+\) ions within the imines doped by Cl\(^-\) ions.

5.2 PANI in polypernigraniline (PB) structure represents the polaron species induced by radiation doing showing N\(^+\) ions within the imines doped by Cl\(^-\) ions.

5.3 SEM micrographs of PANI nanoparticles polymerized by 50 kGy Co-60 \( \gamma \)-rays for 28.6 wt% monomer, taken (a) after preparation (b) 5month later.

5.4 SEM micrographs of 28.6 wt% AniHCl of PVA/PANI nanocomposites polymerized by radiation at 50 kGy illustrating (a) the residual of HCl appear on the foreground and (b) the rectangle crystalline structure of HCl.

5.5 SEM micrograph of Ag\(^0\) nanoparticles induced by \( \gamma \)-radiation at 50 kGy dispersed in PVA matrix

5.6 SEM, micrograph of PANI/Ag\(^0\) nanoparticles dispersed in PVA matrix film irradiated at 50 kGy.

5.7 XRD patterns of pure PVA irradiated at different doses

5.8 XRD patterns of PVA/PANI nanocomposites at different doses.