UNIVERSITI PUTRA MALAYSIA

EFFECTS OF IONIZING RADIATION ON THE ELECTRICAL AND OPTICAL PROPERTIES OF POLYVINYL ALCOHOL/ ANILINE HYDROCHLORIDE BLEND FILMS

AZIAN BINTI OTHMAN

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By

AZIAN BINTI OTHMAN

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

January 2007

DEDICATION

To my parents, Othman Saki and Azizah Hamzah, my family
last but not least to all of my friends.
Thank you very much.

Abstract of thesis presented to Senate of Universiti Putra Malaysia in fulfilment of the requirement for the degree of Master of Science

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Chairman : **Professor Elias Saion, PhD**

Faculty : **Faculty of Science**

An attempt was made to produce polyvinyl alcohol (PVA)/polyaniline (PANI) conducting polymer composites from PVA/Aniline hydrochloride (AniHCl) blends via radiation induction. Films of PVA/AniHCl blends at various AniHCl compositions were initially prepared by solvent casting method. The films were then irradiated with Co-60 gamma rays to doses up to 20 kGy. The optical properties were measured by using a UV-Visible spectrophotometer in the wavelength range of 200-800 nm. The formation of PANI was observed when the films changed colour from colourless to light green at 20 kGy. However the amount of PANI formed was limited as the green colour did not reveal significantly in the absorption spectra, but instead the main absorption band was peaking at 315 nm corresponding to the formation hydrochloric acid by radiation. The absorbance data at 315 nm were fitted to an exponential law and

found to have a relationship between dose sentivity $D_{0''}$ and AniHCl composition C as $D_{0''}$ = 0.3133C + 3.18. The radiation caused bond scission of covalent bonds of AniHCl and hydrolysis of water to produce Cl^-, OH^-, and H^+ ions in the blends and as well as PANI that lead to the changes in optical properties and conductivity of irradiated PVA/AniHCl blends.

The absorption spectra of irradiated PVA/AniHCl films were analyzed further for absorption edge, activation energy, and band gap energy. From the plot of absorption coefficient α versus photon energy $h\nu$, the absorption edge for 9% AniHCl decreases from 4.76 to 4.66 eV when the dose increases from 0 kGy to 20 kGy and that for 29% AniHCl the value decreases from 4.52 to 4.40 eV. From the slope of ln α versus $h\nu$, we found the optical activation energy ΔE decreases from 1.08 to 0.87 eV for 9% AniHCl and from 0.33 eV to 0.25 eV for 23% AniHCl. The optical band gap for the direct allowed transition was determined from the intercepts of the extrapolated linear part of the plot of $(\alpha h\nu)^2$ against $h\nu$,. The band gap energy decreases from 2.60 to 2.38 eV for 9% AniHCl and that for 29% AniHCl the value decreases from 2.46 to 2.14 eV .

The conductivity of irradiated PVA/AniHCl films was measured at room temperature and in the frequency range from 20 Hz to 1 MHz by means of an impedance analyzer. The conductivity at 20 Hz for 9% AniHCl increases from 9.41 x 10^{-7} Sm^{-1} at 0 kGy to 5.01x10^{-6} Sm^{-1} at 20 kGy. The conductivity for 23%

AniHCl increases from 1.85×10^{-5} Sm^{-1} at 0 kGy to 5.78×10^{-5} Sm^{-1} at 20 kGy. The frequency exponent values of s_1 and s_2 were determined from the gradients of the linear plots of log σ(ω) versus log ω. The value of s decreases with the increase of dose and AniHCl composition. The s_1 value varies from 0.04 to 0.20 and that of s_2 its value varies from 0.30 to 0.90. The dc conductivity extracted from the Cole-Cole plots of the complex impedance Z″ vs. Z′, shows the dc conductivity increases with dose by an exponential law. The slope of the linear regressions from ln $\sigma_{dc}(\omega)$ versus D plot was used to determine the value of dose sensitivity $D_{0'}$, for conductivity. The $D_{0'}$ and σ_0 values obtained are AniHCl dependent given by $D_{0'}$=0.3226C +10.904 and σ_0 =1.0×10^{-6} C – 4.0×10^{-6} where C is AniHCl composition.

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

KESAN SINARAN MENGION KEATAS SIFAT ELEKTRIK DAN OPTIKAL BAGI ADUNAN FILEM POLYVINYL ALCOHOL/ ANILINE HYDROCHLORIDE

Oleh

AZIAN BINTI OTHMAN

Januari 2007

Pengerusi : Profesor Elias Saion, PhD

Fakulti : Sains

Satu percubaan telah dibuat untuk menghasilkan komposit alkohol polivinal (PVA)/polianilin (PANI) polimer konduktor daripada adunan polivinal alkohol /aniline hidroklorida (AniHCl) secara aruhan sinaran mengion. Filem campuran PVA/AniHCl pada komposisi AniHCl berbeza telah disediakan dengan menggunakan kaedah acuan pelarut. Filem kemudian disinarkan dengan sinar gama Co-60 dengan dos berbagai sehingga 20 kGy. Ciri-ciri optik adunan ini diukur dengan menggunakan meterspektrum UV-sinar tampak dalam julat panjang gelombang 200-800 nm. Pembentukan PANI telah diperhatikan apabila filem berubah warna daripada tidak berwarna kepada warna hijau pada 20 kGy. Bagaimanapun kandungan terbentuknya PANI adalah terhad ini kerana warna hijau tidak jelas kelihatan dalam spectra penyerapan. Sebaliknya julat penyerapan terbentuk pada 315 nm bersesuaian

dengan spectrum pembentukan asid hidroklorida oleh sinaran. Data penyerapan pada 315 nm dipadankan dengan hukum eksponen dan didapati satu hubungan antara kepekaan dos, $D_{0''}$ dan komposisi AniHCl, C sebagai $D_{0''}$ = 0.3133C + 3.18. Sinaran menyebabkan terputusnya ikatan kovalen AniHCl dan hidrolisis air menghasilkan ion-ion Cl^-, OH^-, and H^+ daripada adunan itu dan juga menghasilkan polaron daripada PANI menyebabkan perubahan kepada ciri-ciri optik dan kekonduksian adunan PVA/AniHCl yang didedahkan dengan sinaran.

Spektra penyerapan filem PVA/AniHCl telah dianalisis berkenaan penyerapan pinggir, tenaga pengaktifan dan jurang jalur tenaga. Daripada lakaran pekali penyerapan α lawan tenaga foton $h\nu$, tenaga penyerapan pinggir untuk 9% AniHCl berkurangan daripada 4.76 kepada 4.66 eV apabila dos ditambahkan daripada 0 kGy kepada 20 kGy dan untuk 29%AniHCl nilainya berkurangan daripada 4.52 kepada 4.40 eV. Daripada kecerunan ln α lawan $h\nu$, didapati tenaga keaktifan optik ΔE berkurangan daripada 1.08 kepada 0.87 eV untuk 9% AniHCl dan daripada 0.33 eV kepada 0.25 eV untuk 23% AniHCl. Jurang jalur tenaga peralihan terus yang dibenarkan telah ditentukan daripada pintasan garis linear graf $(\alpha h\nu)^2$ lawan $h\nu$,. Jurang jalur tenaga berkurangan daripada 2.60 kepada 2.38 eV untuk 9% AniHCl dan daripada 2.46 kepada 2.14 eV untuk 29% AniHCl.

Kekonduksian elektrik filem PVA/AniHCl telah diukur pada suhu bilik pada julat frekuensi daripada 20 Hz kepada 1 MHz. Kekonduksian pada 20 Hz untuk 9% AniHCl bertambah daripada 9.41 x 10^{-7} Sm^{-1} pada 0kGy kepada 5.01x10^{-6} Sm^{-1} pada 20kGy. Kekonduksian pada 23% AniHCl bertambah daripada 1.85×10^{-5} Sm^{-1} pada 0 kGy kepada 5.78×10^{-5} Sm^{-1} pada 20 kGy. Nilai kuasa frekuensi eksponen s_1 dan s_2 telah ditentukan daripada kecerunan graf linear log $\sigma(\omega)$ lawan log ω. Nilai s berkurang dengan bertambahnya dos dan komposisi AniHCl. Nili s_1 berubah daripada 0.04 kepada 0.20 dan nilai s_2 berubah daripada 0.30 kepada 0.90. Kekonduksian arus terus ditentukan daripada lakaran graf Cole-Cole bagi impedans komplek Z″ vs. Z′, dimana ia menunjukkan kekonduksian arus terus bertambah dengan dos menurut hukum exponen. Kecerunan garis linear regerasi ln $\sigma_{dc}(\omega)$ lawan D telah digunakan untuk menentukan dos sensitiviti, $D_{0'}$ bagi kekonduksian. Nilai $D_{0'}$ dan σ_0 didapati bergantung kepada komposisi AniHCl dan masing-masing dinyatakan sebagai $D_{0'}$ =0.3226C +10.904 dan σ_0 = 1.0 x 10^{-6} C – 4.0 x 10^{-6} di mana C adalah komposisi AniHCl.

ACKNOWLEDGEMENTS

بسم الله الر حمن الرحيم

Alhamdulillah, with Allah's blessing, this thesis entitle "*Effects of ionizing radiation on the electrical and optical properties of polyvinyl alcohol/ aniline hydrochloride blend films*" completed. I am grateful to all those who has extended their cooperation and guidance towards the completing of this thesis. I would like to express my sincere gratitude to my supervisor, Professor Dr. Elias Saion for his guidance, patience, advice, contributions, support and understanding throughout the undertaking of this thesis. My grateful appreciations are also due to my supervisor committee members, Dr. Jumiah Hassan, Associate Professor Dr. Zaki Ab. Rahman and Dr. Dahlan Hj. Mohamad for their countless invaluable comments and suggestions to improve this research.

Thanks are also due to Mr Zain from biophysic laboratories, Faculty of Science, UPM foe assistance and providing facilities during laboratories work. Deep thanks and appreciation are extend to all my seniors and friends; Mrs. Susilawati Hambali, Mr. Aris Doyan, Mrs. Azlina baha, Mrs. Nuraihan Harun, Ms. Azimah Yusof, Ms. Noor Haslinda Daud, Mr. Iskandar Shahrim Mustafa, Mr. Asri Tridi, Mr. Ajis Lepit, Mr. Hamzah Harun, Mr. Mohammad Ahmed and Mr. Yusoff Mohammed, for their unfailing friendship and unselfish support. Last but not least, I wish to express my deep thanks to my beloved parents for their moral support, undying love, and prayers.

I certify that an Examination Committee has met on 10 January 2007 to conduct the final examination of Azian Binti Othman on her Master of Science thesis entitled "Effects of Ionizing Radiation on the Electrical and Optical Properties of Polyvinyl alcohol/Aniline Hydrochloride Blend 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:

Zainal Abidin Sulaiman, PhD
Associate Professor
Faculty of Science
Universiti Putra Malaysia
(Chairman)

Abdul Halim Shaari, PhD
Professor
Faculty of Science
Universiti Putra Malaysia
(Internal Examiner)

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

Ibrahim Talib, PhD
Professor
Faculty of Science
Universiti Kebangsaan Malaysia
(External Examiner)

HASANAH MOHD. GHAZALI, PhD
Professor/ Deputy Dean
School of Graduate Studies
Universiti Putra Malaysia

Date: 15 FEBRUARY 2007

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:

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

Mohd Zaki Abdul Rahman, PhD
Associate Professor
Faculty of Science
Universiti Putra Malaysia
(Member)

Jumiah Hassan, PhD
Lecturer
Faculty of Science
Universiti Putra Malaysia
(Member)

Dahlan Haji Mohd, PhD
Secondary Standard Dosimetry Laboratory
Malaysian Institute for Nuclear Technology Research (MINT)
(Member)

____

AINI IDERIS, PhD
Professor/ Dean
School of Graduate Studies
Universiti Putra Malaysia

Date: 8 MARCH 2007

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

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AZIAN BINTI OTHMAN

Date: 12 FEBRUARY 2007

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LIST OF ABBREVIATIONS

PVA	Polyvinyl Alcohol
AniHCl	Aniline Hydrochloride
HCl	Hydrochloric acid
PANI	Polyaniline
UV	Ultraviolet
HOMO	Highly occupied molecular orbital
LUMO	Lowly unoccupied molecular orbital
σ	Conductivity
Z	Impedance
Z′	Real Part of Impedance
Z″	Imaginary Part of Impedance
Z_0	Bulk resistance
Ac	Alternating Current
Dc	Direct Current
ε_0	Permittivity of vacuum
e	Elementary charge
n	Concentration of charge carriers
μ	Mobility
λ	Wavelength
D	Dose

$D_{0'}$	Dose sensitivity of the conductivity
$D_{0''}$	Dose response of the absorbance
A	Absorption
α	Absorption coefficient
s	Power of Frequency
ΔE	Optical activation energy
E_g	Optical band gap energy
C_p	Capacitance
G	Conductance
I	Intensity of transmitted photons
I_0	Intensity of incident photons
T	Transmittance
ω	Frequency
ω_p	Hopping frequency
C	Concentration

CHAPTER 1

INTRODUCTION

Since the first solid poly (ethylene oxide) (PEO) based polymer composite produce by Wright and coworkers (1973) an intensive search for ambient temperature solid ionic conducting polymers (ICPs) that suitable for specific applications is continuing. PEO has low conductivity (10^{-8} Scm^{-1}) at room temperature and is not suitable for use as electrochemical devices. However when it is blended with inorganic salt complexes the composites attract considerable interest as they meet a variety of electrochemical applications: batteries, electrochemical devices, sensors, fuel cell membranes, electronic displays etc. Beside PEO, other polymers have been used as host matrix including poly(vinyl alcohol) (PVA), polyphosphazene (PPA), poly(itaconate) (PIC), poly(vinylidene fluoride) (PVDF), poly(methyl methacrylate)PMMA), and poly(vinyl pyrrolidone) (PVPR), poly(ethylene-alt-tetrafluoroethylene) (ETFE), poly(tetrafluoro ethylene) (PTFE) etc. Some ICPs have unique polymer structure containing functional groups such as negatively charges SO_3^-, CO_2^-, and PO_3^- or positively charges NH_3^+, NR_2^+, and PR_3^+ that are acting as a selective barrier membranes, regulating the transport of positive ions such as H^+ and Li^{2+}or negatively ions such as Cl^- and HSO_4^- to increase the conductivity of polymer composites. The main advantages of ICP composite electrolytes are their favorable mechanical properties including light weight, flexibility, and simple processibility, and their unique ionic transport properties for electrochemical and electrical devices. Works are continuing to produce ICP composites that are suitable for particular applications.

Since the discovery of electrically conducting polymers (CPs) by the 1953 Nobel prize winners, Alan MacDiarmid, Alan J. Heeger, and Hideki Shirakawa in 1976, research on CP composites has been intensive due to their interesting and useful electronic and optical properties (Heeger, 2002). Organic CP is a new generation of polymers that formed as a result of on unpaired π-electron delocalized along the backbone of conjugated polymers. The conjugated polymers have a framework of alternating single and double carbon-carbon bonds or carbon-nitrogen bonds. The electron delocalization in the conjugated polymers provides the highway for charge mobility along the backbone of the chain polymer. The disordered electronic structures are termed as solitons, polarons, and bipolarons that make the conjugated polymers exhibit the electrical properties of semiconductors. The potential advantages of these conjugated CPs or semiconducting polymers lie in their lightweight and in the ease of their synthesis and fabrication.