

**THE EFFECT OF  $\text{Al}_2\text{TiO}_5$  ON ELECTRICAL  
BEHAVIOR OF POLYMER-SALT COMPLEXES**

**FITRIAH BINTI HASSAN**

**FACULTY OF SCIENCE  
UNIVERSITY OF MALAYA  
KUALA LUMPUR**

**2012**

**THE EFFECT OF  $\text{Al}_2\text{TiO}_5$  ON ELECTRICAL  
BEHAVIOR OF POLYMER-SALT COMPLEXES**

**FITRIAH BINTI HASSAN**

**DISSERTATION SUBMITTED IN FULFILLMENT OF  
THE REQUIREMENT FOR THE DEGREE OF  
MASTER OF SCIENCE**

**DEPARTMENT OF PHYSICS  
FACULTY OF SCIENCE  
UNIVERSITY OF MALAYA  
KUALA LUMPUR**

**2012**

## **ACKNOWLEDGEMENT**

First and foremost, in humble way I wish to give all the Praise to Allah S.W.T. for with His mercy has given me blessing to accomplish my study. I wish to express my sincere gratitude to my supervisor, Dr. Siti Rohana Majid for help and guidance in this work and her assistance on experiments.

I am deeply indebted to my co-supervisor, Prof Dr. Abdul Kariem Arof, for his time, critics and hope. I really appreciate it. Thanks so much Prof.

Thanks are also extended to staff from Physics Department, University Malaya especially En. Ismail Che Lah for technical support during the experimental work. Special thanks to all my friends especially Zila, Wani, Hamdi, Teo, Sim, Meor, Leena, Leeana, Den, Fakhrul, Chu, Yap, Thomson and Aziz for their advice and contribution ideas during the research work.

Last but not least, I would like to acknowledge my beloved family especially my husband, Mohamad Adni Wahab for his love and morale support enabled me to complete this study. This is for you.

**FITRIAH BINTI HASSAN**

*In this study, aluminium titanate ( $Al_2TiO_5$ ) has been prepared by the sol gel method. It has been intended for use as a ceramic filler in order to investigate how it affects conductivity and dielectric properties and also the nature of the complexes. Chitosan has been used as the host with ammonium thiocyanate ( $NH_4SCN$ ) as the salt to supply the conducting ions. Films of chitosan acetate (CA) , CA- $NH_4SCN$  complexes, CA- $Al_2TiO_5$  complexes and CA- $NH_4SCN$ - $Al_2TiO_5$  complexes were prepared. The electrical conductivity of all samples has been calculated using the bulk resistance value obtained from the complex impedance plot in the frequency range between 50 Hz to 1 MHz. The film 60 wt.% chitosan – 40 wt.%  $NH_4SCN$  system exhibits the highest room temperature electrical conductivity of  $1.38 \times 10^{-4} S cm^{-1}$ . The highest electrical conductivity of the chitosan- $NH_4SCN$ - $Al_2TiO_5$  is  $2.10 \times 10^{-4} S cm^{-1}$  for the film containing 5 wt.%  $Al_2TiO_5$  at room temperature, 25 °C. The modulus formalism indicates that the samples of chitosan-based electrolytes are ionic conductors. Infrared (IR) spectroscopy shows the occurrence of chitosan-salt complexation. X-ray diffraction (XRD) confirms that the  $Al_2TiO_5$  filler sample with the highest electrical conductivity is the most amorphous. This is supported from the result of scanning electron microscopy (SEM). Hence the effect of  $Al_2TiO_4$  filler is increment of conductivity and changing the degree of amorphousness of the highest conducting chitosan- $NH_4SCN$  system.*

*Dalam kajian ini, aluminum titanate ( $Al_2TiO_5$ ) telah dihasilkan dengan menggunakan kaedah sebatian gel. Tujuan penghasilan  $Al_2TiO_5$  adalah sebagai agen penambah dalam usaha untuk mengkaji kesan terhadap konduktiviti dan sifat dielektrik serta kesan terhadap sifat semula jadi kompleks. Kitosan telah digunakan sebagai perumah dengan ammonium thiocyanate ( $NH_4SCN$ ) sebagai garam pendop untuk membekalkan ion yang berkonduksi. Filem kitosan asetat (CA), kompleks CA- $NH_4SCN$ , kompleks CA- $Al_2TiO_5$  dan kompleks CA- $NH_4SCN$ - $Al_2TiO_5$  telah dihasilkan. Kekonduksian elektrik bagi semua sampel dikira daripada nilai rintangan pukal yang boleh diperolehi daripada plot impedans kompleks dalam julat frekuensi 50 Hz hingga 1 MHz. Filem yang mengandungi 60 wt.% kitosan-40 wt.%  $NH_4SCN$  menunjukkan nilai kekonduksian elektrik tertinggi sebanyak  $1.38 \times 10^{-4} S cm^{-1}$  pada suhu bilik. Nilai kekonduksian elektrik yang tertinggi pada suhu bilik bagi sistem kitosan- $NH_4SCN$ - $Al_2TiO_5$  adalah  $2.10 \times 10^{-4} S cm^{-1}$  bagi filem yang mengandungi 5 wt%  $Al_2TiO_5$ . Tata modulus (modulus formalism) menunjukkan bahawa sampel-sampel elektrolit berasaskan kitosan merupakan konduktor ionik. Spektroskopi inframerah (IR) menunjukkan berlakunya kompleks antara kitosan-garam. Pembelauan sinar-x (XRD) mengesahkan bahawa sampel agen penambah  $Al_2TiO_5$  dengan kekonduksian elektrik tertinggi adalah paling amorfus. Ini disokong oleh keputusan yang diperolehi daripada spektroskopi pengimbasan electron (SEM). Oleh itu, kesan agen penambah ( $Al_2TiO_5$ ) adalah peningkatan kekonduksian dan perubahan darjah keamorfusan bagi sistem kitosan- $NH_4SCN$  yang mempunyai nilai kekonduksian tertinggi.*

	<b>Pages</b>
<i>Acknowledgement</i>	i
<i>Abstract</i>	ii
<i>Abstrak</i>	iii
<i>List of Contents</i>	iv
<i>List of Figures</i>	vii
<i>List of Tables</i>	x
<i>List of Poster Presentation at Conferences</i>	xi
<b>CHAPTER 1 : INTRODUCTION</b>	
1.1 Introduction	1
1.2 Objectives of the Dissertation	3
1.3 Scope of the Dissertation	3
<b>CHAPTER 2 : LITERATURE REVIEW</b>	
2.1 Introduction	5
2.2 Composite Polymer Electrolyte	5
2.3 Aluminium Titanate	7
2.4 Filler	9
2.5 Chitosan as a host polymer	11
2.6 Summary	18
<b>CHAPTER 3 : RESEARCH METHODOLOGY</b>	
3.1 Sample preparation	19
3.1.1 Aluminum Titanate ( $\text{Al}_2\text{TiO}_5$ )	19
3.1.2 Polymer electrolyte	24
3.1.3 Composite Polymer Electrolyte	24
3.2 Characterization	26
3.2.1 Electrochemical Impedance Spectroscopy (EIS)	26
3.2.2 XRD Analysis	29

---

3.2.3 Fourier Transform Infra Red (FTIR)	30
3.2.4 Scanning Electron Microscopy (SEM)	32
3.3 Summary	34
 <b>CHAPTER 4 : PREPARATION AND CHARACTERIZATION OF Al<sub>2</sub>TiO<sub>5</sub> FILLER</b>	
4.1 Introduction	36
4.2 XRD of aluminum titanate	36
4.3 Summary	41
 <b>CHAPTER 5 : ELECTRICAL STUDIES OF CHITOSAN-NH<sub>4</sub>SCN COMPLEXES AND CHITOSAN-NH<sub>4</sub>SCN COMPOSITES</b>	
5.1 Introduction	42
5.2 Conductivity studies of chitosan-NH <sub>4</sub> SCN samples	42
5.3 Conductivity-Temperature dependence in the chitosan-NH <sub>4</sub> SCN system	44
5.4 Conductivity studies of chitosan-NH <sub>4</sub> SCN-Al <sub>2</sub> TiO <sub>5</sub> samples	45
5.5 Conductivity-Temperature relationship of chitosan acetate salt complexes containing aluminum titanate	49
5.6 Dielectric behavior of chitosan acetate-NH <sub>4</sub> SCN-Al <sub>2</sub> TiO <sub>5</sub> complexes	49
5.7 Summary	55
 <b>CHAPTER 6 : INFRARED STUDIES OF CHITOSAN-NH<sub>4</sub>SCN COMPLEXES AND CHITOSAN-NH<sub>4</sub>SCN-Al<sub>2</sub>TiO<sub>5</sub> COMPOSITE</b>	
6.1 Introduction	56
6.2 The FTIR spectrum of chitosan-Al <sub>2</sub> TiO <sub>5</sub>	57
6.3 The FTIR spectrum of chitosan-NH <sub>4</sub> SCN	59
6.4 The FTIR spectrum of chitosan-NH <sub>4</sub> SCN-Al <sub>2</sub> TiO <sub>5</sub>	62
6.5 Summary	64

<b>CHAPTER 7: X-RAY DIFFRACTION AND SCANNING ELECTRON MICROSCOPY ANALYSIS OF CHITOSAN COMPLEXES AND COMPOSITES</b>	
7.1 Introduction	65
7.2 X-ray diffraction of chitosan-NH <sub>4</sub> SCN	65
7.3 Surface Morphology of chitosan-Al <sub>2</sub> TiO <sub>5</sub> composite film	67
7.4 SEM Micrograph of chitosan-NH <sub>4</sub> SCN film	70
7.5 SEM micrograph of (chitosan-NH <sub>4</sub> SCN) + Al <sub>2</sub> TiO <sub>5</sub>	71
7.6 Summary	74
<b>CHAPTER 8: DISCUSSION</b>	75
<b>CHAPTER 9: CONCLUSION AND SUGGESTION FOR FURTHER WORK</b>	83
<b>REFERENCES</b>	86



	<b>Pages</b>	
<b>Fig. 2.1</b>	Structure of chitosan [ <i>Yahya et al., 2002</i> ]	13
<b>Fig. 3.1</b>	The flow chart of preparing Al <sub>2</sub> O <sub>3</sub> -TiO <sub>2</sub> ceramic system	20
<b>Fig. 3.2</b>	Photo of chemicals used for preparation of Al <sub>2</sub> TiO <sub>5</sub> (a) aluminum nitrate, (b) titanium isopropoxide, (c) citric acid and (d) ethanol.	23
<b>Fig. 3.3</b>	Photo of chemical used in preparing polymer composite electrolyte (a) chitosan highly viscous, (b) acetic acid (1%), (c) ammonium thiocyanate and (d) aluminum titanate (homemade)	26
<b>Fig. 3.4</b>	(a) Dielectric constant and (b) dielectric loss as a function of frequency at various temperatures for sample 50 wt% CA:50 wt.% NH <sub>4</sub> CF <sub>3</sub> SO <sub>3</sub>	27
<b>Fig. 3.5</b>	Frequency dependence of (a) real part and (b) imaginary part of electrical modulus at various temperatures for sample 50 wt.% CA:50 wt.% NH <sub>4</sub> CF <sub>3</sub> SO <sub>3</sub> .	28
<b>Fig. 3.6</b>	Typical impedance spectra of 80Al-20Ti (mole %) at 25 °C.	29
<b>Fig. 3.7</b>	Photo of HIOKI 3531 Z-HiTester.	29
<b>Fig. 3.8</b>	XRD patterns of (a) pure CA (chitosan acetate) film (b) CA + 35 wt% AN (aluminium nitrate), (c) CA + 40 wt% AN (d) 45 wt% AN (e) 50 wt% AN and (f) pure NH <sub>4</sub> NO <sub>3</sub>	30
<b>Fig. 3.9</b>	FTIR spectra for (a) NH <sub>4</sub> SCN (b) pure PVAc (c) 95 mol% PVAc: 5 mol% NH <sub>4</sub> SCN (d) 85 mol% PVAc: 15 mol% NH <sub>4</sub> SCN (e) 75 mol% PVAc: 25 mol% NH <sub>4</sub> SCN [ <i>Selvasekarapandian et al., 2005</i> ]	31
<b>Fig. 3.10</b>	SEM images and digital photos of pure PEO (a), PEO <sub>12</sub> -LiClO <sub>4</sub> (b), and PEO-LiClO <sub>4</sub> /X%SBA-15: (c) X=5; (d) X=10; and (e) X=25 [ <i>Xi et al., 2005</i> ]	34
<b>Fig. 4.1</b>	XRD patterns for sample containing (a) 0.01 mole AN (b) 0.02 mole AN (c) 0.04 mole AN (d) 0.06 mole (e) 0.08 mole AN sintered at 1050 °C (*) indicate TiO <sub>2</sub> peaks.	39
<b>Fig. 4.2</b>	XRD patterns for sample containing 0.08 mole AN with different sintering parameter (a) 750 °C (b) 850 °C (c) 950 °C (d) 1050 °C.	41
<b>Fig. 5.1</b>	Room temperature conductivity of NH <sub>4</sub> SCN concentration (wt.%)	43

<b>Fig. 5.2</b>	Arrhenius plot for highest conducting sample in chitosan-NH <sub>4</sub> SCN.	45
<b>Fig. 5.3</b>	Cole-Cole plot for the sample of chitosan-NH <sub>4</sub> SCN-Al <sub>2</sub> TiO <sub>5</sub> system with different wt.% of (a) 1 wt.% (b) 2 wt.% (c) 4 wt.% (d) 5 wt.% and (e) 7 wt.% Al <sub>2</sub> TiO <sub>5</sub> .	46
<b>Fig. 5.4</b>	Conductivity versus amount of Al <sub>2</sub> TiO <sub>5</sub> dopant in the chitosan-NH <sub>4</sub> SCN film.	47
<b>Fig. 5.5</b>	Arrhenius plot for different weights of Al <sub>2</sub> TiO <sub>5</sub> dopant in chitosan acetate-NH <sub>4</sub> SCN film (room temperature to 80 °C)	49
<b>Fig. 5.6</b>	Dielectric constant versus log frequency for chitosan-NH <sub>4</sub> SCN complexes with different concentrations Al <sub>2</sub> TiO <sub>5</sub> .	50
<b>Fig. 5.7</b>	Dielectric constant versus log frequency for the highest conducting chitosan-NH <sub>4</sub> SCN-Al <sub>2</sub> TiO <sub>5</sub> film at various temperature.	51
<b>Fig. 5.8</b>	Dielectric loss versus log frequency for chitosan-NH <sub>4</sub> SCN complexes with different concentrations of Al <sub>2</sub> TiO <sub>5</sub> .	52
<b>Fig. 5.9</b>	Dielectric loss versus log frequency for the highest conducting chitosan-NH <sub>4</sub> SCN-Al <sub>2</sub> TiO <sub>5</sub> film at various temperature.	52
<b>Fig. 5.10</b>	Real part of electric modulus versus log frequency for chitosan-NH <sub>4</sub> SCN complexes with different concentrations of Al <sub>2</sub> TiO <sub>5</sub> .	53
<b>Fig. 5.11</b>	Real part of electric modulus versus log frequency for the highest conducting chitosan-NH <sub>4</sub> SCN-Al <sub>2</sub> TiO <sub>5</sub> film at various temperature.	54
<b>Fig. 5.12</b>	Imaginary part of electric modulus versus log frequency for chitosan-NH <sub>4</sub> SCN complexes with different concentrations of Al <sub>2</sub> TiO <sub>5</sub> .	54
<b>Fig. 5.13</b>	Imaginary part of electric modulus versus log frequency for the highest conducting chitosan-NH <sub>4</sub> SCN-Al <sub>2</sub> TiO <sub>5</sub> film at different temperatures.	55
<b>Fig. 6.1</b>	The FTIR spectra of (I) chitosan and (II) chitosan added 5 wt.% Al <sub>2</sub> TiO <sub>5</sub> in the region from (a) 800 to 1700 and (b) 2700 to 3600 cm <sup>-1</sup> .	58
<b>Fig. 6.2</b>	The FTIR spectra of (I) chitosan and (II) chitosan-NH <sub>4</sub> SCN in the region from 1500 to 1700 cm <sup>-1</sup> .	60
<b>Fig. 6.3</b>	The FTIR spectra of (I) chitosan and (II) chitosan-NH <sub>4</sub> SCN in the region from 500 to 4000 cm <sup>-1</sup> .	60

---

<b>Fig. 6.4</b>	The FTIR spectra of (I) chitosan and (II) chitosan-NH <sub>4</sub> SCN in the region from 1500 to 4000 cm <sup>-1</sup> .	61
<b>Fig. 6.5</b>	The FTIR spectra of (I) chitosan-NH <sub>4</sub> SCN and (II) chitosan-NH <sub>4</sub> SCN-Al <sub>2</sub> TiO <sub>5</sub> in the region from 500 to 4000 cm <sup>-1</sup> .	63
<b>Fig. 6.6</b>	The FTIR spectra of (I) chitosan-NH <sub>4</sub> SCN and (II) chitosan-NH <sub>4</sub> SCN-Al <sub>2</sub> TiO <sub>5</sub> in the region from 1300 to 1800 cm <sup>-1</sup> .	63
<b>Fig. 7.1</b>	XRD patterns of chitosan with (a) 0 wt.% (b) 10 wt.% (c) 20 wt.% (d) 30 wt.% (e) 40 wt.% (f) 50 wt.% NH <sub>4</sub> SCN concentration.	66
<b>Fig. 7.2</b>	SEM surface morphology of chitosan acetate film.	67
<b>Fig. 7.3</b>	SEM surface morphology of chitosan with (a) 5 wt.% (b) 10 wt.% (c) 15 wt.% (d) 20 wt.% (e) 25 wt.% (f) 30 wt.% (g) 35 wt.% (h) 40 wt.% (i) 45 wt.% and (j) 50 wt.% Al <sub>2</sub> TiO <sub>5</sub> film.	69
<b>Fig. 7.4</b>	SEM morphology of chitosan-NH <sub>4</sub> SCN film.	71
<b>Fig. 7.5</b>	SEM surface morphology of chitosan-NH <sub>4</sub> SCN with (a) 1 wt.% (b) 2 wt.% (c) 4 wt.% (d) 5 wt.% and (e) 7 wt.% Al <sub>2</sub> TiO <sub>5</sub> .	72
<b>Fig. 7.6</b>	Conductivity and coherent length against various Al <sub>2</sub> TiO <sub>5</sub> (in wt.%)	73

	<b>Pages</b>
<b>Table 2.1</b>	Physical properties of polymer hosts. 12
<b>Table 2.2</b>	Sources of chitin and chitosan [ <i>Marthur et al., 1990</i> ] 17
<b>Table 2.3</b>	General properties of chitin and chitosan [ <i>Pillai et al., 2009</i> ] 17
<b>Table 3.1</b>	Composition of the samples prepared with different moles of aluminum nitrate and titanium isopropoxide. 20
<b>Table 3.2</b>	Composition of the samples prepared with different moles of aluminum nitrate and titanium isopropoxide with citric acid. 22
<b>Table 3.3</b>	Sintering parameters of the compounds. 22
<b>Table 3.4</b>	Composition of the samples with different weight percent of $\text{NH}_4\text{SCN}$ . 24
<b>Table 3.5</b>	Composition of the samples prepared with different weight percent of $\text{Al}_2\text{TiO}_5$ . 25
<b>Table 4.1</b>	The formation of $\text{Al}_2\text{TiO}_5$ at different sintering temperatures. 37
<b>Table 4.2</b>	The crystallite size of $\text{Al}_2\text{TiO}_5$ . 40
<b>Table 5.1</b>	Conductivity of the polymer electrolyte with respect to the $\text{NH}_4\text{SCN}$ concentration. 43
<b>Table 5.2</b>	Conductivity of the polymer electrolyte with respect to the $\text{Al}_2\text{TiO}_5$ concentration. 48
<b>Table 6.1</b>	Vibrational modes and wavenumbers exhibited by chitosan. 59
<b>Table 6.2</b>	The vibrational modes and wavenumbers exhibited by chitosan and chitosan- $\text{NH}_4\text{SCN}$ . 62
<b>Table 8.1</b>	Examples of conductivity of composite polymer electrolytes. 80

**List of Poster Presentation Presented at Conference:**

1. **F. Hassan**, S. R. Majid and A. K. Arof, “Synthesis and characterization of  $\text{Al}_2\text{TiO}_5$  by sol-gel method”, presented at the National Workshop on Functional Materials (NWFM), 20-21 June 2009, university of Malaya, Kuala Lumpur.