PREPARATION AND CHARACTERIZATION OF CARBOXYMETHYL-CHITIN/SILK FIBROIN BLEND FILMS



Ms. Krittiya Meanjai

A Thesis Submitted in Partial Fulfilment of the Requirements
for the Degree of Master of Science

The Petroleum and Petrochemical College, Chulalongkorn University
in Academic Partnership with

The University of Michigan, The University of Oklahoma
and Case Western Reserve University

2002

ISBN 974-03-1602-6

Thesis Title : Preparation and Characterization of Carboxymethyl-

Chitin/Silk Fibroin Blend Films

By : Krittiya Meanjai

Program : Polymer Science

Thesis Advisors : Dr. Ratana Rujiravanit

Prof. Seiichi Tokura

Accepted by the Petroleum and Petrochemical College, Chulalongkorn University, in partial fulfilment of the requirements for the Degree of Master of Science.

K. Bunyahit. College Director

(Assoc. Prof. Kunchana Bunyakiat)

Thesis Committee:

(Dr. Ratana Rujiravanit)

Ratura Rujuavanit

(Prof. Seiichi Tokura)

(Assoc. Prof. Anuvat Sirivat)

(Asst. Prof. Suwabun Chirachanchai)

ABSTRACT

4372010063: POLYMER SCIENCE PROGRAM

Krittiya Meanjai: Preparation and Characterization of

Carboxymethyl-Chitin/Silk Fibroin Blend Films.

Thesis Advisors: Prof. Seiichi Tokura and Dr. Ratana

Rujiravanit, 63 pp. ISBN 974-03-1602-6

Keywords: CM-chitin/Silk fibroin/Blend film/Swelling behavior/Mechanical

properties

CM-chitin/silk fibroin blend films were prepared by solvent casting method. The effects of CM-chitin to silk fibroin ratio and cross-linking agent on swelling behavior and mechanical properties of the blend films were studied. The blend films exhibited a change in the degree of swelling when the blend films were immersed in both acidic and alkaline solutions. The degree of swelling of the films increased as the CM-chitin content increased. It appeared that cross-linking occurred in the blend films reduced the swelling capacity of the films. For the study on effect of salt type, the films were immersed in various types of aqueous salt solutions, i.e., NaCl, LiCl, CaCl₂, and FeCl₃. Among these salts, the film immersed in NaCl, LiCl, and CaCl₂ had higher degree of swelling than in FeCl₃. The tensile strength increased with the increasing of the amount of cross-linking agent whereas the elongation at break decreased.

บทคัดย่อ

กฤติยา เหมือนใจ: การเตรียมและวิเคราะห์คุณสมบัติของฟิล์มที่ได้จากการผสมระหว่างซี เอ็ม-ไคตินและซิลไฟโบรอีน (Preparation and Characterization of Carboxymethyl-Chitin/Silk Fibroin Blend Films) อ. ที่ปรึกษา: ศ. คร. เซอิชิ โทคุระ และ คร. รัตนา รุจิรวนิช 63 หน้า ISBN 974-03-1602-6

ฟิล์มของสารพอลิเมอร์ผสมระหว่างซีเอ็ม-ไคตินและซิลไฟโบรอินได้ถูกเตรียมขึ้นใน อัตราส่วนของพอลิเมอร์ต่างๆกันทั้งที่เติมและไม่เติมกลูตารัลดีไฮด์ซึ่งเป็นสารก่อการเชื่อมโยง ใน งานวิจัยนี้ ได้ทำการศึกษาถึงอิทธิพลของอัตราส่วนระหว่างซีเอ็ม-ไคตินและซิล ไฟโบรอินและสาร ก่อการเชื่อมโยงต่อพฤติกรรมการบวมตัวและสมบัติทางกลของฟิล์มสารพอลิเมอร์ผสม พฤติกรรมการบวมด้วของฟิล์มของพอลิเมอร์ผสมดังกล่าว พบว่า ฟิล์มของพอลิเมอร์ผสมเกิดการ บวมตัวในสารละลายบัฟเฟอร์ที่เป็นเบสและกรครวมทั้งในสารละลายเกลือโคยเมื่อปริมาณซีเอ็ม-ใคตินเพิ่มขึ้น การบวมตัวของแผ่นฟิล์มของพอลิเมอร์ผสมจะเพิ่มขึ้น นอกจากนี้ เมื่อปริมาณสาร ก่อการเชื่อมโยงที่เติมในฟิล์มของพอลิเมอร์ผสมเพิ่มขึ้นการบวมตัวของแผ่นฟิล์มจะมีค่าลดลง สำหรับผลของสารละลายเกลือต่อค่าการบวมตัว พบว่า ฟิล์มของพอลิเมอร์ผสมจะมีค่าการบวม ตัวสูงเมื่ออยู่ในสารละลายเกลือโซเคียมคลอไรค์ ลิเธียมคลอไรค์ และแคลเซียมคลอไรค์มากกว่า ในสารละลายเกลือเฟอริกคลอไรค์ ในด้านสมบัติทางกล พบว่า ฟิล์มของสารผสมระหว่างซีเอ็ม-ใคตินและซิลไฟโบรอินเมื่อเติมสารก่อการเชื่อมโยงจะมีสมบัติการทนต่อแรงคึงสูงกว่าฟิล์มที่ไม่ ได้เติมสารก่อการเชื่อมโยง นอกจากนี้เมื่อเปรียบเทียบค่าอัตราการเปลี่ยนแปลงความยาวต่อความ ยาวเดิมที่จุดขาดของฟิล์มระหว่างฟิล์มที่เติมและไม่เติมสารก่อการเชื่อมโยง พบว่าฟิล์มที่เติมสาร ก่อการเชื่อมโยงมีค่าอัตราการเปลี่ยนแปลงความยาวต่อความยาวเติมที่จุคขาคสูงกว่าฟิล์มที่ไม่เติม สารก่อการเชื่อมโยง

ACKNOWLEDGEMENTS

I would like to thank the Petroleum and Petrochemical College, Chulalongkorn University where I have gained the knowledge in polymer science. I also would like to thank Surapon Foods Public Co., Ltd. for the support of the raw materials used in this work.

I would like to express the grateful appreciation to my advisors, Prof. Seiichi Tokura and Dr. Ratana Rujiravanit for their invaluable suggestions and criticism.

Finally, I would like to thank my friends for their friendship, helpfulness, cheerfulness, suggestion and encouragement. I am also greatly indebted to my parents for their support, understanding and patience during this pursuit.

TABLE OF CONTENTS

		PAGE
	Title Page	i
	Abstract (in English)	iii
	Abstract (in Thai)	iv
	Acknowledgements	v
	Table of Contents	vi
	List of Tables	ix
	List of Figures	xii
CHAPTER		
I	INTRODUCTION	1
	1.1 Chitin	2
	1.2 Carboxymethyl-Chitin (CM-chitin)	4
	1.3 Silk Fibroin	5
11	LITERATURE SURVEY	8
	2.1 Carboxymethyl-Chitin (CM-chitin)	8
	2.2 Silk Fibroin	9
Ш	EXPERIMENTAL	12
	3.1 Materials	12
	3.2 Equipment	12
	3.2.1 Restch Sieving Machine	12
	3.2.2 Capillary Viscometer	12
	3.2.3 Elemental Analysis	12
	3.2.4 FTIR Spectrophotometer	12
	3.2.5 Wide-angle X-ray Diffractometer (WAXD)	13
	3.2.6 Differential Scanning Calorimeter (DSC)	13
	3.2.7 Thermogravimetric Analysis (TGA)	13
	3.2.8 Lloyd Tensile Tester	13

CHAPTER			PAGE
	3.3 Metho	odology	14
	3.3.1	Preparation of Chitin	14
	3.3.2	Preparation of CM-Chitin	14
	3.3.3	Degree of Deacetylation of Chitin	15
	3.3.4	Degree of Substitution of CM-Chitin	15
	3.3.5	Viscosity-Average Molecular Weight of	
		CM-Chitin	15
	3.3.6	Preparation Silk Fibroin Solution	16
	3.3.7	Preparation CM-Chitin Solution	17
	3.3.8	Preparation of Blend Films	17
	3.3.9	Equilibrium Water Content (EWC)	17
	3.3.10	Swelling Behavior	18
	3.3.11	Mechanical Properties	18
IV	RESULT	S AND DISCUSSION	19
	4.1 Prepar	ration of Chitin	19
	4.2 Prepar	ration of CM-Chitin	20
	4.3 Charac	cterization of CM-Chitin/Silk Fibroin Blend Films	21
	4.3.1 I	FTIR Analysis of Blend Films	21
	4.3.2	X-ray Diffraction Patterns	22
	4.3.3	Thermal Property	23
	4.3.4	Thermal Stability	24
	4.4 Swelli	ng Study	26
	4.4.1 I	Equilibrium Water Content (EWC)	26
	4.4.2 I	Effect of pH	28
	4.4.3 I	Effect of Salt Type	31
	4.5 Mecha	anical Properties	32
	4.5.1	Tensile Strength	32
	4.5.2 I	Elongation at Break	33
V	CONCLU	USIONS	34

CHAPTER		PAGE
	REFERENCES	35
	APPENDICES	40
	Appendix A Characterization of CM-chitin	40
	Appendix B FTIR spectra of CM-chitin/silk fibroin blend	
	films	43
	Appendix C Effect of time on equilibrium water content	
	of blend films	46
	Appendix D Effect of pH on swelling behavior of the blend	i
	films	50
	Appendix E Effect of salt type on swelling behavior of the	
	blend films	58
	Appendix F Mechanical properties of the blend films	60
	Appendix G Decomposition temperature of pure and blend	
	films	62
	CURRICULUM VITAE	63

LIST OF TABLES

ΓABL		PAGE
	.1 Some applications of chitin-based materials	3
	.2 Current practical uses of CM-chitin	4
	.1 Yield of chitin production from shrimp shell	19
	.2 FTIR characteristic absorption bands of CM-chitin	20
	Al Viscosity-average molecular weight of CM-chitin	40
	A2 Degree of substitution of CM-chitin from elemental analysis	42
	21 Effect of time on equilibrium water content (EWC) of blend	
	films at 15 min	46
	22 Effect of time on equilibrium water content (EWC) of blend	
	films at 30 min	47
	23 Effect of time on equilibrium water content (EWC) of blend	
	films at 60 min	47
	24 Effect of time on equilibrium water content (EWC) of blend	
	films at 90 min	48
	25 Effect of time on equilibrium water content (EWC) of blend	
	films at 120 min	48
	26 Effect of time on equilibrium water content (EWC) of blend	
	films at 180 min	49
	27 Effect of time on equilibrium water content (EWC) of blend	
	films at 24 h	49
	Effect of time on equilibrium water content (EWC) of blend	
	films at 48 h	50
	Degree of swelling of blend films in pH buffer solution	
	pH = 3	50
	Degree of swelling of blend films in pH buffer solution	
	pH = 4	51
	Degree of swelling of blend films in pH buffer solution	
	pH = 5	51

D4	Degree of swelling of blend films in pH buffer solution	
	pH = 6	52
D5	Degree of swelling of blend films in pH buffer solution	
	pH = 7	52
D6	Degree of swelling of blend films in pH buffer solution	
	pH = 8	53
D7	Degree of swelling of blend films in pH buffer solution	
	pH = 9	53
D8	Degree of swelling of blend films in pH buffer solution	
	pH = 10	54
D9	Degree of swelling of CM-chitin/silk fibroin: 50/50 in pH	
	buffer solution $pH = 3$	54
D 10	Degree of swelling of CM-chitin/silk fibroin: 50/50 in pH	
	buffer solution $pH = 4$	54
D11	Degree of swelling of CM-chitin/silk fibroin: 50/50 in pH	
	Buffer solution $pH = 5$	55
D12	Degree of swelling of CM-chitin/silk fibroin: 50/50 in pH	
	buffer solution pH = 6	55
D13	Degree of swelling of CM-chitin/silk fibroin: 50/50 in pH	
	buffer solution $pH = 7$	55
D14	Degree of swelling of CM-chitin/silk fibroin: 50/50 in pH	
	buffer solution pH = 8	56
D15	Degree of swelling of CM-chitin/silk fibroin: 50/50 in pH	
	buffer solution $pH = 9$	56
D16	Degree of swelling of CM-chitin/silk fibroin: 50/50 in pH	
	buffer solution $pH = 10$	56
D17	Effect of time on degree of swelling of CM-chitin/silk fibroin:	
	50/50 in pH buffer solution pH = 6 and pH = 10	57
E1	Degree of swelling of blend films in 0.25 M LiCl	58
E2	Degree of swelling of blend films in 0.25 M NaCl	58
E3	Degree of swelling of blend films in 0.25 M CaCl ₂	59
E4	Degree of swelling of blend films in 0.25 M FeCl ₃	59

E5	Degree of swelling of blend films in water	60
F1	Tensile strength of the blend films	60
F2	Tensile strength of the blend films with containing 0.01%	
	glutaraldehyde	61
F3	Elongation at break of the blend films	61
F4	Elongation at break of the blend films with containing	
	0.01% glutaraldehyde	62
G1	Decomposition temperature of pure and blend films	62

LIST OF FIRURES

FIGUE	IGURE	
1.1	Chemical structure of chitin	3
1.1		
	Chemical structure of CM-chitin	4
1.3	Model of microstructure of silk fibroin	6
4.1	FTIR spectrum of chitin powder	20
4.2	1	21
4.3	1 1	
	compositions of CM-chitin to silk fibroin, CM-chitin/	
	silk fibroin composition: (a) 100/0 (CM-chititn); (b) 80/20;	
	(c) 60/40; (d) 50/50; (e) 40/60; (f) 20/80; (g) 0/100 (silk fibroin)	22
4.4	Wide-angle X-ray diffraction patterns of CM-chitin/silk fibroin	
	blend films, CM-chitin/silk fibroin composition: (a) 100/0	
	(CM-chititn); (b) 80/20; (c) 60/40; (d) 50/50; (e) 40/60; (f) 20/80;	
	(g) 0/100 (silk fibroin)	23
4.5	DSC thermograms of CM-chitin/silk fibroin blend films,	
	CM-chitin/silk fibroin composition: (a) 100/0 (CM-chititn);	
	(a) 80/20; (c) 60/40; (d) 50/50; (e) 40/60; (f) 20/80; (g) 0/100	
	(silk fibroin)	24
4.6	Decomposition temperature of CM-chitin/silk fibroin blend	
	films as a function of CM-chitin content	25
4.7	Effect of immersion time on equilibrium water content of	
	CM-chitn/silk fibroin blend films containing 0.01%	
	glutaraldehyde. CM-chitin/silk fibroin composition:	
	● 100/0 (CM-chitin); ○ 80/20; ■ 60/40; □ 50/50; ▲ 40/60;	
	△ 20/80	27
4.8		
	with the addition of 0.01% glutaraldehyde	27

4.9	Degree of swelling of CM-chitn/silk fibroin blend films with the	
	addition of 0.01% glutaraldehyde as a function of pH	
	CM-chitin/silk fibroin composition: ● 100/0 (CM-chitin);	
	○ 80/20; ■ 60/40; □ 50/50; ▲ 40/60; △ 20/80	28
4.10	Effect of glutaraldehyde concentration on degree of swelling of	
	CM-chitin/silk fibroin blends film as a function of pH	
	• 0.005% glutaraldehyde; • 0.01% glutaraldehyde;	
	■ 0.05% glutaraldehyde	29
4.11	Degree of swelling of CM-chitin/silk fibroin blend films with	
	50/50 blend ratio containing 0.01% glutaraldehyde on a step	
	change in pH	30
4.12	Effect of salt types on degree of swelling of CM-chitin/silk	
	fibroin blend films containing 0.01% glutaraldehyde as a	
	function of CM-chitin content. ● LiCl 100/0; ○ NaCl; ■ CaCl ₂ ;	
	\Box FeCl ₃ ; \blacktriangle H ₂ O	31
4.13	Tensile strength of CM-chitin/silk fibroin blend films as a	
	function of CM-chitin content, □: films without glutaraldehyde;	
	O: films with 0.01% glutaraldehyde	32
4.14	Elongation at break of CM-chitin/silk fibroin blend films as a	
	function of CM-chitin content, □: films without glutaraldehyde;	
	O: films with 0.01% glutaraldehyde	33
A1	η_{sp}/c and $\ln(\eta_{rel})/c$ against concentration of CM-chitin solution	41
В1	FTIR spectrum of CM-chitin film	43
B2	FTIR spectrum of the blend film containing 80%CM-chitin	43
В3	FTIR spectrum of the blend film containing 60%CM-chitin	44
B4	FTIR spectrum of the blend film containing 50%CM-chitin	44
B5	FTIR spectrum of the blend film containing 40%CM-chitin	45
B6	FTIR spectrum of the blend film containing 20%CM-chitin	45
В7	FTIR spectrum of silk fibroin film	46