



**EFFECT OF CHEMICAL MODIFICATIONS AND
ELECTRON BEAM IRRADIATION ON PROPERTIES
OF CORN COB FILLED CHITOSAN BIOCOMPOSITE
FILMS**

by

**CHAN MING YENG
(1340410865)**

A thesis submitted in fulfillment of the requirements for the degree of
Doctor of Philosophy

**School of Materials Engineering
UNIVERSITI MALAYSIA PERLIS**

2015

UNIVERSITI MALAYSIA PERLIS

DECLARATION OF THESIS

Author's full name : CHAN MING YENG
Date of birth : 1ST MAY 1988
Title : EFFECT OF CHEMICAL MODIFICATIONS AND ELECTRON BEAM IRRADIATION ON PROPERTIES OF CORN COB FILLED CHITOSAN BIOCOMPOSITE FILMS.
Academic Session : 2013

I hereby declare that the thesis becomes the property of Universiti Malaysia Perlis (UniMAP) and to be placed at the library of UniMAP. This thesis is classified as :

- CONFIDENTIAL** (Contains confidential information under the Official Secret Act 1972)*
- RESTRICTED** (Contains restricted information as specified by the organization where research was done)*
- OPEN ACCESS** I agree that my thesis is to be made immediately available as hard copy or on-line open access (full text)

I, the author, give permission to the UniMAP to reproduce this thesis in whole or in part for the purpose of research or academic exchange only (except during a period of _____ years, if so requested above).

Certified by:

SIGNATURE

SIGNATURE OF SUPERVISOR

880501-03-5040

ASSOC. PROF. DR.IR. SALMAH HUSSEINSYAH

(NEW IC NO. / PASSPORT NO.)

NAME OF SUPERVISOR

Date : _____

Date : _____

NOTES : * If the thesis is CONFIDENTIAL or RESTRICTED, please attach with the letter from the organization with period and reasons for confidentiality or restriction.

ACKNOWLEDGEMENT

First of all, I would like to express my special appreciation and thanks to my supervisor, Associate Professor Ir. Dr. Salmah Husseinsyah, who have been a tremendous guide me throughout the completion of my Doctoral of Philosophy (Ph.D) study. Without her guidance, monitoring and encouragement, which this work would have never been accomplished. I also thanks to Dr. Sam Sung Ting as my co-supervisor for his supervision and supporting me during the period of my research work.

Besides that, I would like to thanks to Dean of School of Materials Engineering, Dr. Khairel Rafezi, and technicians for their guidance and assistance in laboratory works. Furthermore, I would like to acknowledge the program of MyBrain15 by Ministry of Higher Education Malaysia for providing the scholarship throughout my Ph.D study. I also wish to thank Dr. Chantara Thevy Ratnam and her staffs from Malaysia Nuclear Agency (Bangi) for the assistance during irradiation process.

I wish to express my gratitude to my partner, Mr. Koay Seong Chun who always supporting me and accompany me throughout the journey of study and sharing the sweets and bitters of my life all the time. I also would like to thank my friends who had a great influence in my life during the graduate program.

At last but not least, I am also greatly thankful for my family, my father, sisters and brother who supported me throughout my educational endeavor and provided me with a great strength along the way.

~ Chan Ming Yeng ~

TABLE OF CONTENTS

	PAGE
THESIS DECLARATION	i
ACKNOWLEDGEMENT	ii
TABLE OF CONTENTS	iii
LIST OF TABLES	x
LIST OF FIGURES	xiv
LIST OF ABBREVIATIONS	xxv
LIST OF SYMBOLS	xxvii
ABSTRAK	xxviii
ABSTRACT	xxix
CHAPTER 1: INTRODUCTION	
1.1 Research Background	1
1.2 Problem Statement	5
1.3 Research Objectives	6
1.4 Scope of Study	7
1.5 Thesis Preface	7
CHAPTER 2: LITERATURE REVIEW	
2.1 Biocomposites	9
2.1.1 Biocomposite Films	12
2.2 Polymer Matrix	13

2.3	Biopolymer	14
2.3.1	Chitosan (CS)	15
2.3.1.1	Chitosan Based Biocomposite Films	22
2.4	Fillers	24
2.4.1	Natural Fillers	26
2.5	Corn Cob (CC)	30
2.5.1	Corn Cob Based Biocomposites	32
2.6	Filler-matrix Interface	33
2.6.1	Type of Bonding at the Interface	33
2.6.2	Nicolais and Narkis Theory	37
2.6.3	Nielsen Theory	39
2.7	Chemical Modification	40
2.7.1	Acrylic Acid (AA)	42
2.8	Crosslinking	44
2.8.1	Crosslinking agent	46
2.8.1.1	Glutaraldehyde (GLA)	48
2.8.1.2	Salicylaldehyde (SAL)	49
2.8.1.3	Phthalic Anhydride (PTH)	51
2.8.1.4	Epichlorohydrin (EP)	52
2.9	Electron Beam Irradiation	54
2.10	Biodegradation	58
2.10.1	Enzymatic Biodegradation	61
2.10.2	Soil Biodegradation	63
2.11	Summary of Literature Review	65

CHAPTER 3: RESEARCH METHODOLOGY

3.1	Materials	66
3.2	Preparation of CS/CC Biocomposite Films with Different CC Content	67
3.3	Chemical Modification of Corn Cob	68
3.4	Preparation of Treated CS/CC Biocomposite Films with Acrylic Acid (AA) at Different CC Content	68
3.5	Preparation of Modified CS/CC Biocomposite Films with Different Crosslinking Agent at Different CC Content	68
3.6	Tensile Properties and Characterization of CS/CC Biocomposite Films	69
	3.6.1 Tensile Properties	69
	3.6.2 Thermogravimetry Analysis (TGA)	71
	3.6.3 Fourier Transform Infrared (FTIR) Analysis	71
	3.6.4 Gel Fraction	71
	3.6.5 Enzymatic Biodegradation	72
	3.6.6 Soil Biodegradation	72
	3.6.7 Electron Beam Irradiation	73
	3.6.8 Morphology Analysis	73

CHAPTER 4: RESULTS AND DISCUSSION

4.1	Effect of Corn Cob Content on Properties of CS/CC Biocomposite Films	74
	4.1.1 Tensile Properties	74
	4.1.2 Morphology Analysis	79
	4.1.3 Thermogravimetry Analysis (TGA)	81
	4.1.4 Gel Fraction	85

4.1.5	Enzymatic Biodegradation	86
4.1.6	Soil Biodegradation	92
4.2	Effect of Glutaraldehyde Crosslinking Agent on Properties of CS/CC Biocomposite Films	94
4.2.1	Tensile Properties	94
4.2.2	Morphology Analysis	99
4.2.3	Thermogravimetry Analysis (TGA)	101
4.2.4	Fourier Transform Infrared (FTIR) Analysis	104
4.2.5	Gel Fraction	107
4.2.6	Enzymatic Biodegradation	108
4.2.7	Soil Biodegradation	111
4.3	Effect of Salicylaldehyde Crosslinking Agent on Properties of CS/CC Biocomposite Films	113
4.3.1	Tensile Properties	113
4.3.2	Morphology Analysis	118
4.3.3	Thermogravimetry Analysis (TGA)	119
4.3.4	Fourier Transform Infrared (FTIR) Analysis	121
4.3.5	Gel Fraction	123
4.3.6	Enzymatic Biodegradation	124
4.3.7	Soil Biodegradation	128
4.4	Effect of Epichlorohydrin Crosslinking Agent on Properties of CS/CC Biocomposite Films	129
4.4.1	Tensile Properties	129

4.4.2 Morphology Analysis	134
4.4.3 Thermogravimetry Analysis (TGA)	135
4.4.4 Fourier Transform Infrared (FTIR) Analysis	138
4.4.5 Gel Fraction	140
4.4.6 Enzymatic Biodegradation	140
4.4.7 Soil Biodegradation	144
4.5 Effect of Phthalic Anhydride Crosslinking Agent on Properties of CS/CC Biocomposite Films	145
4.5.1 Tensile Properties	145
4.5.2 Morphology Analysis	150
4.5.3 Thermogravimetry Analysis (TGA)	151
4.5.4 Fourier Transform Infrared (FTIR) Analysis	153
4.5.5 Gel Fraction	155
4.5.6 Enzymatic Biodegradation	156
4.5.7 Soil Biodegradation	159
4.6 Comparison on Properties of CS/CC Biocomposite Films with Different Crosslinking Agent	161
4.6.1 Tensile Properties	161
4.6.2 Thermogravimetry Analysis (TGA)	162
4.6.3 Enzymatic Biodegradation	163
4.6.4 Soil Biodegradation	163
4.7 Effect of Acrylic Acid on Properties of CS/CC Biocomposite Films	164
4.7.1 Tensile Properties	164

4.7.2 Morphology Analysis	169
4.7.3 Thermogravimetry Analysis (TGA)	170
4.7.4 Fourier Transform Infrared (FTIR) Analysis	173
4.7.5 Gel Fraction	175
4.7.6 Enzymatic Biodegradation	175
4.7.7 Soil Biodegradation	178
4.8 Effect of Irradiation on Properties of CS/CC Biocomposite Films	180
4.8.1 Tensile Properties	180
4.8.2 Morphology Analysis	185
4.8.3 Thermogravimetry Analysis (TGA)	187
4.8.4 Fourier Transform Infrared (FTIR) Analysis	189
4.8.5 Gel Fraction	192
4.8.6 Enzymatic Biodegradation	193
4.8.7 Soil Biodegradation	197
4.9 Effect of Irradiation on Properties of Modified CS/CC Biocomposite Films with Salicylaldehyde	199
4.9.1 Tensile Properties	199
4.9.2 Morphology Analysis	204
4.9.3 Thermogravimetry Analysis (TGA)	205
4.9.4 Fourier Transform Infrared (FTIR) Analysis	207
4.9.5 Gel Fraction	208
4.9.6 Enzymatic Biodegradation	209
4.9.7 Soil Biodegradation	212

CHAPTER 5: CONCLUSIONS AND FUTURE WORK	214
5.1 Conclusions	214
5.2 Recommendations for Future Works	218
REFERENCES	220
LIST OF PUBLICATIONS	237
LIST OF AWARDS	238
APPENDICES	239

©This item is protected by original copyright

LIST OF TABLES

NO.		PAGE
2.1	Chemical properties of chitosan	18
2.2	Physicochemical and biological properties of chitosan	19
2.3	Chemical families of fillers for polymers	24
2.4	Summary of the general polymer schemes which are susceptible to either crosslinking or chain scission upon radiation with absence of oxygen	55
2.5	Major commercial application of electron beam processing of polymeric materials	57
2.6	Environmental factor active at soil surface and their possible effects on polymer degradation	64
3.1	Properties of chitosan	67
3.2	Composition of corn cob	67
3.3	Formulations of CS/CC biocomposite films with different CC content	68
3.4	Formulations of treated CS/CC biocomposite films with AA at different CC content	68
3.5	Formulations of modified CS/CC biocomposite films with different crosslinking agent at different CC content	69
4.1	The T_{onset} , T_{dmax} and percentage residue of CS/CC biocomposite films at different temperature	83
4.2	Gel fraction of CS/CC biocomposite films at different CC content	85
4.3	Weight loss of CS/CC biocomposite films after 14 days on enzymatic biodegradation	87

4.4	Weight loss of CS/CC biocomposite films after 14 weeks on soil biodegradation	93
4.5	The T_{onset} , T_{dmax} and percentage residue of unmodified and modified CS/CC biocomposite films with GLA at different temperature	104
4.6	The major spectra of unmodified and modified CS/CC biocomposite films with GLA	106
4.7	Gel fraction of unmodified and modified CS/CC biocomposite films with GLA	108
4.8	Weight loss of unmodified and modified CS/CC biocomposite films with GLA after 14 days on enzymatic biodegradation	109
4.9	Weight loss of unmodified and modified CS/CC biocomposite films with GLA after 14 weeks on soil biodegradation	113
4.10	The T_{onset} , T_{dmax} and percentage residue of unmodified and modified CS/CC biocomposite films with SAL at different temperature	121
4.11	The major spectra of modified CS/CC biocomposite films with SAL	123
4.12	Gel fraction of unmodified and modified CS/CC biocomposite films with SAL	124
4.13	Weight loss of unmodified and modified CS/CC biocomposite films with SAL after 14 days on enzymatic biodegradation	125
4.14	Weight loss of unmodified and modified CS/CC biocomposite films with SAL after 14 weeks on soil biodegradation	129
4.15	The T_{onset} , T_{dmax} and percentage residue of unmodified and modified CS/CC biocomposite films EP at different temperature	138
4.16	The major spectra of modified CS/CC biocomposite films with EP	139
4.17	Gel fraction of unmodified and modified CS/CC biocomposite films with EP	140
4.18	Weight loss of unmodified and modified CS/CC biocomposite films with EP after 14 days on enzymatic biodegradation	141
4.19	Weight loss of unmodified and modified CS/CC biocomposite films with EP after 14 weeks on soil biodegradation	145

4.20	The T_{onset} , T_{dmax} and percentage residue of unmodified and modified CS/CC biocomposite films with PTH at different temperature	153
4.21	The major spectra of modified CS/CC biocomposite films with PTH	155
4.22	Gel fraction of unmodified and modified CS/CC biocomposite films with PTH	156
4.23	Weight loss of unmodified and modified CS/CC biocomposite films with PTH after 14 days on enzymatic biodegradation	157
4.24	Weight loss of unmodified and modified CS/CC biocomposite films with PTH after 14 weeks on soil biodegradation	160
4.25	Tensile properties of unmodified and modified CS/CC biocomposite films with different crosslinking agent	161
4.26	TGA and DTG data of unmodified and modified CS/CC biocomposite films with different crosslinking agent	162
4.27	Weight loss on enzymatic biodegradation of unmodified and modified CS/CC biocomposite films after 14 days	163
4.28	Weight loss on soil biodegradation of unmodified and modified CS/CC biocomposite films after 14 weeks	164
4.29	The T_{onset} , T_{dmax} and percentage residue of untreated and treated CS/CC biocomposite films with AA at different temperature	173
4.30	The major spectra of treated CS/CC biocomposite films with AA	174
4.31	Gel fraction of untreated and treated CS/CC biocomposite films with AA	175
4.32	Weight loss of untreated and treated CS/CC biocomposite films with AA after 14 days on enzymatic biodegradation	176
4.33	Weight loss of untreated and treated CS/CC biocomposite films with AA after 14 weeks on soil biodegradation	179
4.34	The T_{onset} , T_{dmax} and percentage residue of unirradiated and irradiated neat CS film and CS/CC biocomposite films at different temperature	189
4.35	The major spectra of irradiated neat CS film and CS/CC biocomposite films	191

4.36	Gel fraction of unirradiated and irradiated neat CS film and CS/CC biocomposite films	193
4.37	Weight loss of unirradiated and irradiated neat CS film and CS/CC biocomposite films after 14 days on enzymatic biodegradation	194
4.38	Weight loss of unirradiated and irradiated CS/CC biocomposite films after 14 weeks on soil biodegradation	199
4.39	The T_{onset} , T_{dmax} and percentage residue of unirradiated and irradiated modified CS/CC biocomposite films with SAL at different temperature	207
4.40	The major spectra of irradiated modified CS/CC biocomposite films with SAL	208
4.41	Gel fraction of unirradiated and irradiated modified CS/CC biocomposite films with SAL	209
4.42	Weight loss of unirradiated and irradiated modified CS/CC biocomposite films with SAL after 14 days on enzymatic biodegradation	210
4.43	Weight loss of unirradiated and irradiated modified CS/CC biocomposite films with SAL after 14 weeks on soil biodegradation	213
4.44	Comparison tensile properties on CS/CC biocomposite films with different modifications at 20 wt % of CC content	216
4.45	Comparison T_{onset} , T_{dmax} and percentage of residue on CS/CC biocomposite films with different modifications at 20 wt % CC content	217
4.46	Comparison percentage weight loss of enzymatic biodegradation on CS/CC biocomposite films with of different modifications at 20 wt% of CC content	218
4.47	Comparison percentage weight loss of soil biodegradation on CS/CC biocomposite films with of different modifications at 20 wt% of CC content	218

LIST OF FIGURES

NO.		PAGE
2.1	The schematic of biocomposites	9
2.2	Classification of biocomposites	10
2.3	Concept of “ sustainable” bio-based product	11
2.4	Carbon dioxide sequestration	11
2.5	Classification of biopolymers	15
2.6	Structure of chitosan	16
2.7	Scheme of deacetylated chitosan from chitin via alkaline treatment	16
2.8	The scheme of solubility of chitosan in acetic acid	18
2.9	Overview of current and prospective applications of chitosan	20
2.10	General schematic representation of filler-matrix interaction	26
2.11	Classification of natural fillers	27
2.12	Structure of plant fiber showing the cellobiose repeat unit	28
2.13	Structure of cellulose	28
2.14	Structure of hemicellulose	29
2.15	Structure of lignin	30
2.16	(a) Part of corn: (1) corn kernel; and (2) corn cob; (b) part of corn cob: (1) beeswing; (2) chaff; (3) woody ring; and (4) pith	31
2.17	Mechanical bond between matrix and filler	34
2.18	(a) Good mechanical bond; (b) lack of wettability can make a polymer unable to penetrate the asperities on the filler surface, owing to interfacial void	34
2.19	Electrostatic bond	35
2.20	Chemical bonding (R and X represent compatible chemical groups)	35

2.21	Chemical bonding as applied to a silane coupling agent	36
2.22	Interfacial layer formed by interdiffusion	36
2.23	Reaction bonding involving polymer	37
2.24	Structure of acrylic acid	43
2.25	Schematic reaction scheme between acrylic acid and cellulose	43
2.26	Schematic of polymer crosslinking	44
2.27	Schematic diagram of (a) intermolecular crosslinking; (b) intramolecular crosslinking	46
2.28	Structure of glutaraldehyde	48
2.29	Schematic crosslinking reaction between chitosan and glutaraldehyde	49
2.30	Structure of salicylaldehyde	50
2.31	Schematic crosslinking reaction between salicylaldehyde and amine polymer	50
2.32	Structure of phthalic anhydride	52
2.33	A chemical reaction between an amine and anhydride	52
2.34	Structure of epichlorohydrin	53
2.35	Schematic crosslinking reaction between epichlorohydrin and chitosan	53
2.36	The free radical reaction in radiation-induced polymer oxidation with presence of oxygen	56
2.37	Crosslinking occur for same polymer and different polymers through radiation	57
2.38	Schematic classification of different degradation environments for polymer	60
4.1	Effect of CC content on tensile strength of CS/CC biocomposite films	76
4.2	SEM micrograph of corn cob	76
4.3	Effect of CC content on elongation at break of CS/CC biocomposite films	77

4.4	Effect of CC content on modulus of elasticity of CS/CC biocomposite films	79
4.5	SEM micrograph of tensile fracture surface of neat CS film	80
4.6	SEM micrograph of tensile fracture surface of unmodified CS/CC biocomposite film at 20 wt % of CC content	80
4.7	SEM micrograph of tensile fracture surface of unmodified CS/CC biocomposite film at 40 wt % of CC content	81
4.8	TGA curves of CS/CC biocomposite films.	83
4.9	DTG curves of CS/CC biocomposite films.	83
4.10	Weight loss of CS/CC biocomposite films on enzymatic biodegradation	87
4.11	Proposed mechanism of enzymatic biodegradation of CS/CC biocomposite films	88
4.12	SEM micrograph on surface of neat CS film before enzymatic biodegradation	89
4.13	SEM micrograph on surface of neat CS film after 14 days of enzymatic biodegradation	89
4.14	SEM micrograph on surface of CS/CC biocomposite film at 20 wt % of CC content before enzymatic biodegradation	90
4.15	SEM micrograph on surface of CS/CC biocomposite film at 40 wt % of CC content before enzymatic biodegradation	91
4.16	SEM micrograph on surface of CS/CC biocomposite film at 20 wt % of CC content after 14 days of enzymatic biodegradation	91
4.17	SEM micrograph on surface of CS/CC biocomposite film at 40 wt % of CC content after 14 days of enzymatic biodegradation	92
4.18	Weight loss of CS/CC biocomposite films on soil biodegradation	93
4.19	Effect of CC content on tensile strength of unmodified and modified CS/CC biocomposite films with GLA	95
4.20	Relative yield strength of theoretical, unmodified and modified CS/CC biocomposite films with GLA	96
4.21	Effect of CC content on elongation at break of unmodified and modified CS/CC biocomposite films with GLA	97
4.22	Relative elongation at yield of theoretical, unmodified and modified CS/CC biocomposite films with GLA	98

4.23	Effect of CC content on modulus of elasticity of unmodified and modified CS/CC biocomposite films with GLA	99
4.24	SEM micrograph of tensile fracture surface of modified CS/CC biocomposite film with GLA at 20 wt % of CC content	100
4.25	SEM micrograph of tensile fracture surface of modified CS/CC biocomposite film with GLA at 40 wt % of CC content	100
4.26	TGA curves of unmodified and modified CS/CC biocomposite films with GLA	103
4.27	DTG curves of unmodified and modified CS/CC biocomposite films with GLA	103
4.28	FTIR spectra of unmodified and modified CS/CC biocomposite films with GLA	105
4.29	The proposed schematic reaction of CS and GLA	106
4.30	Weight loss of unmodified and modified CS/CC biocomposite films with GLA on enzymatic biodegradation	109
4.31	SEM micrograph on surface of modified CS/CC biocomposite film with GLA at 20 wt % of CC content before enzymatic biodegradation	110
4.32	SEM micrograph on surface of modified CS/CC biocomposite film with GLA at 40 wt % of CC content before enzymatic biodegradation	110
4.33	SEM micrograph on surface of modified CS/CC biocomposite film with GLA at 20 wt % of CC content after 14 days enzymatic biodegradation	111
4.34	SEM micrograph on surface of modified CS/CC biocomposite film with GLA at 40 wt % of CC content after 14 days enzymatic biodegradation	111
4.35	Weight loss of unmodified and modified CS/CC biocomposite films with GLA on soil biodegradation	112
4.36	Effect of CC content on tensile strength of unmodified and modified CS/CC biocomposite films with SAL	114
4.37	Relative yield strength of theoretical, unmodified and modified CS/CC biocomposite films with SAL	115
4.38	Effect of CC content on elongation at break of unmodified and modified CS/CC biocomposite films with SAL	116

4.39	Relative elongation at yield of theoretical, unmodified and modified CS/CC biocomposite films with SAL	117
4.40	Effect of CC content on modulus of elasticity of unmodified and modified CS/CC biocomposite films with SAL	118
4.41	SEM micrograph of tensile fracture surface of modified CS/CC biocomposite film with SAL at 20 wt % of CC content	119
4.42	SEM micrograph of tensile fracture surface of modified CS/CC biocomposite film with SAL at 40 wt % of CC content	119
4.43	TGA curves of unmodified and modified CS/CC biocomposite films with SAL	120
4.44	DTG curves of unmodified and modified CS/CC biocomposite films with SAL	121
4.45	FTIR spectra of unmodified and modified CS/CC biocomposite films with SAL	122
4.46	The proposed schematic reaction of CS and SAL	123
4.47	Weight loss of unmodified and modified CS/CC biocomposite films with SAL on enzymatic biodegradation	125
4.48	SEM micrograph on surface of modified CS/CC biocomposite film with SAL at 20 wt % of CC content before enzymatic biodegradation	126
4.49	SEM micrograph on surface of modified CS/CC biocomposite film with SAL at 40 wt % of CC content before enzymatic biodegradation	127
4.50	SEM micrograph on surface of modified CS/CC biocomposite film with SAL at 20 wt % of CC content after 14 days enzymatic biodegradation	127
4.51	SEM micrograph on surface of modified CS/CC biocomposite film with SAL at 40 wt % of CC content after 14 days enzymatic biodegradation	128
4.52	Weight loss of unmodified and modified CS/CC biocomposite films with SAL on soil biodegradation	129
4.53	Effect of CC content on tensile strength of unmodified and modified CS/CC biocomposite films with EP	130
4.54	Relative yield strength of theoretical, unmodified and modified CS/CC biocomposite films with EP	131

4.55	Effect of CC content on elongation at break of unmodified and modified CS/CC biocomposite films with EP	132
4.56	Relative elongation at yield of theoretical, unmodified and modified CS/CC biocomposite films with EP	133
4.57	Effect of CC content on modulus of elasticity of unmodified and modified CS/CC biocomposite films with EP	134
4.58	SEM micrograph of tensile fracture surface of modified CS/CC biocomposite film with EP at 20 wt % of CC content	135
4.59	SEM micrograph of tensile fracture surface of modified CS/CC biocomposite film with EP at 40 wt % of CC content	135
4.60	TGA curves of unmodified and modified CS/CC biocomposite films with EP	137
4.61	DTG curves of unmodified and modified CS/CC biocomposite films with EP	137
4.62	FTIR spectra of unmodified and modified CS/CC biocomposite films with EP	139
4.63	The proposed schematic reaction of CS and EP	139
4.64	Weight loss of unmodified and modified CS/CC biocomposite films with EP on enzymatic biodegradation	141
4.65	SEM micrograph on surface of modified CS/CC biocomposite film with EP at 20 wt % of CC content before enzymatic biodegradation	142
4.66	SEM micrograph on surface of modified CS/CC biocomposite film with EP at 40 wt % of CC content before enzymatic biodegradation	143
4.67	SEM micrograph on surface of modified CS/CC biocomposite film with EP at 20 wt % of CC content after 14 days enzymatic biodegradation	143
4.68	SEM micrograph on surface of modified CS/CC biocomposite film with EP at 40 wt % of CC content after 14 days enzymatic biodegradation	144
4.69	Weight loss of unmodified and modified CS/CC biocomposite films with EP on soil biodegradation	145
4.70	Effect of CC content on tensile strength of unmodified and modified CS/CC biocomposite films with PTH	146

4.71	Relative yield strength of theoretical, unmodified and modified CS/CC biocomposite films with PTH	147
4.72	Effect of CC content on elongation at break of unmodified and modified CS/CC biocomposite films with PTH	148
4.73	Relative elongation at yield of theoretical, unmodified and modified CS/CC biocomposite films with PTH	149
4.74	Effect of CC content on modulus of elasticity of unmodified and modified CS/CC biocomposite films with PTH	150
4.75	SEM micrograph of tensile fracture surface of modified CS/CC biocomposite film with PTH at 20 wt % of CC content	151
4.76	SEM micrograph of tensile fracture surface of modified CS/CC biocomposite film with PTH at 40 wt % of CC content	151
4.77	TGA curves of unmodified and modified CS/CC biocomposite films with PTH	152
4.78	DTG curves of unmodified and modified CS/CC biocomposite films with PTH	153
4.79	FTIR spectra of unmodified and modified CS/CC biocomposite films with PTH	154
4.80	The proposed schematic reaction of CS and PTH	155
4.81	Weight loss of unmodified and modified CS/CC biocomposite films with PTH on enzymatic biodegradation	157
4.82	SEM micrograph on surface of modified CS/CC biocomposite film with PTH at 20 wt % of CC content before enzymatic biodegradation	158
4.83	SEM micrograph on surface of modified CS/CC biocomposite film with PTH at 40 wt % of CC content before enzymatic biodegradation	158
4.84	SEM micrograph on surface of modified CS/CC biocomposite film with PTH at 20 wt % of CC content after 14 days enzymatic biodegradation	159
4.85	SEM micrograph on surface of modified CS/CC biocomposite film with PTH at 40 wt % of CC content after 14 days enzymatic biodegradation	159
4.86	Weight loss of unmodified and modified CS/CC biocomposite films with PTH on soil biodegradation	160

4.87	Effect of CC content on tensile strength of untreated and treated CS/CC biocomposite films with AA	165
4.88	Relative yield strength of theoretical, untreated and treated CS/CC biocomposite films with AA	166
4.89	Effect of CC content on elongation at break of untreated and treated CS/CC biocomposite films with AA	167
4.90	Relative elongation at yield of theoretical, untreated and treated CS/CC biocomposite films with AA	168
4.91	Effect of CC content on modulus of elasticity of untreated treated CS/CC biocomposite films with AA	169
4.92	SEM micrograph of tensile fracture surface of treated CS/CC biocomposite film with AA at 20 wt % of CC content	170
4.93	SEM micrograph of tensile fracture surface of treated CS/CC biocomposite film with AA at 40 wt % of CC content	170
4.94	TGA curves of untreated and treated CS/CC biocomposite films with AA	172
4.95	DTG curves of untreated and treated CS/CC biocomposite films with AA	172
4.96	FTIR spectra of untreated and treated CC with AA	174
4.97	The proposed schematic reaction between acrylic acid, corn cob and chitosan	174
4.98	Weight loss of untreated and treated CS/CC biocomposite films with AA on enzymatic biodegradation	176
4.99	SEM micrograph on surface of treated CS/CC biocomposite film with AA at 20 wt % of CC content before enzymatic biodegradation	177
4.100	SEM micrograph on surface of treated CS/CC biocomposite film with AA at 40 wt % of CC content before enzymatic biodegradation	177
4.101	SEM micrograph on surface of treated CS/CC biocomposite film with AA at 20 wt % of CC content after 14 days enzymatic biodegradation	178
4.102	SEM micrograph on surface of treated CS/CC biocomposite film with AA at 40 wt % of CC content after 14 days enzymatic biodegradation	178

4.103	Weight loss of untreated and treated CS/CC biocomposite films with AA on soil biodegradation	179
4.104	Effect of CC content on tensile strength of unirradiated and irradiated CS/CC biocomposite films	181
4.105	Relative yield strength of theoretical, unirradiated and irradiated CS/CC biocomposite films	182
4.106	Effect of CC content on elongation at break of unirradiated and irradiated CS/CC biocomposite films	183
4.107	Relative elongation at yield of theoretical, unirradiated, and irradiated CS/CC biocomposite films	184
4.108	Effect of CC content on modulus of elasticity of unirradiated and irradiated CS/CC biocomposite films	185
4.109	SEM micrograph of tensile fracture surface of irradiated neat CS film	186
4.110	SEM micrograph of tensile fracture surface of irradiated CS/CC biocomposite film at 20 wt % of CC content	186
4.111	SEM micrograph of tensile fracture surface of irradiated CS/CC biocomposite film at 40 wt % of CC content	187
4.112	TGA curves of unirradiated and irradiated neat CS film and CS/CC biocomposite films	188
4.113	DTG curves of unirradiated and irradiated neat CS film and CS/CC biocomposite films	189
4.114	FTIR spectra of unirradiated and irradiated neat CS films	190
4.115	FTIR spectra of unirradiated and irradiated CS/CC biocomposite films	191
4.116	The proposed schematic crosslinking reaction between CS and itself upon irradiation.	192
4.117	Weight loss of unirradiated and irradiated neat CS film and CS/CC biocomposite films on enzymatic biodegradation	194
4.118	SEM micrograph on surface of irradiated neat CS film before enzymatic biodegradation	195
4.119	SEM micrograph on surface of irradiated neat CS film after 14 days enzymatic biodegradation	195

4.120	SEM micrograph on surface of irradiated CS/CC biocomposite film at 20 wt % of CC content before enzymatic biodegradation	196
4.121	SEM micrograph on surface of irradiated CS/CC biocomposite film at 40 wt % of CC content before enzymatic biodegradation	196
4.122	SEM micrograph on surface of irradiated CS/CC biocomposite film at 20 wt % of CC content after 14 days enzymatic biodegradation	197
4.123	SEM micrograph on surface of irradiated CS/CC biocomposite film at 40 wt % of CC content after 14 days enzymatic biodegradation	197
4.124	Weight loss of unirradiated and irradiated CS/CC biocomposite films on soil biodegradation	198
4.125	Effect of CC content on tensile strength of unirradiated and irradiated modified CS/CC biocomposite films with SAL	200
4.126	Relative yield strength of theoretical, unirradiated and irradiated modified CS/CC biocomposite films with SAL	201
4.127	Effect of CC content on elongation at break of unirradiated and irradiated modified CS/CC biocomposite films with SAL	202
4.128	Relative elongation at yield of theoretical, unirradiated and irradiated modified CS/CC biocomposite films with SAL	203
4.129	Effect of CC content on modulus of elasticity of unirradiated and irradiated modified CS/CC biocomposite films with SAL	204
4.130	SEM micrograph of tensile fracture surface of irradiated modified CS/CC biocomposite film with SAL at 20 wt% of CC content	205
4.131	SEM micrograph of tensile fracture surface of irradiated modified CS/CC biocomposite film with SAL at 40 wt% of CC content	205
4.132	TGA curves of unirradiated and irradiated modified CS/CC biocomposite films with SAL	206
4.133	DTG curves of unirradiated and irradiated modified CS/CC biocomposite films with SAL	207
4.134	FTIR spectra of unirradiated and irradiated modified CS/CC biocomposite films with SAL	208
4.135	Weight loss of unirradiated and irradiated modified CS/CC biocomposite films with SAL on enzymatic biodegradation	210
4.136	SEM micrograph surface on of irradiated modified CS/CC biocomposite film with SAL at 20 wt % of CC content before enzymatic biodegradation	211