## TABLE OF CONTENTS

	Page
Acknowledgements	iii
Abstract (Thai)	v
Abstract (English)	vii
Table of Contents	ix
List of Tables	XV
List of Figures	xvi
List of Abbreviations	XX
Chapter 1 Introduction	<b>1</b> 2
References	5
	-
Chapter 2 Literature review	9
2.1 Biodegradable biopolymers	9
2.2 Biopolymer classifications	10
2.3 Biopolymer films	12
2.3.1 Polysaccharide films	12
2.3.1.1 Starch films	13
2.3.1.2 Cellulose derivatives films	18
2.3.2 Protein films	20
2.3.3 Biopolymer-blended films	22
Co 2.4 Active packaging Chiang Mai University	25
2.5 Antioxidant	28
2.5.1 Types of antioxidants <b>CONTROL</b>	30
2.5.1.1 Synthetic antioxidants	31
2.5.1.2 Natural Antioxidants	32
2.6 Antioxidant films	35

#### References

Chapter 3		er 3	3 Effect of carboxymethyl cellulose concentration					
			on physical properties of biodegradable cassava					
			starch based films	62				
	Abstrac	rt		62				
	3.1	Introdu	uction	63				
	3.2	Materi	ials and methods	66				
	1	3.2.1	Materials	66				
	6	3.2.2	Cassava starch-CMC film preparation	66				
		3.2.3	Mechanical characterization	67				
	302	3.2.4	Water solubility of cassava starch-CMC films	67				
		3.2.5	Fourier transform infrared spectroscopy (FT-IR)	68				
	1 306	3.2.6	Differential scanning calorimetry (DSC)	68				
		3.2.7	Film morphology	68				
		3.2.8	Statistical analysis	69				
	3.3	Result	s and discussion	69				
		3.3.1	FT-IR spectrum of cassava starch films with and without					
			carboxymethyl cellulose (CMC)	69				
	,	3.3.2	Effects of CMC concentration and % relative humidity (RH)					
			on tensile strength and elongation at break of cassava starch					
			based films	72				
		3.3.3	Effects of CMC concentration on water solubility of cassava					
			starch based films	73				
		3.3.4	Thermal properties of cassava starch films with and without					
Со	ovri	gh	carboxymethyl cellulose ang Mai Universi	75				
		3.3.5	Morphology of blended films	78				
ΑΙ	3.4	Conclu	usions <b>g n t s f e s e r v e</b>	79				
	Referen	ices		81				

## Chapter 4 Mechanical and physical properties of cassava starchgelatin blended films

86

40

Abstra	ostract					
4.1	Introduction					
4.2	Materials and Methods					
	4.2.1	Materials	89			
	4.2.2	Cassava starch blended films preparation	89			
	4.2.3	Fourier transform infrared spectroscopy (FT-IR)	90			
	4.2.4	Mechanical characterization	90			
	4.2.5	Water solubility of cassava starch blended films	91			
	4.2.6	Film morphology	91			
16	4.2.7	X-ray diffraction (XRD)	92			
	4.2.8	Differential scanning calorimetry (DSC)	92			
-50	4.2.9	Statistical analysis	92			
4.3	Result	s and discussion	92			
	4.3.1	FT-IR	93			
	4.3.2	Mechanical properties	95			
Ŷ	4.3.3	Water solubility of films	96			
	4.3.4	Film microstructures	98			
	4.3.5	X-ray diffraction patterns	101			
	4.3.6	DSC	102			
4.4	Conclu	usions	105			
Refere	ences	UNIVU	106			

Chapter 5	Water vapour permeability and sorption isotherms of							
cassava starch based films blended with gelatin and								
	carboxymethyl cellulose	114						
Abstract	it <sup>©</sup> by Chiang Mai Unive	rs 114/						
5.1 Introd	luction	115						
5.2 Mate	rials and Methods	<b>C</b> 118						
5.2.1	Materials	118						
5.2.2	Cassava starch based film preparation	118						
5.2.3	Water vapor permeability (WVP)	118						
5.2.4	Determination of water sorption isotherms	120						

	5.2.5	Moisture sorption isotherm curve fitting	120
5.3	Result	s and Discussion	122
	5.3.1	Water vapor permeabilities WVP	122
	5.3.2	Moisture sorption isotherms	123
	5.3.2.1	Moisture sorption curves	123
	5.3.2.2	2 Fitting sorption isotherm models to experimental data	125
5.4	Conclu	Isions	131
Refere	ences		131
Chapt	ter 6	Properties and antioxidant activities of cassava starch/gelatin	

Chapter 6	Properties and antioxidant activities of cassava starch/getath		
	blended films incorporated with quercetin and TBHQ and		
ATC	their applications in food packaging	137	
Abstract			
6.1 Introd	uction	138	
6.2 Mater	ials and methods	140	
6.2.1	Materials	140	
6.2.2	Film preparation	141	
6.2.3	Mechanical properties	141	
6.2.4	Fourier transform infrared spectroscopy (FT-IR)	142	
6.2.5	Differential scanning calorimetry (DSC)	142	
6.2.6	X-ray diffraction (XRD)	142	
6.2.7	Film morphology	142	
6.2.8	Water solubility of cassava starch/gelatin films	143	
6.2.9	Water Vapor Transmission Rate (WVTR)	143	
6.2.10	Total phenolic content assay	144	
<b>CODV</b> 6.2.11	Determination of antioxidant activity in the blended films	145	
6.2.12	Application of antioxidant films on lard	146	
AII r	6.2.12.1 Effect of antioxidants incorporations into		
	cassava starch/gelatin films on lard storage	146	
	6.2.12.2 Estimation of peroxide value	146	
6.2.13	Application of antioxidant films on fresh pork	147	
6.2.14	Statistical analysis	148	

	6.3	Result	s and discussion	148
		6.3.1	Mechanical properties	148
		6.3.2	Fourier transform infrared spectroscopy (FT-IR)	151
		6.3.3	Thermal properties of the blended films	154
		6.3.4	X-ray diffraction patterns	157
		6.3.5	Film morphology	157
		6.3.6	Water solubility of blended films	159
		6.3.7	Water vapor transmission rate (WVTR) of blended films	161
		6.3.8	Total phenolic assay	162
	6	6.3.9	Determination of antioxidant activity in the blended films	164
		6.3.10	Application of antioxidant films on lard	164
	20	6.3.11	Application of antioxidant films on fresh pork	165
	6.4	Conclu	isions	169
	Refere	nces		170
	Chapt	er 7	Physical properties and applications of cassava starch-	
			carboxymethyl cellulose films incorporated with	
			quercetin and TBHQ	178
	Abstra	ct	quercetin and TBHQ	<b>178</b> 178
	Abstra 7.1	ct Introdu	quercetin and TBHQ	<b>178</b> 178 179
	Abstra 7.1 7.2	ct Introdu Materi	quercetin and TBHQ action als and methods	<ol> <li>178</li> <li>178</li> <li>179</li> <li>181</li> </ol>
	Abstra 7.1 7.2	ct Introdu Materi 7.2.1	quercetin and TBHQ action als and methods Materials	<ol> <li>178</li> <li>178</li> <li>179</li> <li>181</li> <li>181</li> </ol>
	Abstra 7.1 7.2	ct Introdu Materi 7.2.1 7.2.2	quercetin and TBHQ action als and methods Materials Film preparation	<ol> <li>178</li> <li>178</li> <li>179</li> <li>181</li> <li>181</li> <li>182</li> </ol>
	Abstra 7.1 7.2	ct Introdu Materi 7.2.1 7.2.2 7.2.3	quercetin and TBHQ nction als and methods Materials Film preparation Mechnical properties	<ol> <li>178</li> <li>178</li> <li>179</li> <li>181</li> <li>181</li> <li>182</li> <li>182</li> </ol>
	Abstra 7.1 7.2	ct Introdu Materi 7.2.1 7.2.2 7.2.3 7.2.4	quercetin and TBHQ nction als and methods Materials Film preparation Mechnical properties Fourier transform infrared spectroscopy (FT-IR)	<ol> <li>178</li> <li>178</li> <li>179</li> <li>181</li> <li>181</li> <li>182</li> <li>182</li> <li>182</li> <li>182</li> </ol>
ີ ຄີປ Col	Abstra 7.1 7.2	ct Introdu Materi 7.2.1 7.2.2 7.2.3 7.2.4 7.2.5	quercetin and TBHQ action als and methods Materials Film preparation Mechnical properties Fourier transform infrared spectroscopy (FT-IR) Differential scanning calorimetry (DSC)	<ol> <li>178</li> <li>178</li> <li>179</li> <li>181</li> <li>181</li> <li>182</li> <li>182</li> <li>182</li> <li>182</li> <li>183</li> </ol>
ີດ ເດີ ເດີ	Abstra 7.1 7.2	ct Introdu Materi 7.2.1 7.2.2 7.2.3 7.2.4 7.2.5 7.2.6	quercetin and TBHQ action als and methods Materials Film preparation Mechnical properties Fourier transform infrared spectroscopy (FT-IR) Differential scanning calorimetry (DSC) X-ray diffraction (XRD)	<ol> <li>178</li> <li>178</li> <li>179</li> <li>181</li> <li>181</li> <li>182</li> <li>182</li> <li>182</li> <li>182</li> <li>183</li> <li>183</li> </ol>
ດີ ເດິ ໄ A	Abstra 7.1 7.2	ct Introdu Materi 7.2.1 7.2.2 7.2.3 7.2.4 7.2.5 7.2.6 7.2.7	quercetin and TBHQ action als and methods Materials Film preparation Mechnical properties Fourier transform infrared spectroscopy (FT-IR) Differential scanning calorimetry (DSC) X-ray diffraction (XRD) Film morphology	<ol> <li>178</li> <li>179</li> <li>181</li> <li>181</li> <li>182</li> <li>182</li> <li>182</li> <li>183</li> <li>183</li> <li>183</li> </ol>
ີດ I A	Abstra 7.1 7.2	ct Introdu Materi 7.2.1 7.2.2 7.2.3 7.2.4 7.2.5 7.2.6 7.2.7 7.2.8	quercetin and TBHQ action als and methods Materials Film preparation Mechnical properties Fourier transform infrared spectroscopy (FT-IR) Differential scanning calorimetry (DSC) X-ray diffraction (XRD) Film morphology Water solubility of blended films	<ol> <li>178</li> <li>179</li> <li>181</li> <li>181</li> <li>182</li> <li>182</li> <li>182</li> <li>183</li> <li>183</li> <li>183</li> <li>183</li> </ol>
ີດ ເດິ A I	Abstra 7.1 7.2	ct Introdu Materi 7.2.1 7.2.2 7.2.3 7.2.4 7.2.5 7.2.6 7.2.7 7.2.8 7.2.9	quercetin and TBHQ action als and methods Materials Film preparation Mechnical properties Fourier transform infrared spectroscopy (FT-IR) Differential scanning calorimetry (DSC) X-ray diffraction (XRD) Film morphology Water solubility of blended films Water vapor transmission rate (WVTR) of blended films	<ol> <li>178</li> <li>179</li> <li>181</li> <li>181</li> <li>182</li> <li>182</li> <li>182</li> <li>183</li> <li>183</li> <li>183</li> <li>183</li> <li>183</li> <li>184</li> </ol>
ດີ Col A l	Abstra 7.1 7.2	ct Introdu Materi 7.2.1 7.2.2 7.2.3 7.2.4 7.2.5 7.2.6 7.2.7 7.2.8 7.2.9 7.2.10	quercetin and TBHQ action als and methods Materials Film preparation Mechnical properties Fourier transform infrared spectroscopy (FT-IR) Differential scanning calorimetry (DSC) X-ray diffraction (XRD) Film morphology Water solubility of blended films Water vapor transmission rate (WVTR) of blended films Total phenolic assay	<ol> <li>178</li> <li>179</li> <li>181</li> <li>181</li> <li>182</li> <li>182</li> <li>182</li> <li>183</li> <li>183</li> <li>183</li> <li>183</li> <li>184</li> <li>185</li> </ol>

		7.2.12	Application	n of antiox	idant films	on lard				186
			7.2.12.1 H	Effect of an	tioxidants	incorporat	tions into	cassava	l	
			S	tarch-CMC	C films on l	lard storag	ge			186
			7.2.12.2 H	Estimation	of peroxide	e value				186
		7.2.13	Application	n of antiox	idant films	on fresh p	oork			187
		7.2.14	Statistical a	analysis	•					188
	7.3	Results	and discus	sion	10/		62			188
		7.3.1	Effect of a	ntioxidants	concentrat	tions on m	echnical	properti	es	
			of the blen	ded films	町の					188
	1 6	7.3.2	Fourier tran	nsform infr	ared spectr	roscopy (F	T-IR)			191
		7.3.3	X-ray diffr	action patte	erns					193
	1	7.3.4	Thermal pr	operties of	the blende	ed films		3	22	195
		7.3.5	Film morpl	nology					5	198
	80	7.3.6	Water solu	bility of bl	ended film	s		30	6	198
		7.3.7	Water vapo	or transmis	sion rate (V	WVTR) of	blended	films	- //	201
	Ŷ	7.3.8	Total phene	olic assay	J Å					202
		7.3.9	Determinat	ion of anti	oxidant act	ivity in th	e blende	d films		204
		7.3.10	Effect of a	ntioxidants	incorporat	ed into ca	ssava sta	rch-CM	С	
			films on la	rd storage	abec					205
		7.3.11	Effect of an	ntioxidants	incorporat	ed into ca	ssava sta	rch-CM	С	
			films on di	scoloration	of pork					205
	7.4	Conclu	sions							209
	Refere	ences								210
	Chap	ter 8	Future wo	rks and re	ecommend	ations				218
Co	ovr			oy Cl		g Ma			ers	ity
	Curri	culum v	itae	h +	0		0 0			219
AI			I B		S		<b>5</b> e			

## LIST OF TABLES

Tabl	e 0.91813409 8	Page
2.1	Mechanisms of food quality loss	27
2.2	Examples of sachet and film type releasing active packaging	
	systems for preservation and self-life extension of foodstuffs	
	or improving their quality	29
2.3	Natural antioxidants for active food packaging applications	34
3.1	Composition of CMC/cassava starch in 100 mL film solution	66
3.2	Melting temperature and heat of fusion of cassava starch film	,
R	without and with CMC	77
4.1	Composition of film solutions	90
4.2	Melting temperature $(T_m)$ and heat of fusion ( $\Delta H$ ) of cassava starch	
	film without and with gelatin	103
5.1	Composition of film solutions	119
5.2	Sorption isotherm model constants of cassava starch based film with	
	gelatin and CMC plasticized with 30% (w/w) glycerol at 22±1°C	129
6.1	Wavenumbers of FT-IR peaks of cassava-CMC film with and without	
	quercetin (Q) and TBHQ (T)	153
6.2	Melting temperature $(T_m)$ and heat of fusion ( $\Delta H$ ) of cassava	
	starch/gelatin film incorperated with quercetin (Q) and TBHQ (T)	155
7.1	Wavenumbers of FT-IR peaks of cassava-CMC film with and without	
Conv	quercetin (Q) and TBHQ (T)	193
7.2	Melting temperature (T <sub>m</sub> ) and heat of fusion ( $\Delta$ H) of cassava starch-	JILY
	CMC film incorperated with quercetin (Q) and TBHQ (T)	196

## LIST OF FIGURES

Figure	• งามยนติ	Page
1.1	Scheme of experimental design	4
2.1	Structure of (a) starch, (b) cellulose, and (c) CMC	15
2.2	Transparent biodegradable film made from CMC	19
2.3	Structure of (a) BHA, (b) BHT, (c) PG and (d) TBHQ	31
2.4	Structure of qurcetin	35
3.1	FT-IR spectra of cassava starch film with and without CMC.	
50	(a) cassava starch film; (b) cassava starch-10% CMC film;	
70	(c) cassava starch-20% CMC film; (d) cassava starch-30% CMC film;	
	(e) cassava starch-40% CMC film; and (f) CMC film	70
3.2	Effect of CMC concentrations on mechanical properties of the films.	
	(a) tensile strength and (b) elongation at break of cassava based films	
	at 34% and 54% RH	74
3.3	Effect of CMC concentration on cassava starch-CMC blended film	
	solubility at 25°C	76
3.4	DSC thermograms of cassava starch film, blended film and	
	CMC film. (a) control cassava starch film; (b) cassava starch-30% CMC	
	film; and (c) CMC film	78
3.5	SEM observations of cross-sections of cassava starch film, blended	
	film and CMC film. (a) control cassava starch film; (b) cassava starch-	
Convr	30% CMC film; and (c) CMC film at 54% RH	-80
4.1	FTIR spectra of (a) cassava starch film, cassava starch films with	
	(b) 10% gelatin, (c) 20% gelatin, (d) 30% gelatin, (e) 40% gelatin and	
	(f) 100% gelatin film	94
4.2	Effect of gelatin concentration and relative humidity (% RH) on	
	tensile strength (a), and elongation at break (b) of cassava starch	
	based films	97

97

	4.3	Effect of gelatin concentrations on films solubility at 25°C	99
	4.4	SEM observations of cross sections of cassava starch films;	
		(a) cassava starch film, (b) the film with 30% gelatin and (c) gelatin film	100
	4.5	XRD patterns of (a) cassava starch film, (b) cassava starch film +	
		10% gelatin, (c) cassava starch film + 20% gelatin, (d) cassava starch film	
		+ 30% gelatin, (e) cassava starch film + 40% gelatin, and	
		(f) 100% gelatin film	102
	4.6	Thermograms of (a) cassava starch film, (b) cassava starch film +	
		30% gelatin, and (c) gelatin film	104
	5.1	WVPs of cassava starch based films with various amount of	
		(a) gelatin and (b) CMC at 33 and 54% RH, 22±1°C	124
	5.2	Moisture sorption isotherms of 100% cassava starch, CMC, gelatin,	
		and glycerol at 22±1°C	126
	5.3	Moisture sorption isotherms of cassava starch based films plasticized	
		with 30% (w/w) glycerol with and without (a) gelatin and (b) CMC	
		at 22±1°C	128
	5.4	Comparison between experimental moisture content and those predicted	
		by (a) GAB model, (b) BET model and (c) Oswin model of cassava	
		starch films with various gelatin and CMC concentrations	130
	6.1	Effect of antioxidant contents on (a) tensile strength and (b) elongation	
		at break of cassava starch/gelatin films with quercetin (Q) and TBHQ (T)	150
	6.2	FT-IR spectra of cassava starch/gelatin films with (a) quercetin and	
		(b) TBHQ	152
	6.3	DSC thermograms of cassava starch/gelatin films with (a) quercetin and	
		(b) TBHQ	156
Co	6.4	XRD of cassava starch/gelatin films with (a) quercetin (Q) and	itv
		(b) TBHQ (T)	158
	6.5	SEM micrographs of cassava starch/gelatin blended films (a) without	
		antioxidant (x1000), (b) with quercetin (x1000), and (c) with TBHQ	
		(x1000)	159
	6.6	Water solubility of cassava starch/gelatin films with quercetin (Q) and	
		TBHQ (T)	160

xvii

6.7 WVTR of cassava starch- gelatin films with quercetin (Q) and 162 TBHQ (T) 6.8 Effect of aging on total phenolic content of cassava starch/gelatin films with (a) quercetin and (b) TBHQ 163 6.9 Effect of aging on antioxidative activity of cassava starch/gelatin films with quercetin (Q) and TBHQ (T) 164 6.10 Effect of (a) quercetin and (b) TBHQ contents in cassava starch/gelatin films on peroxide value of lard 166 6.11 Effect quercetin and TBHQ content in cassava starch/gelatin films on peroxide value of lard Redness decrease (%) of pork uncovered (control) and covered with cassava starch/gelatin film containing (a) quercetin and (b) TBHQ 168 7.1 Effect of quercetin and TBHQ contents on (a) tensile strength and (b) elongation at break of cassava starch/CMC films at 34 and 54 %RH 190 FT-IR spectra of cassava starch-CMC films with (a) quercetin and 7.2 (b) TBHQ 192 7.3 XRD of cassava starch-CMC films with quercetin and TBHQ 194 DSC thermograms of cassava starch-CMC films with (a) quercetin and 7.4 197 (b) TBHQ 7.5 SEM micrographs of cassava starch-CMC blended films (a) without antioxidant (x1000), (b) with quercetin (x1000), and (c) with TBHQ (x1000) 199 Water solubility of cassava starch-CMC films with quercetin and TBHQ 200WVTR of cassava starch-CMC films with quercetin (Q) and TBHQ (T) 202 Effect of aging on total phenolic content of cassava starch-CMC 7.8 films with (a) quercetin and (b) TBHQ 203

# 7.9 Effect of aging on antioxidative activity of cassava starch-CMC films with quercetin and TBHQ 7.10 Effect (c) and the transmission of transmission o

204

207

7.10 Effect (a) quercetin and (b) TBHQ content in cassava starch-CMC films on peroxide value of lard

xviii

- AL UNIVERSITA
- 7.11 Redness decrease (%) of pork uncovered (control) and covered with cassava starch-CMC film containing (a) quercetin and (b) TBHQ

**ลิขสิทธิ์มหาวิทยาลัยเชียงใหม่** Copyright<sup>©</sup> by Chiang Mai University All rights reserved

208

#### LIST OF ABBREVIATIONS

	лн	Heat of fusion
		American Sector STrating and Material
	ASIM	American Society of Testing and Material
	BET	Brunauer-Emmett-Teller
	СМС	Carboxymethyl cellulose
	DPPH	1,1-diphenyl-2-picrylhydrazyl
	DSC	Differential scanning calorimetry
	EAB	Elongation at break
30%	EMC	Equillibrium moisture content
-563	FT-IR	Fourier transform infrared spectroscopy
200	GAB	Guggenheim-Anderson-deBoer
	Q	Quercetin
	RH	Relative humidity
	RMS	Root mean square
T I	SEM	Scanning electron microscopy
	твно	Tertiary butylhydroquinone
	T <sub>m</sub>	Melting temperature
	TS	Tensile strength
	WVP	Water vapor permeability
	WVTR	Water vapor trasmission rate
	xrd	X-ray diffraction

IJ

Copyright<sup>©</sup> by Chiang Mai University All rights reserved