



# **UNIVERSITI PUTRA MALAYSIA**

EFFECTS OF OIL-DISPERSED PHASE COMPOSITION AND SELECTED POLYSACCHARIDES ON THE PHYSICAL PROPERTIES AND STABILITY OF SOYBEAN-PALM KERNEL OLEIN BLEND OIL-IN-WATER EMULSIONS MODEL SYSTEM

# **NOR HAYATI BINTI IBRAHIM**

FSTM 2008 6

EFFECTS OF OIL-DISPERSED PHASE COMPOSITION AND SELECTED POLYSACCHARIDES ON THE PHYSICAL PROPERTIES AND STABILITY OF SOYBEAN-PALM KERNEL OLEIN BLEND OIL-IN-WATER EMULSIONS MODEL SYSTEM

NOR HAYATI BINTI IBRAHIM

DOCTOR OF PHILOSOPHY UNIVERSITI PUTRA MALAYSIA

2008



### EFFECTS OF OIL-DISPERSED PHASE COMPOSITION AND SELECTED POLYSACCHARIDES ON THE PHYSICAL PROPERTIES AND STABILITY OF SOYBEAN-PALM KERNEL OLEIN BLEND OIL-IN-WATER EMULSIONS MODEL SYSTEM

By

## NOR HAYATI BINTI IBRAHIM

Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia in Fulfillment of the Requirements for the Degree of Doctor of Philosophy

September 2008



To my husband, family, teachers and lecturers



Abstract of thesis presented to the Senate of University Putra Malaysia in fulfilment of the requirement for the degree of Doctor of Philosophy

### EFFECTS OF OIL-DISPERSED PHASE COMPOSITION AND SELECTED POLYSACCHARIDES ON THE PHYSICAL PROPERTIES AND STABILITY OF SOYBEAN-PALM KERNEL OLEIN BLEND OIL-IN-WATER EMULSIONS MODEL SYSTEM

By

#### NOR HAYATI BINTI IBRAHIM

September 2008

Chairman:Professor Yaakob Bin Che Man, PhDFaculty:Food Science and Technology

An oil-in-water (O/W) emulsion is a system that consists of oil droplets dispersed in an aqueous continuous phase. Soybean oil (SBO) is commonly being used as oildispersed phases in many O/W-based food products. The products sometimes exhibit poor physical properties and stability against temperature fluctuations that can be attributed to a high unsaturation degree of SBO. These problems can be reduced by blending of SBO with more saturated oils such as palm kernel olein (PKO). However, crystallizing tendency of PKO at low storage temperatures may lead to partial droplet coalescence, causing destabilization of the emulsion. The use of certain polysaccharides however can reduce this problem and indirectly improve the overall emulsion properties. The objective of this research was to investigate the effects of oil-dispersed phase composition and selected polysaccharides on the physical properties and stability of SBO:PKO blend O/W emulsions model system. In the first stage of this study, the effect of palm kernel olein (PKO) incorporation



on physical properties and stability of O/W emulsions was investigated. Soybean oil and blends of SBO:PKO at 10-40% PKO levels were used as dispersed phases (70%) volume fraction) of egg yolk-stabilized O/W emulsions. The use of PKO caused a significant (p < 0.05) increase in droplet size but a significant (p < 0.05) decrease in rheological properties of the freshly prepared emulsions. With 10-30% PKO replacements, the emulsions were stable after storage at 25°C, most probably promoted by a significant content of C8-C12 fatty acids in PKO. With 30 and 40% PKO replacements, the emulsions were unstable after storage at 5°C due to high solid fat content (14-20%) which caused a severe partial coalescence. This was mainly evidence by increases in droplet equivalent surface mean diameter from 3.65-3.70 µm to 7.80-8.97 µm and decreases in emulsion yield stress from 1.72-1.82 Pa to 0.27-0.30 Pa after 30 days of storage. Throughout the storage, peroxide and anisidine values were found to be lower in the emulsions with PKO incorporated than in the emulsion with fully SBO. Under an accelerated oxidation condition (60°C, 12 days), a calibration model based on a Fourier-transform infrared spectral region (1800-1480 cm<sup>-1</sup>) was developed to predict the peroxide value in oxidized emulsions over the range of 6-45 meq/kg.

In the second stage, physical properties and stability of emulsions as affected by the presence of individually 0.5% (wt/wt) xanthan gum (XG), carboxymethyl cellulose (CMC), guar gum (GG) and locust bean gum (LBG) were evaluated. A blend of SBO:PKO at 30% PKO level was used as a dispersed phase (40% volume fraction) of the emulsions. The microstructure of stored (5°C) XG emulsion showed the presence of partially coalesced droplets, explaining a large increase in its droplet size and the presence of 'free oil' after centrifugation at 3,500 rpm. However,



partially coalesced droplets were not observed in stored CMC, GG and LBG emulsions and no 'free oil' could be separated under centrifugation force. The results support the ability of these polysaccharides in reducing partial coalescence by acting as a protective coating for oil droplets. Blends of XG, CMC and LBG were also prepared according to an augmented simplex-centroid mixture design with 10 points to investigate interaction effects of these polysaccharides on the emulsion rheological properties. The strongest synergistic effect was shown by ternary blends of XG:CMC:LBG at approximately 33-67% XG levels. Yield stress, apparent viscosity, elastic modulus and loss tangent responses were successfully fitted with a special quartic model ( $R^2 > 0.89$ ). Hence, the mixture design with regression modelling approach was shown to be a valuable tool in better elucidating and predicting the interaction effects beyond the two-component blends.



Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Doktor Falsafah

### KESAN KOMPOSISI FASA MINYAK-TERSEBAR DAN POLISAKARIDA TERPILIH KE ATAS CIRI-CIRI FIZIKAL DAN KESTABILAN SISTEM MODEL EMULSI MINYAK-DALAM-AIR BERASASKAN ADUNAN MINYAK SOYA-OLEIN ISIRUNG SAWIT

Oleh

#### NOR HAYATI BINTI IBRAHIM

September 2008

Pengerusi:Profesor Yaakob Bin Che Man, PhDFakulti:Sains dan Teknologi Makanan

Emulsi minyak-dalam-air (O/W) ialah satu sistem yang terdiri daripada titisan-titisan minyak yang tersebar di dalam fasa akuas yang berterusan. Minyak soya (SBO) biasanya digunakan sebagai fasa minyak-tersebar di dalam kebanyakan produk makanan berasaskan emulsi O/W. Produk-produk berkenaan kadang-kala mempamerkan ciri-ciri fizikal dan kestabilan terhadap perubahan suhu yang kurang baik, yang boleh dikaitkan dengan darjah ketidaktepuan SBO yang tinggi. Masalahmasalah tersebut boleh dikurangkan dengan cara mengadunkan SBO dengan minyak yang lebih tepu seperti olein isirung sawit (PKO). Namun demikian, kecenderungan PKO untuk menghablur pada suhu penyimpanan yang rendah boleh membawa kepada percantuman separa titisan minyak, menyebabkan ketidakstabilan emulsi. Penggunaan polisakarida yang tertentu bagaimanapun boleh mengurangkan masalah berkenaan dan secara tidak lasungnya memperbaiki ciri-ciri keseluruhan emulsi.



tersebar dan polisakarida terpilih ke atas ciri-ciri fizikal dan kestabilan sistem model emulsi minyak-dalam-air berasaskan adunan minyak soya-olein isirung sawit. Di peringkat pertama kajian ini, kesan penggunaan olein isirung sawit (PKO) terhadap ciri-ciri fizikal dan kestabilan emulsi O/W telah dikaji. Minyak soya dan adunan-adunan SBO:PKO pada paras 10-40% PKO telah digunakan sebagai fasa tersebar (70% pecahan isipadu) beberapa emulsi yang distabilkan oleh kuning telur. Penggunaan PKO telah menyebabkan peningkatan dan penurunan yang signifikan (p < 0.05), masing-masing pada saiz titisan minyak dan ciri-ciri rheologi emulsiemulsi tersebut. Dengan gantian 10-30% PKO di dalam fasa minyak tersebar, emulsi-emulsi berkenaan didapati stabil selepas disimpan pada suhu 25°C, kemungkinan disumbangkan oleh kandungan asid lemak C8-C12 yang signifikan di dalam PKO. Dengan gantian 30 dan 40% PKO di dalam fasa minyak tersebar, emulsi-emulsi berkenaan didapati tidak stabil selepas disimpan pada suhu 5°C, disebabkan oleh kandungan lemak pepejal yang tinggi (14-20%) di dalam fasa minyak yang tersebar telah menggalakkan percantuman separa titisan-titisan minyak yang ketara. Ini telah dibuktikan terutamanya oleh peningkatan pada min diameter 'equivalent surface' titisan minyak daripada 3.65-3.70 μm kepada 7.80-8.97 μm dan penurunan pada nilai 'yield stress' daripada 1.72-1.82 Pa kepada 0.27-0.30 Pa selepas 30 hari simpanan. Di sepanjang simpanan, nilai-nilai peroksida dan anasidina pada emulsi-emulsi yang mengandungi gantian PKO didapati lebih rendah berbanding dengan emulsi yang mengandungi SBO tulen. Di bawah keadaan pengoksidaan yang dipercepatkan (60°C, 12 hari), satu model kalibrasi telah dibina berasaskan spektrum-spektrum inframerah peralihan-Fourier pada julat gelombang 1800-1480 cm<sup>-1</sup>, untuk meramal nilai peroksida pada julat 6-45 meq/kg yang terdapat di dalam emulsi yang teroksida.



Di peringkat kedua, kesan kehadiran 0.5% (berat/berat) gum xanthan (XG), karboksimetil sellulosa (CMC), gum guar (GG) dan gum kacang locust (LBG) (secara individu) ke atas ciri-ciri dan kestabilan fizikal emulsi telah dikaji. Adunan SBO:PKO pada paras 30% PKO telah digunakan sebagai fasa tersebar (40% pecahan isipadu) emulsi-emulsi tersebut. Selepas simpanan (5°C), mikrostruktur emulsi yang mengandungi XG menunjukkan kehadiran titisan-titisan minyak yang tercantum secara separa. Ini dapat menerangkan peningkatan pada saiz titisan minyak dan juga kehadiran 'minyak bebas' selepas pengemparan pada 3,500 rpm pada emulsi tersebut. Namun demikian, kehadiran 'minyak bebas' di bawah tekanan emparan dan titisan-titisan minyak yang tercantum secara separa tidak dapat dicerap pada emulsi-emulsi yang mengandungi CMC, GG dan LBG. Dengan ini, keputusan yang diperolehi dapat menyokong keupayaan polisakarida-polisakarida tersebut dalam mengurangkan proses percantuman separa dengan bertindak sebagai salutan pelindung kepada titisan-titisan minyak. Selanjutnya, adunan-adunan yang mengandungi XG, CMC dan LBG telah disediakan berpandukan rekabentuk percampuran 'augmented simplex-centroid' untuk mengkaji kesan interaksi polisakarida-polisakarida berkenaan ke atas ciri-ciri rheologi emulsi. Kesan sinergi yang paling kuat telah ditunjukkan oleh adunan pertigaan XG:CMC:LBG, pada paras XG secara kasarnya sebanyak 33-67%. Data-data 'yield stress', kelikatan, modulus elastik dan 'loss tangent' telah berjaya dipadankan dengan model 'special quartic' ( $R^2 > 0.89$ ). Maka, rekabentuk percampuran bersama pemodelan regrasi ini merupakan satu pendekatan yang berguna bagi meramal dan memahami dengan lebih jelas kesan-kesan interaksi di kalangan polisakarida-polisakarida, selain daripada adunan-adunan dua komponen.



#### ACKNOWLEDGEMENTS

My deepest appreciation goes to my academic supervisors, Prof. Dr. Yaakob bin Che Man, Dr. Tan Chin Ping and Dr. Nor Aini Idris (Malaysian Palm Oil Board) for their support, encouragement and friendship throughout my study. It is their valuable advice and great patience that has made my doctoral research a reality.

I would like to enthusiastically thank all the lecturers who have involved in my postgraduate courses and also to the staffs and students of Faculty of Food Science and Technology for their assistance and friendship.

I would like to acknowledge the PhD Scholarship from Universiti Malaysia Terengganu for making this doctoral program possible for me. This research was also partly financed by IRPA grants no. 09-02-04-0457-EA001 (Prof. Dr. Yaakob bin Che Man) and 54260 (Dr. Tan Chin Ping) of Universiti Putra Malaysia. This acknowledgement is also extended to Malaysian Palm Oil Board and Research Instruments (Malaysia) Sdn. Bhd. for the scientific instrument support.

Finally, my appreciation also goes to my beloved husband and family for their love, patience, understanding and support.



I certify that an Examination Committee has met on 23<sup>rd</sup> September 2008 to conduct the final examination of Nor Hayati Binti Ibrahim on her Doctor of Philosophy thesis entitled "Effects of Oil-Dispersed Phase Composition and Selected Polysaccharides on Physical Properties and Stability of Soybean-Palm Kernel Olein Blend Oil-in-Water Emulsions Model System" in accordance with Universiti Pertanian Malaysia (Higher Degree) Act 1980 and Universiti Pertanian Malaysia (Higher Degree) Regulations 1981. The Committee recommends that the student be awarded the relevant degree.

Members of the Examination Committee were as follows:

#### Alejandro G. Marangoni, PhD

Professor Food and Soft Materials Science University of Guelph, Canada (External Examiner)

#### Hasanah Mohd. Ghazali, PhD

Professor and Deputy Dean School of Graduate Studies Universiti Putra Malaysia (Internal Examiner 1)

### Zulkefly Kuang Bin Abdullah, PhD

Professor Faculty of Science Universiti Putra Malaysia (Internal Examiner 2)

HASANAH MOHD. GHAZALI, PhD

Professor and Deputy Dean School of Graduate Studies Universiti Putra Malaysia

Date:



This thesis was submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfilment of the requirement for the degree of Doctor of Philosophy. The members of the Supervisory Committee were as follows:

#### Yaakob Bin Che Man, PhD

Professor Faculty of Food Science and Technology Universiti Putra Malaysia (Chairman)

#### Tan Chin Ping, PhD

Lecturer Faculty of Food Science and Technology Universiti Putra Malaysia (Member)

#### Nor Aini Idris, PhD Head

Food Technology & Nutrition Unit Product Development & Advisory Services Division Malaysian Palm Oil Board (Member)

> HASANAH MOHD. GHAZALI, PhD Professor and Dean

School of Graduate Studies Universiti Putra Malaysia

Date: 19 December 2008



## DECLARATION

I declare that the thesis is my original work except for quotations and citations which have been dully acknowledged. I also declare that it has not been previously, and is not concurrently, submitted for any other degree at Unversiti Putra Malaysia or at any other institution.

## NOR HAYATI BINTI IBRAHIM

Date:



# TABLE OF CONTENTS

# Page

DEDICATION	ii
ABSTRACT	iii
ABSTRAK	vi
ACKNOWLEDGEMENTS	ix
APPROVAL	Х
DECLARATION	xii
LIST OF TABLES	xvii
LIST OF FIGURES	XX
LIST OF ABBREVIATIONS	xxxi

## CHAPTER

1	INT	INTRODUCTION			
	1.1	Backgro	ound and Justifications	1	
	1.2	Objectiv	ves	6	
2	LIT	LITERATURE REVIEW			
	2.1	Emulsic	on – Definition, Rheology and Stability	8	
		2.1.1	Oil-in-water (O/W) Emulsion	10	
		2.1.2	Rheological Properties of O/W Emulsion	11	
		2.1.3	Emulsion Stability - Mechanism and	19	
			Types of Instability		
		2.1.4	Relationship between Rheology and	22	
			Physical Stability of O/W Emulsion		
	2.2	Fat Crys	stallization in O/W Emulsion	23	
		2.2.1	Mechanism and Measurement of Fat	23	
			Crystallization		
		2.2.2	Influential Factors for Fat Crystallization	30	
	2.3	Lipid O	xidation in O/W Emulsion	35	
		2.3.1	Mechanism and Measurement of Lipid	35	
			Oxidation		
		2.3.2	Influential Factors for Lipid Oxidation	47	
	2.4	Polysac	charides in O/W Emulsion	55	
		2.4.1	Stabilization Effect of Polysaccharides	60	
		2.4.2	Destabilization Effect of Polysaccharides	65	
		2.4.3	Synergistic Interaction among	68	
			Polysaccharides		
	2.5	Soybear	n Oil and Palm Kernel Olein	73	
		2.5.1	General Introduction	73	
		2.5.2	Physicochemical Characteristics	76	
3	PHY	SICOC	HEMICAL CHARACTERISTICS OF	80	
			NEL OLEIN, SOYBEAN OIL AND		
	TH	EIR BIN	ARY BLENDS		
	3.1	Introduc	ction	80	



3.2	Materia	ls and Methods	82
	3.2.1	Materials and Oil Blends Preparation	82
	3.2.2	Fatty Acid Composition Analysis	82
	3.2.3	Triacylglycerol Analysis	83
	3.2.4	Iodine Value Analysis	84
	3.2.5	Solid Fat Content Analysis	84
	3.2.6	Fourier-transform Infrared Spectra	85
		Acquisition	
3.3	Results	and Discussion	86
	3.3.1	Chemical Composition	86
	3.3.2	Iodine Value and Solid Fat Content	90
		Profile	
	3.3.3	Fourier-transform Infrared Spectra	92
	3.3.4	PLS Calibration Models for IV and SFC	98
		Prediction of the Oil Blends	
3.4	Conclus	sions	101
		BEHAVIOUR OF SOYBEAN OIL	103
		RNEL OLEIN BLENDS AND THEIR	
		TER EMULSIONS	100
4.1			103
4.2		ls and Methods	107
	4.2.1	Materials	107
	4.2.2	Emulsion Preparation	107
	4.2.3	Thermal Analysis	108
	4.2.4	Statistical Analysis	109
4.3		and Discussion	109
	4.3.1	Thermal Behaviour of Bulk oil and Oil Blends	109
	4.3.2	Thermal Behaviour of O/W Emulsions	120
		and Effect of Thermal Cycle on Their	
4 4	Constant	Stability	100
4.4	Conclus	sions	133
рн	VSICAL	PROPERTIES AND STABILITY OF	135
		OIL /PALM KERNEL OLEIN OIL-IN-	
		IULSIONS	
5.1	Introdu	ction	135
5.2	Materia	ls and Methods	138
	5.2.1	Materials and Emulsion Preparation	138
	5.2.2	Storage Procedure	138
	5.2.3	Droplet Size Distribution Analysis	138
	5.2.4	Rheological Analyses	140
	5.2.5	Microstructure Observation	142
	5.2.6	Centrifugation Assay	142
	5.2.7	Oxidation Procedures	142
	5.2.8	Chemical Oxidation Analyses	142
	5.2.9	Fatty Acid Composition Analysis	143
	5.2.10	FTIR Spectra Acquisition, Calibration	144
	5.2.10	Development and Validation	144
		Development and vanuation	

4

5



	5.2.111	Statistical Analysis	145
5.3	Results	and Discussions	146
	5.3.1	Droplet Size Distribution	146
	5.3.2	Flow Behaviour	158
	5.3.3	Viscoelastic Behaviour	165
	5.3.4	Droplet Microstructure	172
	5.3.5	Phase Separation	175
	5.3.6	Oxidative Stability under Normal Storages	185
	5.3.7	FTIR-prediction of Peroxide Value under	198
		an Accelerated Storage	
5.4	Conclu	sions	210
PH	YSICAL	PROPERTIES AND STABILITY OF	211
SO	YBEAN	OIL /PALM KERNEL OLEIN O/W	
EM	ULSIO	NS – INDIVIDUAL EFFECT	
		TED POLYSACCHARIDES	
	Introdu		211
6.2		als and Methods	213
	6.2.1	Materials	213
	6.2.2	Polysaccharide Dispersion Preparation	214
	6.2.3	L	214
	6.2.4	Emulsion Characterization	215
	6.2.5	Statistical Analysis	216
6.3		and Discussion	216
	6.3.1	Thermal Behaviour and Effect of Thermal	216
		Cycle on Emulsion Stability	
	6.3.2	Droplet Size Distribution	227
	6.3.3	Flow Behaviour	234
	6.3.4	Viscoelastic Behaviour	239
	6.3.5	Droplet Microstructure	244
	6.3.6	Phase Separation	248
6.4	Conclu	sions	253
		ICAL STUDY OF SOYBEAN OIL/	255
		RNEL OLEIN EMULSIONS AS D BY XANTHAN GUM,	
		METHYL CELLULOSE AND LOCUST	
		<b><i>I</i></b> INTERACTIONS USING A MIXTURE	
		PPROACH	
7.1	Introdu		255
7.2		als and Methods	259
	7.2.1	Materials	259
	7.2.2	Preparation of Polysaccharides Blends	259
	7.2.3	Emulsion Preparation and Rheological Analyses	260
	7.2.4	Experimental Design and Statistical Analysis	260
7.3	Results	and Discussion	264
	7.3.1	Experimental Rheological Responses	264
	7.3.2	Fitted Regression Models, Contour and	274
		-	



	Surface Plots 7.3.3 Model Validation 7.4 Conclusions	289 291
8	SUMMARY, CONCLUSION AND RECOMMENDATIONS FOR FUTUR RESEARCH	292 E
REFERE		297
APPEND		320
-	A OF STUDENT	338
LIST OF	PUBLICATIONS	339



## LIST OF TABLES

Table		Page
2.1	Rheological Models Describe the Flow Behaviour of Concentrated Emulsions Applied by Selected Current Researches	16
2.2	List of Selected References (Published in 2000 and Onwards) on Lipid Oxidation Determination in O/W Emulsions	40
2.3	Important Infrared Band Assignments of Model Compound Emulsions	46
2.4	Properties of Selected Polysaccharides	59
2.5	Elastic Component, Viscous Component and Elastic Yield Stress of Selected Polysaccharides Measured at 4°C and 50 s <sup>-1</sup> as Determined by an Oscillating Capillary Rheometer	60
2.6	Selected Current Publications on the Role of Xanthan Gum in Promoting the Emulsion Stability through a Rheological Control	62
2.7	Physicochemical Characteristics of Soybean Oil and Palm Kernel Olein	77
3.1	Fatty Acid Composition (% Peak Area) of Soybean Oil and Palm Kernel Olein as Determined by Gas Chromatograph	87
3.2	Iodine Value (IV) and Solid Fat Content (SFC) (as Determined by a Pulsed Nuclear Magnetic Resonance) for Soybean Oil and Palm Kernel Olein (SBO:PKO) Blends	91
3.3	Infrared Band Assignments of Soybean Oil (SBO) and Palm Kernel Olein (PKO) as Fully Referred to the Work Done by Yang and Irudayaraj (2000)	97
3.4	Cross-Validation Results from Partial Least Squares (PLS) Models for % of Palm Kernel Olein Prediction	98
3.5	Cross-Validation Results from Partial Least Squares (PLS) Models for Iodine Value (IV) and Solid Fat Content (SFC) Prediction	99



4.1	Differential Scanning Calorimetry Crystallization Parameters of Soybean Oil, Palm Kernel Olein and Their Binary Blends (SBO:PKO) Determined at a Scanning Rate of 10°C/min	111
4.2	Differential Scanning Calorimetry Melting Parameters of Soybean Oil, Palm Kernel Olein and Their Binary Blends (SBO:PKO) Determined at a Scanning Rate of 10°C/min	116
5.1	Droplet Mean Diameters $(\mu m)$ of Freshly Prepared Emulsions	147
5.2	Droplet Mean Diameters (µm) of Stored Emulsions (25°C, 30 Days)	152
5.3	Droplet Mean Diameters (µm) of Stored Emulsions (10°C, 30 Days)	154
5.4	Droplet Mean Diameters (µm) of Stored Emulsions (5°C, 30 Days)	156
5.5	Modelling of the Flow Curve between 1 and 100 s <sup>-1</sup> of Shear Stress of Freshly Prepared Emulsions using Herschel-Bulkley Model: $\sigma = \sigma_0 + K\gamma^n$	160
5.6	Modelling of the Flow Curve between 1 and 100 s <sup>-1</sup> of Shear Stress of Stored (25°C, 30 Days) Emulsions using Herschel-Bulkley Model: $\sigma = \sigma_0 + K\gamma^n$	163
5.7	Modelling of the Flow Curve between 1 and 100 s <sup>-1</sup> of Shear Stress of Stored Emulsions (10°C, 30 Days) using Herschel-Bulkley Model: $\sigma = \sigma_0 + K\gamma^n$	164
5.8	Modelling of the Flow Curve between 1 and 100 s <sup>-1</sup> of Shear Stress of Stored Emulsions (5°C, 30 Days) using Herschel-Bulkley Model: $\sigma = \sigma_0 + K\gamma^n$	165
5.9	Elastic (G') and Viscous (G") Moduli of Stored (30 Days) Emulsions at 1 Hz	170
5.10	Total Oxidation (Totox) Value of Emulsions Stored at 25°C	193
5.11	Total Oxidation (Totox) Value of Emulsions Stored at 5°C	193
5.12	Fatty Acid Composition (%) of Oil Phases Extracted from Fresh and Oxidized Emulsions Stored at 25°C	196



for 30 Days

5.13	Important Infrared Band Assignments of Emulsions	201
5.14	Calibration and Cross-Validation Results from Partial Least Square (PLS) Models for Peroxide Value Prediction	207
6.1	Droplet Mean Diameters $(\mu m)$ of Freshly Prepared Emulsions	228
6.2	Droplet Mean Diameters (µm) of Stored (5°C, 30 Days) Emulsions	232
6.3	Modelling of the Flow Curve between 1 and 100 s <sup>-1</sup> of Shear Stress of Freshly Prepared Emulsions using Herschel-Bulkley Model: $\sigma = \sigma_0 + K\gamma^n$	236
6.4	Modelling of the Flow Curve between 1 and 100 s <sup>-1</sup> of Shear Stress of Stored (5°C, 30 Days) Emulsions using Herschel-Bulkley Model: $\sigma = \sigma_0 + K\gamma^n$	237
7.1	An Augmented Simplex Centroid Design with Ten Ratios of Xanthan Gum $(X_1)$ , Carboxlymethyl Cellulose $(X_2)$ and Locust Bean Gum $(X_3)$ Blends and Rheological Responses of the Respective Emulsion	262
7.2	Analysis of Variance of Model Fits	275
7.3	Estimated Regression Coefficients (with Reduced Terms) and Adjusted Coefficient of Determination $(R^2)$ of Model Fits	276
7.4	Predicted Value for Responses of Emulsions with New Component Proportions as Compared to Actual Value	290



## LIST OF FIGURES

Figure		Page
2.1	Typical Dimensions of Structural Entities Commonly Found in Emulsion-based Food Products	9
2.2	A Shear-thinning Behaviour of an Emulsion that Contains Flocculated Droplets with Deformation and Disruption of Flocculated Droplets in the Shear Field	13
2.3	Viscosity Profiles (at 25°C) of Mayonnaise-type Emulsions with Different Formulation i.e. F1 (0.10/0.20/0.70), F2 (0.20/0.20/0.60), F3 (0.10/0.25/0.65), F4 (0.20/0.25/0.55), and F5 (0.15/0.225/0.625) with the Proportion Refers to Water/Soybean Oil/Banana Green Pulp	14
2.4	Evolution of the Storage ( $G'$ ) and Loss ( $G''$ ) Moduli as a Function of Frequency for Salad Dressing-type Emulsions Stabilized by 8% Egg Yolk and 2% Starch, with Different Salt Concentration	17
2.5	Schematic Diagram of Emulsion Instability through Various Physical Mechanisms	19
2.6	Micrograph of a Confectionery Coating Fat Emulsion during Cooling Observed under Polarized Light	25
2.7	Diagrams Illustrating the Process Shown in Figure 2.6	25
2.8	Typical Thermograms of (a) n-Hexadecane and (b) Confectionery Coating Fat Recorded at 1.5°C/min. (1) Emulsified Fat; (2) A Mixture of Emulsified and Bulk Fat (3) Bulk Fat	28
2.9	Primary Structure of Xanthan Gum with Functional Trisaccharide Group	57
2.10	Primary Structure of Carboxymethyl Cellulose with Functional Carboxymethyl Group	57
2.11	Primary Structure of Guar Gum with Functional Galactose Group	58
2.12	Primary Structure of Locust Bean Gum with Functional Galactose Group	58



2.13	Droplet Microstructures of 40% Sunflower Oil-in- water Emulsions Stabilized with 1% $\beta$ - Lactoglobulin, Demonstrating (a) Bridging Flocculation at pH 3 and (b) Depletion Flocculation at pH 6	68
3.1	High Performance Liquid Chromatography Triacylglycerols Profiles for (a) Soybean Oil and (b) Palm Kernel Olein. Ca, C, La, M, P, S, O, L, and Ln Represent Caprlic, Capric, Lauric, Myristic, Palmitic, Stearic, Oleic, Linoleic and Linolenic Acids, Respectively	89
3.2	Fourier Transform Infrared Spectra of Soybean Oil and Palm Kernel Olein. Numbers of the Bands Assigned Refer to Table 3.2. The Absorbance Scale was Normalized	94
3.3	Fourier-Transform Infrared Spectra of Soybean Oil (A) And Palm Kernel Olein (J) and Their Binary Blends (B-I). The Absorbance Scale was Normalized	95
3.4	Evolution of Representative Spectra of Soybean Oil and Palm Kernel Olein Blends (A-I) in the Region 3500-2500 cm <sup>-1</sup> Range. IV, Iodine Value; SFC, Solid Fat Content at 5°C. The Absorbance Scale was Normalized	101
4.1	Differential Scanning Calorimetry Crystallization Thermograms of Soybean Oil (A), Palm Kernel Olein (J) and their Binary Blends (Code B to I) Determined at a Scanning Rate of 10°C/min. The Thermograms are Presented in Normalized Scale	110
4.2	Differential Scanning Calorimetry Melting Thermograms of Soybean Oil (A), Palm Kernel Olein (J) and their Binary Blends (Code B To I) Determined at a Scanning Rate of 10°C/min. The Thermograms are Presented in Normalized Scale	115
4.3	Differential Scanning Calorimetry Cooling (A) and Melting (B) Thermograms (Original) of Fully Soybean Oil Emulsion, Determined at a Scanning Rate of 10°C/min	122
4.4	Differential Scanning Calorimetry Cooling (A) and Melting (B) Thermograms of Fully Soybean Oil Emulsion (SBOE) in the Dispersed Phase Volume Fraction, after Three Successive Cool-Heat Cycles at a Scanning Rate of 10°C/min. The Thermograms are	124



Presented in Normalized Scale

4.5	Differential Scanning Calorimetry Cooling (A) and Melting (B) Thermograms of Emulsion Containing 10% Palm Kernel Olein in the Dispersed Phase Volume Fraction (10PKOE), after Three Successive Cool-Heat Cycles at a Scanning Rate of 10°C/min. The Thermograms are Presented in Normalized Scale	125
4.6	Differential Scanning Calorimetry Cooling (A) and Melting (B) Thermograms of Emulsion Containing 20% Palm Kernel Olein in the Dispersed Phase Volume Fraction (20PKOE), after Three Successive Cool-Heat Cycles at a Scanning Rate of 10°C/min. The Thermograms are Presented in Normalized Scale	126
4.7	Differential Scanning Calorimetry Cooling (A) and Melting (B) Thermograms of Emulsion Containing 30% Palm Kernel Olein in the Dispersed Phase Volume Fraction (30PKOE), after Three Successive Cool-Heat Cycles at a Scanning Rate of 10°C/min. The Thermograms are Presented in Normalized Scale	130
4.8	Differential Scanning Calorimetry Cooling (A) and Melting(B) Thermograms of Emulsion Containing 40% Palm Kernel Olein in the Dispersed Phase Volume Fraction (40PKOE), after Three Successive Cool-Heat Cycles at a Scanning Rate of 10°C/min. The Thermograms are Presented in Normalized Scale	131
5.1	Droplet Size Distribution of Freshly Prepared Emulsions. Data Points are Presented in Average of Three Replications with Maximum Standard Deviation of 0.5%. SBOE, 100% Soybean Oil Emulsion, 10PKOE-40PKOE, Emulsions Containing 10–40% Palm Kernel Olein Replacements in the Dispersed Phase Volume Fraction, Accordingly	147
5.2	Droplet Size Distribution of Stored Emulsions (25°C, 30 Days). Data Points are Presented in Average of Three Replications with Maximum Standard Variation of 0.9%. See Figure 5.2 for Abbreviation of the Samples	152
5.3	Droplet Size Distribution of Stored Emulsions	154



(10°C, 30 Days). Data Points are Presented in Average of Three Replications with Maximum Standard Variation of 0.5%. See Figure 5.2 for Abbreviation of the Samples

5.4	Droplet Size Distribution of Stored Emulsions (5°C, 30 Days). Data Points are Presented in Average of Three Replications with Maximum Standard Variation of 0.8%. See Figure 5.1 For Abbreviation of the Samples	156
5.5	Percent of Coalescence and Flocculation (C+F)% The Emulsions Stored for 30 Days at Different Temperature. Data are Presented in Average of Three Replications with Maximum Standard Variation of 2%. <sup>a-e</sup> Means with the Same Small Letter within the Same Temperature are Not Significantly Different (p < 0.05). See Figure 5.1 for Abbreviation of the Samples	158

- 5.6 Rheogram (Raw Data) of Selected Freshly Prepared 160 Emulsions Representing the Evolution of Viscosity ( $\eta$ ) as a Function of Shear Rate ( $\gamma$ ). See Figure 5.1 for Abbreviation of the Samples
- 5.7 Representative Flow Curve (Shear Stress vs. Shear Rate) of Freshly Prepared Emulsion Containing 100% Soybean Oil (SBOE) Fitted with Herschel-Bulkley Model
- 5.8 Representative Rheogram of Freshly Prepared 166
  Emulsion with 100% Soybean Oil from Strain Sweep Experiment at Frequency 1 Hz. G', Storage Modulus; G", Loss Modulus; γ, Strain. See Figure 5.1 for Abbreviation of the Samples
- 5.9 Selected Rheograms of Freshly Prepared Emulsions
  from Frequency Sweep Experiment at 0.5% Strain.
  G', Storage Modulus; G", Loss Modulus; f,
  Frequency. See Figure 5.1 for Abbreviation of the
  Samples
- 5.10 Storage (G') and Loss (G") Moduli of Freshly 169 Prepared Emulsions Obtained from Frequency Sweep Experiment at 0.5% Strain. Data are Presented in Average of Three Replications with Maximum Standard Variation Of 1.2, 0.6 Pa for G' and G", Respectively. <sup>A-D, a-b</sup> Means with the Same Capital or Small Letter are Not Significantly Different (p < 0.05). See Figure 5.1 for Abbreviation of the Samples



161