



UNIVERSITI PUTRA MALAYSIA

**PROPERTIES OF FRYING SHORTENING PREPARED FROM
LIPASE-TRANSESTERIFIED PALM STEARIN
AND PALM KERNEL OLEIN BLEND**

TEE SIOK BEE

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**MASTER OF SCIENCE
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LIPASE-CATALYZED TRANSESTERIFIED PALM STEARIN
AND PALM KERNEL OLEIN BLEND**

By

TEE SIOK BEE

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PROPERTIES OF FRYING SHORTENING PREPARED FROM LIPASE-TRANSESTERIFIED PALM STEARIN AND PALM KERNEL OLEIN BLEND

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July 2001

Chairman : Professor Hasanah Mohd. Ghazali, Ph. D.
Faculty : Food Science and Biotechnology

Transesterification process is a vital tool to tailor-make *trans*-free fats and oils products. Palm stearin (PS) is the solid fraction of palm oil, while palm kernel olein (PKO) is the liquid fraction extract from the palm kernel. The combination of this hard stock and the liquid oil in a transesterification process may result in the production of a *trans*-free plastic frying shortening that can replace the conventional hydrogenated base product. This study was conducted to produce a *trans*-free frying shortening from PS:PKO blend, via transesterification process using the lipase from *Rhizomucor miehei* (Lipozyme IM60, Novo Nordisk, Denmark).

The physical and chemical properties of five domestic and imported plastic frying shortenings were analysed so as to obtain information on the functional characteristics of a typical plastic frying shortening. By taking the plastic range of the samples at solid fat content (SFC) of 15-25%, the imported samples (Samples D and E) fell in the lower temperature range (11-26°C) compared to domestic sample (Samples A, B and C) (21-40°C).



The PS:PKO (w/w) (1:4, 3:7, 2:3, 1:1 and 3:2) blends were transesterified using Lipozyme IM60 lipase at 60°C for 6 h. Results showed that the plastic range of all PS:PKO blends shifted to a lower temperature range as the PKO level increased in the blends. For each of the PS:PKO blends, transesterification also shifted their plastic range to a lower range as compared to their respective control blends.

Transesterification utilized the short carbon chains TG (such as LaDD, LaLaD, LaLaM and LaMM) and long carbon chain TG (such as PPP, PPS and POS) to produce TG with the carbon chains that fell within the two ranges. The alteration in TG composition of PS:PKO blends through enzymatic transesterification had led to the changes in their slip melting point (SMP), SFC, polymorphic form, crystallisation and melting behaviour, especially at high temperature range (35-40°C) and therefore explained the improvement in their plastic range. Result of the increase in medium chains TG *via* transesterification was also exhibited by the change in the melting behaviour. In their melting behaviour studies, results showed that the higher melting temperature TG was found to reduce corresponding to the increase in the lower melting temperature TG. However, the polymorphic forms of the transesterified samples remained largely unchanged.

As the PS level increased in the blends, the concentration of TG with longer chains FA (such as PPP, PPS and POS) also increased, resulting in the increase in SMP and SFC levels, especially at the high temperature ranges (35-40°C). Similar changes were also found in their crystallisation and melting behaviour studies. The polymorphic forms of the PS:PKO blends also changed as the PS level increased. The higher the PS level, the more β' dominating the sample became.



In the rheological studies, the viscoelasticity (VE) for both commercial and test shortenings were studied. The maximum stress of the samples was found to increase with the increase in SMP and SFC. Transesterification process shifted the maximum yield stress of all PS:PKO blends to a higher level yield value. This may be related to their β' dominating polymorphic forms, which has a higher retention capacity for oil.

In summary, transesterification transformed the 2:3 (w/w) and 3:2 (w/w) PS:PKO blends into firmer textured plastic shortenings, which are similar to commercial shortenings Sample A and B, respectively. The findings in this study provide a better understanding on commercial plastic frying shortening for production of similar products in the industries.



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**CIRI-CIRI LELEMAK PENGOORENGAN YANG DIHASILKAN MELALUI
TRANSESTERIFIKASI CAMPURAN STEARIN KELAPA SAWIT DENGAN
MINYAK OLEIN ISIRONG KELAPA SAWIT OLEH LIPASE**

Oleh

TEE SIOK BEE

Julai 2001

Pengerusi : Professor Hasanah Mohd. Ghazali, Ph. D.
Fakulti : Food Science and Biotechnology

Transesterifikasi adalah suatu cara untuk menghasilkan produk lemak ang tanpa asid lemak *trans*. Stearin kelapa sawit (PS) ialah bahagian pejal minyak sawit, manakala minyak olein isirong kelapa sawit (PKO) ialah bahagian cecair yang diekstrak daripada isirong kelapa sawit. Pencampuran lemak pejal dan minyak PKO melalui proses transesterifikasi boleh menghasilkan lemak penggorengan yang tanpa asid lemak *trans*. LelemaK penggorengan ini dapat menggantikan lelemaK penggorengan yang disediakan dengan kaedah lama iaitu melalui penghidrogenan. Tujuan kajian ini adalah untuk menghasilkan lelemaK penggorengan tanpa asid lemak *trans* daripada campuran PS:PKO melalui proses transesterifikasi dengan lipas dari *Rhizomucor miehei* (Lipozyme IM60, Novo Nordisk, Denmark).

Ciri-ciri fizikal dan kimia lima lelemaK penggorengan komersial dari dalam dan luar negara (Sampel A, B, C, D dan E) telah dikaji untuk memahami dan mendapatkan maklumat tentang cirri-ciri lelemaK penggorengan yang tipikal. Dengan menganggap julat



plastik lemak penggorengan adalah dalam lingkungan 15-20% kandungan lemak pejal (SFC), sample-sample import (Sampel D dan E) didapati wujud dalam lingkungan suhu yang lebih rendah (11-26°C) berbanding dengan sample-sample tempatan (21-40°C) (Sampel-sample A, B dan C).

Campuran PS:PKO (w/w) (1:4, 3:7, 2:3, 1:1 dan 3:2) telah ditransesterifikasi dengan menggunakan lipase Lipozyme IM60 pada suhu 60°C selama 6 jam. Keputusan menunjukkan julat plastik bagi semua campuran PS:PKO berubah kepada lingkungan suhu rendah sejajar dengan penambahan PKO. Bagi semua sample campuran PS:PKO, julat plastiknya berubah ke suhu yang lebih rendah berbanding dengan sample kawalan campuran PS:PKO masing-masing.

Transesterifikasi menghidrolisiskan trigliserida (TG) dengan asid lemak rantai pendek (seperti LaDD, LaLaD, LaLaM, dan LaMM) dan TG dengan asid lemak berantai panjang (seperti PPP, PPS dan POS) untuk menghasilkan TG dengan panjang rantai lemak yang jatuh di antara kedua-dua tersebut. Perubahan pada komposisi TG dalam campuran-campuran PS:PKO yang telah ditransesterifikasi oleh enzim telah menyebabkan perubahan pada takat lebur (SMP), SFC, bentuk hablur, proses pembentukan hablur dan sifat-sifat peleburan, terutamanya pada julat suhu yang tinggi (35-40°C) dalam sample-sample. Dalam pengajian sifat-sifat peleburan sample-sample tersebut, keputusan menunjukkan TG bertakat lebur tinggi di dapati berkurangan sejajar dengan peningkatan dalam TG bertakat lebur rendah. Walau bagaimanapun, perubahan komposisi TG tidak membawa perubahan yang nyata dalam bentuk hablur yang diperolehi selepas transesterifikasi.

Apabila kadar PS dalam campuran PS:PKO meningkat, kepekatan TG berantai panjang (seperti PPP, PPS dan POS) juga meningkat. Ini mengakibatkan peningkatan dalam nilai SMP dan SFC, terutamanya pada lingkungan suhu yang tinggi (35-40°C). Perubahan yang sama juga berlaku pada sifat pembekuan dan peleburan. Bentuk hablur campuran PS:PKO juga berubah apabila kandungan PS meningkat. Campuran yang mengandungi kandungan PS yang tinggi cenderung membentuk hablur dengan β' sebagai hablur yang dominan.

Dalam kajian rheologi, kelakuan viscoelastik (VE) bagi sample-sample komersial dan sampel-sampel kajian telah dijalankan. Nilai tekanan maksimum didapati berkadar terus dengan nilai-nilai SMP dan SFC. Transesterifikasi meningkatkan nilai tekanan maksimum campuran PS:PKO. Ini mungkin disebabkan oleh kehadiran hablur β' yang mempunyai kapasiti untuk memerangkap minyak.

Secara keseluruhan, transesterifikasi telah menukar campuran PS:PKO dengan nisbah 2:3 (w/w) dan 3:2 (w/w) kepada lemak penggorengan yang mempunyai tekstur seakan-akan sampel komersial A dan B. Maklumat yang diperolehi daripada kajian ini boleh digunakan sebagai panduan menghasilkan lemak penggorengan produk-produk lain yang serupa dalam industri.

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LIST OF TABLES

Table		Page
1.	Grade of palm stearin (PS)	7
2.	Physical and chemical properties of palm stearin	8
3.	Triacylglycerol (TG) composition of palm kernel olein	9
4.	Physical and chemical properties of palm kernel olein	10
5.	Classes of microbial lipases	16
6.	Typical X-ray short spacing for α , β' and β polymorphs.	35
7.	Fatty acid (FA) composition of five commercial plastic frying shortenings and their high melting glycerides (HMG).	55
8.	X-ray Diffraction (XRD) pattern and polymorphic forms of the five commercial plastic frying shortenings.	65
9.	Slip melting point (SMP), melting point determined by DSC, crystallization temperatures and iodine value (IV) of five commercial plastic frying shortenings.	71
10.	Fatty acids (FA) composition (% peak area) of palm stearin (PS) and palm kernel olein (PKO).	76
11.	Fatty acids (FA) composition (% peak area) of transesterified PKO at different transesterification time (h).	77
12.	Fatty acids (FA) composition (% peak area) of transesterified palm stearin (PS) at different transesterification times (h).	78
13.	Fatty acids (FA) composition (% peak area) of transesterified palm stearin:palm kernel olein (PS:PKO) blends (w/w).	79
14.	Fatty acids (FA) composition (% peak area) of high melting glycerides (HMG) of five transesterified palm stearin:palm kernel olein (PS:PKO) blends (w/w).	80
15.	Triacylglycerol (TG) composition (% peak area) of transesterified palm kernel olein (PKO) at different transesterification time (h).	84
16.	Triacylglycerol (TG) composition (% peak area) of transesterified palm stearin (PS) at different transesterified time (h).	85



17.	Triacylglycerol (TG) composition (% peak area) of transesterified palm stearin:palm kernel olein (PS:PKO) blends (w/w) and their control.	92
18.	Triacylglycerol (TG) composition by degree of saturation of transesterified palm stearin:palm kernel olein (PS:PKO) blends (w/w) and their control.	93
19.	Triacylglycerol (TG) composition (% peak area) of high melting glycerides (HMG) of transesterified palm stearin:palm kernel olein (PS:PKO) blends (w/w) and their control.	95
20.	Triacylglycerol (TG) composition (% peak area) by degree of saturation of high melting glycerides (HMG) of transesterified palm stearin:palm kernel olein (PS:PKO) blends (w/w) and their control.	96
21.	Phase transitions of heating thermograms determined by Differential Scanning Calorimetry (DSC) for transesterified palm kernel olein (PKO) at different transesterification time (h).	100
22.	Phase transitions of heating thermograms determined by Differential Scanning Calorimetry (DSC) for transesterified palm stearin (PS) at different transesterification time (h).	102
23.	Phase transitions of determined by Differential Scanning Calorimetry (DSC) for five 6 h transesterification palm stearin:palm kernel olein (PS:PKO) blends (w/w).	106
24.	Phase transitions of determined by Differential Scanning Calorimetry (DSC) for the high melting glycerides (HMG) of 6 h transesterification palm stearin:palm kernel olein (PS:PKO) blends (w/w).	108
25.	Crystallisation temperature from cooling thermogram determined by Differential Scanning Calorimetry (DSC) for transesterified palm kernel olein (PKO) at different transesterification time (h).	112
26.	Crystallisation temperature from cooling thermogram determined by Differential Scanning Calorimetry (DSC) for transesterified palm stearin (PS) at different transesterification time (h).	113
27.	Crystallisation temperature from cooling thermogram determined by Differential Scanning Calorimetry (DSC) for five 6 h transesterification palm stearin:palm kernel olein (PS:PKO) blends (w/w).	116

28.	Crystallisation temperature from cooling thermogram determined by Differential Scanning Calorimetry (DSC) for the high melting glycerides (HMG) of five 6 h transesterification palm stearin/palm kernel olein (PS/PKO) blends and their control.	118
29.	Polymorphic forms of five transesterified palm stearin:palm kernel olein (PS:PKO) blends and their control.	120
30.	Slip melting point (SMP) and melting point determined by Differential Scanning Calorimetry (DSC) of transesterified palm stearin (PS) and palm kernel olein (PKO) at different transesterification time (h).	122
31.	Slip melting point (SMP), melting point determined by Differential Scanning Calorimetry (DSC) and iodine value (IV) of five transesterified PS:PKO blends (w/w) and their control.	123
32.	Slip melting point (SMP), melting point determined by Differential Scanning Calorimetry (DSC) and iodine value (IV) of the high melting glycerides (HMG) of five transesterified PS:PKO blends (w/w) and their control.	124
33.	Comparing maximum stress of linear viscoelastic region of five commercial plastic frying shortenings with their slip melting point (SMP) and solid fat content.	134
34.	Maximum stress of linear viscoelastic region for five transesterified PS:PKO blends (w/w) and their controls.	143

LIST OF FIGURES

Figure		Page
1.	Model for lipase action on soluble and insoluble substrates, by lipases that undergo conformational changes upon activation.	18
2.	The Ping-Pong Bi-Bi mechanism for lipase-catalysed tranesterification with the transfer of an acyl group from one triacylglyceride (TAG ₁) to a diacylglycerol (DAG ₂) to form a new triacylglycerol (TAG ₂).	21
3.	Diagrammatic representations of ideal rheological behaviour : (a) The Hookean spring; (b) The Newtonian dashpot.	42
4.	HPLC chromatograms of (a) Sample A and its (b) high melting glycerides (HMG) fraction (M, myristic; P, palmitic; L, linoleic; O, oleic and S, stearic acid).	59
5.	HPLC chromatograms of (a) Sample B and its (b) high melting glycerides (HMG) fraction (M, myristic; P, palmitic; L, linoleic; O, oleic and S, stearic acid).	60
6.	HPLC chromatograms of (a) Sample C and its (b) high melting glycerides (HMG) fraction (M, myristic; P, palmitic; L, linoleic; O, oleic and S, stearic acid).	61
7.	HPLC chromatograms of (a) Sample D and its (b) high melting glycerides (HMG) fraction (M, myristic; P, palmitic; L, linoleic; O, oleic and S, stearic acid).	62
8.	HPLC chromatograms of (a) Sample E and its (b) high melting glycerides (HMG) fraction (M, myristic; P, palmitic; L, linoleic; O, oleic and S, stearic acid).	63
9.	Differential Scanning Calorimetry (DSC) cooling thermograms of five commercial plastic frying shortenings at cooling rate 5°C/min from 80°C to -40°C.	67
10.	Differential Scanning Calorimetry (DSC) melting thermograms of five commercial plastic frying shortenings at heating rate 5°C/min from -40°C to 80°C.	69
11.	The changes in solid fat content (SFC) profile as a function of temperature (°C) for five commercial plastic frying shortenings (A, B, C, D and E).	73



12.	HPLC chromatograms of (a) palm kernel olein (PKO) and (b) PKO after transesterification for 12 h.	82
13.	HPLC chromatograms of (a) palm stearin (PS) and (b) PS after transesterification for 12 h.	83
14.	HPLC chromatograms of (a) 1:4:PS:PKO (w/w), (b) its high melting glycerides (HMG) (c) transesterified 1:4:PS:PKO (w/w) and (d) its HMG	87
15.	HPLC chromatograms of (a) 3:7:PS:PKO (w/w), (b) its high melting glycerides (HMG) (c) transesterified 3:7:PS:PKO (w/w) and (d) its HMG	88
16.	HPLC chromatograms of (a) 2:3:PS:PKO (w/w), (b) its high melting glycerides (HMG) (c) transesterified 2:3:PS:PKO (w/w) and (d) its HMG	89
17.	HPLC chromatograms of (a) 1:1:PS:PKO (w/w), (b) its high melting glycerides (HMG) (c) transesterified 1:1:PS:PKO (w/w) and (d) its HMG	90
18.	HPLC chromatograms of (a) 3:2:PS:PKO (w/w), (b) its high melting glycerides (HMG) (c) transesterified 3:2:PS:PKO (w/w) and (d) its HMG	91
19.	Differential Scanning Calorimetry (DSC) melting thermograms of palm kernel olein (PKO) at different transesterification time (h) at heating rate 5°C/min from -40°C to 80°C.	98
20.	Differential Scanning Calorimetry (DSC) melting thermograms of palm stearin (PS) at different transesterification time (h) at heating rate 5°C/min from -40°C to 80°C.	101
21.	Differential Scanning Calorimetry (DSC) melting thermograms of five 6 h transesterified palm stearin:palm kernel olein (PS:PKO) blends and their respective control at heating rate 5°C/min from -40°C to 80°C.	104
22.	Differential Scanning Calorimetry (DSC) melting thermograms of the high melting glycerides (HMG) of five 6 h transesterified palm stearin:palm kernel olein (PS:PKO) blends and their respective control at heating rate 5°C/min from -40°C to 80°C.	105
23.	Differential Scanning Calorimetry (DSC) cooling thermograms of palm kernel olein (PKO) at different transesterification time (h) at cooling rate 5°C/min from 80°C to -40°C.	110

24.	Differential Scanning Calorimetry (DSC) cooling thermograms of palm stearin (PS) at different transesterification time (h) at cooling rate 5°C/min from 80°C to -40°C.	111
25.	Differential Scanning Calorimetry (DSC) cooling thermograms of five palm stearin:palm kernel olein (PS:PKO) blends at cooling rate 5°C/min from 80°C to -40°C.	115
26.	Differential Scanning Calorimetry (DSC) cooling thermograms of the high melting glycerides (HMG) of five palm stearin:palm kernel olein (PS:PKO) blends at cooling rate 5°C/min from 80°C to -40°C.	117
27.	The changes in solid fat content (SFC) profile as a function of temperature (°C) for palm kernel olein (PKO) at different transesterification time (2 h, 4 h, 6h and 12 h) and control (0 h).	126
28.	The changes in solid fat content (SFC) profile as a function of temperature (°C) for palm stearin (PS) at different transesterification time (2h, 4 h, 6 h and 12 h) and control (0 h).	127
29.	The changes in solid fat content (SFC) profile as a function of temperature (°C) for five transesterified palm stearin:palm kernel olein (PS:PKO) blends (1:4, 3:7, 2:3, 1:1 and 3:2).	129
30.	Linear viscoelastic region of five commercial frying shortenings.	132
31.	Storage modulus (G') versus frequency of five commercial plastic frying shortenings (A, B, C, D and E) at 25°C.	136
32.	Loss modulus (G'') versus frequency of five commercial plastic frying shortenings at 25°C.	137
33.	Complex viscosity (η^*) versus frequency of five commercial plastic frying shortenings at 25°C.	138
34.	Tan δ versus frequency of five commercial plastic frying shortenings (A, B, C, D and E) at 25°C.	139
35.	Stress Sweep profile of transesterified (TE) palm stearin:palm kernel olein (PS:PKO) blends with ratios of 2:3, 1:1 and 3:2 (w/w) and their respective controls (C) at 25°C.	142
36.	Storage modulus (G') versus frequency for three transesterified palm stearin:palm kernel olein (PS:PKO) blends with ratios 2:3, 1:1 and 3:2 and their respective controls (C) at 25°C.	145



LIST OF ABBREVIATIONS

AOCS	American Oil Chemists' Society
α	alpha
β'	beta prime
β	beta
<i>c</i>	cis
<i>t</i>	trans
C6:0	caproic acid
C8:0	caprylic acid
C10:0	capric acid
C12:0	lauric acid
C14:0	myristic acid
C16:0	palmitic acid
C18:0	stearic acid
C18:1	oleic acid
C18:2	linoleic acid
C18:3	linolenic acid
DSC	Differential Scanning Calorimetry
FA	fatty acid (s)
FFA	free fatty acids
GC	gas Liquid Chromatography
HMG	high melting glycerides



HPLC	high Performance Liquid Chromatography
IV	iodine value
PKO	palm kernel olein
PS	palm stearin
PORIM	Palm Oil Research Institute of Malaysia
sp.	species
SMP	slip melting point
SFC	solid fat content
TG	triacylglycerol(s)
TFA	<i>trans</i> fatty acid(s)
w/w	weight/weight
X	rate of transesterification

TABLE OF CONTENTS

	Page
ABSTRACT	i
ABSTRAk	iv
ACKNOWLEDGEMENTS	vii
LIST OF TABLES	xii
LIST OF FIGURES	xv
LIST OF ABBREVIATIONS	xviii
CHAPTER	
1 INTRODUCTION	1
2 LITERATURE REVIEW	5
Oil Palm in Malaysia	5
General Descriptions of the Oil Palm	5
Malaysia Palm Oil	6
Physical and Chemical Properties of Palm Stearin (PS)	7
Physical and Chemical Properties of Palm Kernel Olein (PKO)	9
Shortening	11
Definition	11
Composition	11
Classification	12
Frying Shortening	13
Lipase	15
Interesterification	18
Transesterification	19
Chemical Transesterification Vs Enzymatic Transesterification	19
Enzymatic Transesterification	20
Acidolysis	25
Alcoholysis	26
Factor Affecting Lipase Activity During Transesterification	27
Water Content/ Moisture Content	28
Temperature	29
Crystallisation of Fats	30
Fat Crystal Network	32
Polymorphism of Fats	33
Factors Affecting Type of Crystal Formed during Product	
Processing	35



	Rheology of Fats	38
	Viscoelastic Properties	40
	Measuring Methods	42
	Stress Sweep	43
	Frequency Sweep	44
3	MATERIALS AND METHODS	45
	Materials	45
	Methods	46
	Preparation of Test Shortenings	46
	Extraction of High Melting Glycerides (HMG) from the Commercial Plastic Shortenings and Transesterified PS:PKO Blends	46
	Determination of Hydrolytic Activity	47
	Determination of Triacylglycerol (TG) Profile	47
	Removal of Free Fatty Acids (FFA)	48
	Determination of Fatty Acids (FA) Composition	49
	Determination of Iodine Value (IV)	50
	Determination of Melting and Crystallisation Behaviour	50
	Determination of Slip Melting Point (SMP)	51
	Determination of Solid Fat Content (SFC)	52
	Polymorphic Form	52
	Viscoelasticity Measurement	52
4	RESULTS AND DISCUSSION	54
	Characterisation of Five Commercial Plastic Frying Shortenings	54
	Fatty Acids (FA) Composition	54
	Triacylglycerol (TG) Composition	58
	Polymorphic Forms	64
	Cooling Profile	66
	Melting Profile	68
	Slip Melting Point (SMP)	70
	Iodine Value (IV)	70
	Solid Fat Content (SFC)	72
	Physical and Chemical Properties of Transesterification of Palm Kernel Olein (PKO), Palm Stearin (PS) and Five PS:PKO Blends	75
	Fatty Acids (FA) Composition of PS:PKO Blends and their High Melting Glycerides (HMG)	75
	Triacylglycerol (TG) Composition of PKO, PS, PS:PKO Blends and their High Melting Glycerides (HMG)	81

Melting Profile of PKO, PS, PS:PKO Blends and their transesterified products	97
Cooling	
transesterified samples	109
Polymorphic Form	119
Slip Melting Point (SMP) and Iodine Value (IV)	121
Solid Fat Content (SFC)	125
Rheological Study	131
Viscoelastic (VE) Changes on Commercial Plastic Frying Shortenings	131
Stress Sweep	131
Frequency Sweep	135
Viscoelastic (VE) Changes on Transesterified PS/PKO Blends	141
Stress Sweep	141
Frequency Sweep	144
Comparing VE Properties between Commercial Plastic Frying Shortenings and Transesterified PS:PKO Blends	149
5 SUMMARY, CONCLUSION AND RECOMMENDATIONS	150
BIBLIOGRAPHY	155
APPENDICES	167
VITA	169



CHAPTER 1

INTRODUCTION

Lipases are endowed with a substrate specificity that surpasses that of any other known enzyme (McNeil *et al.*, 1995; Gandhi *et al.*, 1997). The unique of lipase is in its selective action toward its substrate such as triacylglycerol, fatty acid in 1,3 position and fatty acids (Macrae, 1983). This confers on these enzymes an application potential that is literally boundless. Lipases can be employed in the production of pharmaceuticals, cosmetics, leather, detergents, food, perfumery, medical diagnostics, and other organic synthetic materials (Gandhi, 1997).

In the food industry, lipase is a vital tool in fats and oils modification to "tailor-make" specific functional fats and oils to suit specific applications in food products. Application of a commercial food-grade lipase, Lipozyme (Novo Nordisk, 1997), has been studied excessively. Lipozyme has been used in production of margarines (Graille *et al.*, 1992; Vimont *et al.*, 1998; Lai *et al.*, 1998a), structured triacylglycerol (ST) (Soumanou and Bournscheuer, 1997; Mangos *et al.*, 1999; Yankah and Akoh, 2000), enrichment of fatty acids (Akoh *et al.*, 1995; Schmitt-Rozieres *et al.*, 2000), frying shortening (Chu *et al.*, 2001).

Transesterification process involves the rearrangement of acyl groups among triacylglycerols (TG) and alters the original TG profile of a fat or oil. This causes changes in the physical properties of the fat or oil, such as, slip melting point (SMP), solid fat

