



UNIVERSITI PUTRA MALAYSIA

**PHYSICO-CHEMICAL PROPERTIES OF PALM-BASED
DIACYLGLYCEROL OILS IN BLEND WITH PALM-BASED OILS**

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By

AMIR HOSSEIN SABERI

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Chairman: Assoc. Prof. Lai Oi Ming, PhD

Faculty: Biotechnology and Biomolecular Sciences

Physico-chemical properties of palm-based diacylglycerol (P-DAG) oils as new functional fats were studied individually and in blends with palm-based oils (P-oil) to obtain basic information for development of functional palm-based DAG-enriched plastic fat products. P-DAG oils were produced through enzymatic glycerolysis of palm kernel oil (PKO), palm oil (PO), palm olein (POL), palm mid fraction (PMF) and palm stearin (PS) with the high DAG purity range of 83-90% (w/w). Reversed-phase high-performance liquid chromatography method using charged aerosol detector (CAD) was developed for separation of 1,3- and 1,2(2,3)-positional isomers of P-DAG oils including PKO-based DAG (PKO-DAG) as the sources of short- and medium-chain DAGs, and PO-based DAG (PO-DAG), PMF-based DAG (PMF-DAG), POL-based DAG (POL-DAG) and PS-based DAG (PS-DAG) as sources of long-chain DAG but with different ratios. In this method, linear gradient of acetone



and acetonitrile was used and total retention time (RT) of 28 min was attained. Identification of P-DAG molecular species was accomplished using synthetic DAG standards.

Physico-chemical properties of P-DAG oils were also evaluated and compared with their corresponding P-oils. P-DAG oils as compared to P-oils were found to have significantly ($P < 0.05$) different FACs, Iodine values (IV) and slip melting points (SMP) and less steep solid fat content (SFC) profiles with higher complete melting temperatures. Also, P-DAG oils in contrast with P-oils showed endothermic as well as exothermic peaks at higher temperature regions, higher crystallization onset (T_0) and higher heat of fusion (ΔH_f) and crystallization. Crystal forms for P-DAG oils were mostly β .

Crystallization kinetics of PO in the presence of different concentrations (2, 5, 10, 30 and, 50% w/w) of PO-DAG were investigated using Avrami model. Comparison of induction time (T_i), Avrami exponent (n), Avrami constant (k) and half-time of crystallization ($t_{1/2}$) of blends showed that addition of 5% of PO-DAG in most of the supercooling ranges significantly ($P < 0.05$) reduced nucleation rate as well as crystal growth velocity of PO. On the other hand, high concentrations of PO-DAG were found to significantly ($P < 0.05$) reduce T_i as well as $t_{1/2}$ and also increase k suggesting their promoting effects on nucleation and crystallization rate of PO. PO and PO blends with 2 and 5% of PO-DAG showed crystal transformation at crystallization temperatures (T_{Cr}) of 26, 26, 26.5°C, respectively as reflected in corresponding changes of the

Avrami parameters at below and above these T_{Cr} . Presence of 10% PO-DAG showed β' -stabilizing effect on PO.

Phase behaviour of binary blends containing PO and PO-DAG with 10% interval was also studied. The minor eutectic effects were observed at around 20-50% PO-DAG in SFC iso-lines of 20-50%. Phase behavior predicted by iso-solid diagram as well as isothermal SFC did not account for hardness variations observed between PO and PO blends with 10-40% PO-DAG. However, as concentration of PO-DAG increased from 40 to 100%, iso-lines temperatures, isothermal SFC and also hardness were found to steadily increase. On the other hand, hardness variations observed among PO and PO blends with 10-40% PO-DAG could be attributed to the respective DSC data as well as polymorphism changes. PO-DAG at 10% concentration was found to have β' -stabilizing effect on PO polymorphism while a β -form increasing trend was observed as concentration of PO-DAG increased from 10% to 90%.

Ternary phase behaviour of sunflower oil (SFO), palm kernel olein (PKOL) and POL-DAG, and POL, PKO and PO-DAG were analyzed using isosolid diagrams of SFC and Δ SFC, and melting and solidification properties in two different ternary systems. The eutectic behaviour was observed along the binary line of PKOL/POL-DAG at temperature ranges of 5-20°C in the former system. However, no eutectic interaction was observed along the binary lines of SFO/PKOL as well as SFO/POL-DAG despite showing deviation from SFC (Δ SFC) within temperature range of 5-25°C. The most intensive eutectic

interaction was observed along the binary line of PKO/PO-DAG followed by POL/PKO and POL/PO-DAG in the latter system. In general, it was found that Δ SFC does not always lead to eutectic behaviour and also the higher Δ SFC did not always lead to more intensive eutectic behaviour among the blends. Palm-based DAG-enriched soft tub margarine (PDAG-TM) containing SFO/PKOL/POL-DAG (35/15/50, (w/w)) was optimally formulated through analysis of multiple isosolid diagrams, and was found to have quite similar SFC profile as well as SMP but also lower saturated fatty acid (SAFA) as compared to the commercial soft tub margarine (CTM). Palm-based DAG-enriched shelf-stable margarine (PDAG-SSM) consisting of POL/PKO/PO-DAG (42.5/42.5/15, (w/w)) was also optimally formulated through analysis of multiple isosolid diagrams and was found to have quite similar SFC profile with commercial shelf-stable margarine (CSM).

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

**SIFAT FIZIK-KIMIA DIASILGLISEROL MINYAK SAWIT
BERCAMPUR DENGAN MINYAL SAWIT**

Oleh

AMIR HOSSEIN SABERI

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Pengerusi: Profesor Madya Lai Oi Ming, PhD

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Sifat fiziko-kimia diasilgliserol minyak sawit (P-DAG) sebagai lemak berfungsi baru telah dikaji secara individu dan seterusnya dicampur dengan minyak sawit (P-oil) untuk mendapatkan maklumat asas yang akan diguna untuk pembangunan produk lemak plastik yang diperkayakan dengan P-DAG berfungsi. Minyak P-DAG telah dihasilkan melalui gliserolisis berenzim minyak isirong sawit (PKO), minyak sawit (PO), minyak sawit olein (POL), fraksi pertengahan sawit (PMF), dan stearin minyak sawit (PS) dengan ketulenan DAG yang tinggi antara 83–90% (w/w). Kaedah fasa-terbalik kromatografi cecair berprestasi-tinggi dengan pengesan aerosol bercas telah dibangunkan untuk pemisahan kedudukan isomer 1,3- and 1,2(2,3)- minyak P-DAG termasuk DAG berdasarkan PKO (PKO-DAG) sebagai sumber DAG berantai pendek dan sederhana dan DAG berdasarkan PO (PO-DAG), DAG berdasarkan PMF (PMF-DAG), DAG berdasarkan POL (POL-DAG) dan DAG



berdasarkan PS (PS-DAG) sebagai sumber DAG berantai panjang dengan nisbah berlainan. Dalam kaedah ini, aseton dan asetonitril kecerunan linear telah digunakan dan jumlah waktu retensi yang dicapai adalah 28 min. Pengenalan spesis molekul P-DAG telah dicapai dengan menggunakan DAG piawai sintetik.

Sifat fiziko-kimia P-DAG juga telah dinilai dan dibandingkan dengan P-oil masing-masing. Minyak P-DAG jika dibandingkan dengan P-oil didapati mempunyai perbezaan signifikan ($P < 0.05$) dari segi komposisi asid lemak, nilai iodine (IV) dan titik peleburan slip (SMP) dan profil kandungan lemak padat (SFC) yang kurang curam dengan suhu peleburan lengkap yang lebih tinggi. P-DAG juga didapati berbeza daripada P-oil di mana ia menunjukkan puncak endotemik dan eksotemik dengan kawasan suhu lebih tinggi, pengkristalan onset lebih tinggi, dan gabungan haba dan pengkristalan lebih tinggi. Bentuk kristal untuk P-DAG kebanyakannya adalah β .

Kinetik pengkristalan PO dengan kepekatan PO-DAG yang berbeza (2, 5, 10, 30 dan, 50% w/w) telah dikaji dengan menggunakan model Avrami. Perbandingan masa induksi (T_i), Avrami eksponen (n), Avrami malar (k) dan setengah masa pengkristalan ($t_{1/2}$) campuran-campuran ini menunjukkan bahawa penambahan 5% PO-DAG dalam kebanyakan lingkungan penyejukan super mengurangkan kadar nukleasi dan kelajuan pertumbuhan kristal PO secara signifikan ($p < 0.05$). Di samping itu, PO-DAG pada kepekatan tinggi

didapati mengurangkan T_i dan $t_{1/2}$ secara signifikan ($P < 0.05$). Peningkatan k mencadangkan kesan promosi ke atas nukleasi dan kadar pengkristalan PO. PO dan campuran PO dengan 2 and 5% PO-DAG menunjukkan transformasi kristal pada suhu pengkristalan (T_{Cr}) 26, 26, 26.5°C, masing-masing mencerminkan perubahan berkaitan dengan parameter Avrami di bawah dan atas T_{Cr} ini. Kehadiran 10% PO-DAG menunjukkan kesan penstabilan β' ke atas PO.

Perilaku fasa campuran-campuran binari yang mengandungi PO dan PO-DAG pada selang 10% juga telah dikaji. Kesan eutetik minor telah diperhatikan bagi PO-DAG antara 20-50% dalam SFC garis-iso. Perilaku fasa yang dijangkakan oleh diagram iso-solid dan SFC isothermal tidak menjelaskan variasi kekerasan yang diperhatikan antara PO dan campuran-campuran PO dengan 10-40% PO-DAG. Walau bagaimanapun, apabila kepekatan PO-DAG bertambah dari 40% kepada 100%, suhu garis-iso, SFC isothermal dan kekerasan didapati terus meningkat. Di samping itu, variasi kekerasan diperhatikan antara PO dan campuran-campuran PO dengan 10-40% PO-DAG mungkin disebabkan oleh data DSC dan perubahan polimorfik. PO-DAG pada kepekatan 10% didapati mempunyai kesan penstabilan β' ke atas polimorfik PO sementara peningkatan kecenderungan bentuk β telah diperhatikan apabila kepekatan PO-DAG bertambah dari 10 % kepada 90%.

Perilaku fasa ternari antara minyak bunga matahari (SFO), minyak isirong sawit olein (PKOL) dan POL-DAG, dan POL, PKO, dan PO-DAG telah dianalisa menggunakan diagram isosolid SFC dan Δ SFC, dan sifat-sifat peleburan dan kepadatan dalam dua sistem ternari yang berbeza. Perilaku eutetik telah diperhatikan dalam garis binari PKOL/POL-DAG pada lingkungan suhu antara 5-20°C dalam sistem sebelumnya. Walau bagaimanapun, tidak ada interaksi eutetik diperhatikan dalam garis binari SFO/PKOL dan SFO/POL-DAG walaupun penyimpangan dari SFC (Δ SFC) dalam lingkungan suhu antara 5-25°C telah diperhatikan. Interaksi eutetik paling intensif diperhatikan dalam garis binari PKO/PO-DAG diikuti dengan POL/PKO dan POL/PO-DAG dalam sistem yang lain. Umumnya, didapati bahawa Δ SFC tidak semestinya mengakibatkan perilaku eutektik. Δ SFC lebih tinggi juga tidak selalunya mengakibatkan perilaku eutektik yang lebih intensif antara campuran-campuran tersebut. Marjerin lembut jenis tub yang diperkayakan dengan P-DAG dan mengandungi SFO/PKOL/POL-DAG (35/15/50, (w/w)) telah diformulasi secara optimal melalui analisa diagram isosolid berganda. Ia didapati mempunyai profil SFC dan SMP yang hampir sama dan asid lemak tepu yang lebih rendah jika dibanding dengan marjerin lembut tub yang komersial. Marjerin rak-stabil yang diperkayakan dengan P-DAG mengandungi POL/PKO/PO-DAG (42.5/42.5/15 (w/w)) yang diformulasi secara optimal melalui analisa diagram isosolid berganda telah didapati mempunyai profil SFC yang hampir sama dengan marjerin komersial.

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DECLARATION

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

AMIR HOSSEIN SABERI

Date: 22 APRIL 2011

TABLE OF CONTENTS3

	Page
ABSTRACT	II
ABSTRAKT	VI
ACKNOWLEDGEMENT	X
APPROVAL	XI
DECLARATION	XIII
LIST OF TABLES	XIX
LIST OF FIGURES	XXII
LIST OF ABBREVIATIONS	XXVIII
CHAPTER	
1 INTRODUCTION	1
2 LITERATURE REVIEW	7
2.1. Palm Oil and Its Fractions	7
2.2. Overweight, Obesity and High Fat Intake	8
2.3. Diacylglycerol	11
2.3.1. Physico-chemical Properties	12
2.3.2. Digestion, Absorption, and Metabolism	14
2.3.3. Potential Health Benefit	16
2.3.4. Safety Assessment of DAG Consumption	17
2.3.5. Production of DAG	18
2.3.6. Application of DAG In Food Products	21
2.4. Lipid Phase Behavior	22
2.4.1. Lipid Phase Behavior Determination	25
2.5. Crystallization	26
2.5.1. Crystallization Kinetic	27
2.5.2. Experimental Techniques for Study of Isothermal Crystallization Kinetics	28
2.5.3. Mathematical Models Used for Study of Isothermal Crystallization Kinetics	30
2.6. Margarine	35
2.6.1. Fat Phase in Margarine	35
2.6.2. Use Of Palm Oil and Its Derivatives for Formulation of Margarine Fat Blend	37
2.6.3. Use of DAG In Plastic Fat Products	39
3 REVERSED-PHASE HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY ANALYSIS OF 1,3- AND 1,2(2,3)-POSITIONAL ISOMERS OF PALM-BASED DIACYLGLYCEROLS	41



3.1.	Introduction	41
3.2.	Materials and Methods	45
3.2.1.	Materials	45
3.2.2.	Production of DAG Oils	46
3.2.3.	Purification of DAG Oils	46
3.2.4.	Fatty Acid Composition Analysis	47
3.2.5.	Synthesis of DAG Standards	48
3.2.6.	HPLC Condition	48
3.3.	Results and Discussion	49
3.3.1.	Fatty Acid Composition Analysis	49
3.3.2.	Separation, Identification and Quantification of Palm- Based Diacylglycerol Molecular Species	51
3.3.3.	Elution Orders of Synthetic Standards	64
3.4.	Conclusion	69
4	PHYSICO-CHEMICAL PROPERTIES OF VARIOUS PALM-BASED DIACYLGLYCEROL OILS IN COMPARISON WITH THEIR CORRESPONDING PALM-BASED OILS	70
4.1.	Introduction	70
4.2.	Materials and Methods	72
4.2.1.	Materials	72
4.2.2.	Production of DAG	72
4.2.3.	Purification of DAG	72
4.2.4.	Fatty Acid Composition Analysis	73
4.2.5.	Synthesis of DAG Standards	73
4.2.6.	Slip Melting Point Analysis	73
4.2.7.	Iodine Value Analysis	73
4.2.8.	Dynamic DSC Analysis	74
4.2.9.	Solid Fat Content Analysis	74
4.2.10.	Polymorphism	75
4.2.11.	Statistical Analysis	75
4.3.	Results and Discussion	76
4.3.1.	Fatty Acid Composition, Slip Melting Point and Iodine Value	76
4.3.2.	Acylglycerol Compositions and DAG Compositions	81
4.3.3.	Solid Fat Content Profile of Palm-Based DAG Oils and Palm-Based Oils	83
4.3.4.	DSC Heating and Cooling Profile of Palm-Based DAG Oils	87
4.3.5.	Crystal Structure	92
4.4.	Conclusion	93

5	CRYSTALLIZATION KINETICS OF PALM OIL IN BLENDS WITH PALM-BASED DIACYLGLYCEROL	94
5.1.	Introduction	94
5.2.	Materials and Methods	96
5.2.1.	Materials	96
5.2.2.	Production of DAG	96
5.2.3.	Purification of DAG	96
5.2.4.	Blend Preparation	96
5.2.5.	Fatty Acid Composition Analysis	97
5.2.6.	Acylglycerol Composition Analysis	97
5.2.7.	Dynamic DSC Analysis	97
5.2.8.	Isothermal DSC Analysis	97
5.2.9.	Solid Fat Content Analysis	99
5.2.10.	Statistical Analysis	99
5.3.	Results and Discussions	100
5.3.1.	Acylglycerol and Fatty Acid Compositions	100
5.3.2.	DSC Thermogram	103
5.3.3.	Isothermal Crystallization	106
5.3.4.	Solid Fat Content Profile	131
5.4.	Conclusion	133
6	PHASE BEHAVIOR OF PALM OIL IN BLENDS WITH PALM-BASED DIACYLGLYCEROL	135
6.1.	Introduction	135
6.2.	Materials and Methods	137
6.2.1.	Materials	137
6.2.2.	Production of DAG	137
6.2.3.	Purification of DAG	137
6.2.4.	Blend Preparation	138
6.2.5.	Iso-Solid Diagram	138
6.2.6.	Fatty Acid Composition Analysis	138
6.2.7.	Acylglycerol Composition Analysis	139
6.2.8.	Dynamic DSC Analysis	139
6.2.9.	Dynamic SFC Analysis	139
6.2.10.	Isothermal SFC Analysis	139
6.2.11.	Crystal Polymorphism	140
6.2.12.	Hardness	140
6.3.	Results and Discussion	141
6.3.1.	Acylglycerol and Fatty Acid Compositions	141
6.3.2.	Iso-Solid Diagram	141
6.3.3.	Hardness	143



6.3.4.	DSC Thermogram	144
6.3.5.	Polymorphism	151
6.4.	Conclusion	154
7	MELTING AND SOLIDIFICATION PROPERTIES OF PALM-BASED DIACYLGLYCEROL, PALM KERNEL OLEIN AND SUNFLOWER OIL IN THE PREPARATION OF PALM-BASED DIACYLGLYCEROL-ENRICHED SOFT TUB MARGARINE	156
7.1.	Introduction	156
7.2.	Materials and methods	158
7.2.1.	Materials	158
7.2.2.	Production of DAG	158
7.2.3.	Purification of DAG	159
7.2.4.	Blend Preparation	159
7.2.5.	Fatty Acid Composition Analysis	159
7.2.6.	Acylglycerol Composition Analysis	159
7.2.7.	Solid Fat Content Analysis	159
7.2.8.	Slip Melting Point	160
7.2.9.	DSC Analysis	161
7.2.10.	Experimental Design and Statistical Analysis	161
7.3.	Results and Discussion	162
7.3.1.	Chemical Properties	162
7.3.2.	Solid Fat Content and Ternary Phase Behaviour	162
7.3.3.	Compatibility of Mixture Components In Ternary Phase Diagram	173
7.3.4.	Melting and Crystallization Properties	177
7.3.5.	Optimization of Ternary Mixture Components for Soft Tub Margarine Formulation	181
7.4.	Conclusion	186
8	PHYSICAL PROPERTIES OF PALM- BASED DIACYLGLYCEROL AND PALM-BASED OILS IN THE PREPARATION OF SHELF-STABLE MARGARINE	188
8.1.	Introduction	188
8.2.	Materials and methods	190
8.2.1.	Materials	190
8.2.2.	Production of DAG	190
8.2.3.	Purification of DAG	190
8.2.4.	Blend Preparation	190
8.2.5.	Fatty Acid Composition Analysis	191

8.2.6.	Acylglycerol Composition Analysis	191
8.2.7.	Solid Fat Content Analysis	191
8.2.8.	Slip Melting Point	191
8.2.9.	DSC Analysis	191
8.2.10.	Experimental Design and Statistical Analysis	192
8.3.	Results and Discussion	192
8.3.1.	Chemical Properties	192
8.3.2.	Solid Fat Content and Ternary Phase Behaviour	193
8.3.3.	Compatibility of Mixture Components In Ternary Phase Diagram	203
8.3.4.	Melting and Crystallization Properties	208
8.3.5.	Optimization of Ternary Mixture Components for Shelf-Stable Margarine Formulation	212
8.4.	Conclusion	216
9	SUMMARY, CONCLUSIONS AND RECOMMENDATION	217
9.1.	Summary	217
9.2.	Conclusions and Recommendations	221
	REFERENCES	223
	APPENDICES	
A	Melting and Crystallization Thermogram of Palm-Based Oils and Palm-Based DAG Oils	247
B	X-Ray Diffraction Curve for Palm-Based DAG Oils	252
C	DSC ISO Thermal profile for PO blend with 10% PO-DAG	254
D	Example of Avrami parameters Calculation for Isothermal Crystallization of PO at 25°C	255
	BIODATA OF STUDENT	257
	PUBLICATION LIST	258

