UNIVERSITI PUTRA MALAYSIA

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

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FBSB 2011 2

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By

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

April 2011

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

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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_O) and higher heat of fusion (ΔHf) 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 ΔSFC, 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 (ΔSFC) 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 ∆SFC does not always lead to eutectic behaviour and also the higher ∆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

April 2011

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 isotermal 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 isotermal 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 ΔSFC, 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 peyimpangan dari SFC (ΔSFC) 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 ΔSFC tidak semestinya mengakibatkan perilaku eutektik. ΔSFC 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.

ACKNOWLEDGEMENT

First, I must start by extending my sincere appreciation to ALLAH who gives me the breath of life every morning, it would have been impossible for me to carry out and finish the work presented in this doctoral thesis without His gift of hope, encouragement and life every day.

I would like to express much gratitude to my supervisor, Associate Professor Dr. Lai Oi Ming, for her insightful guidance in developing this thesis, and her encouragement and support throughout my studies. I would also like to thank Associate Professor Dr. Tan Chin Ping, and Dr. Mat Sahri Miskandar, the co-supervisors, for their thought provoking comments, challenging questions and valuable suggestions. I am also grateful to Mr. Beh Boon Kee and Dr. Seong Koon for their kind cooperation throughout the work and for taking the time to share their experiences, knowledge and wisdom. I also appreciatively thank, Mr. Razam, Mr. Ananthan, Mr. Radha Krishnan, Mr. Vijay Krishnan and, Ms. Sri Nesa from Sime Darby, Banting for their kind technical assistance. Many thanks are also due to faculty members, staffs and technicians for their individual assistance and support.

Finally, I take this opportunity to express my whole gratitude to my parents and family in Iran for their invaluable love, encouragement and support all through the years. My deepest love and heartfelt thanks go to my wife, for her limitless support, love, understanding, and patience. Without the blessings, encouragement and guidance of all these people, I could never have completed my research.

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:

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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

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