

# MICROSTRUCTURE, RHEOLOGICAL PROPERTIES AND STABILITY OF OLEOGELS DERIVED FROM PALM OLEIN, PALM MID FRACTION AND SOYBEAN OIL BLENDS

SAW MEI HUEY

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By

SAW MEI HUEY

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

June 2020

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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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**June 2020** 

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Organogelation is an alternative method of structuring edible oils used to produce low saturation solid fat products. Many studies on oleogels involve the use of soft vegetable oils. However, these highly unsaturated oils are mostly thermally unstable and exhibit poor physical properties. Therefore, palm-based liquid oil could be a better choice for the preparation of oleogels due to its balanced fatty acid composition. In oleogel systems, the rheology, stability, physical and microstructural properties of the oleogels are greatly influenced by the preparation temperature and gelator type and dosage, as well as the type of liquid oil used. Therefore, this dissertation focuses on the influence of various factors on the characteristics of palm-based oleogels and the possibility of using palm-based liquid oil in the formation of oleogels.

First, gelator screening was conducted through the inverted vial method. Polyglycerol behenice acid ester (PBA), sunflower wax (SFW) and fully hydrogenated palm-based monoacylglycerol with high stearic (MGHO) were selected, whereas fully hydrogenated palm stearin iodine value of 2 (PSIV2), hard palm stearin iodine value of 14 (PSIV14) and fully hydrogenated palm-based monoacylglycerol with high palmitic (MGHP) were removed from further investigation due to their low effectiveness in gelling palm superolein. The results indicated that storage temperature and duration significantly affected the characteristics of the superolein oleogels. Palm superolein tended to crystallize at 5 °C, causing a tremendous increase in the hardness from 1.6 g to 340 g when storage temperature for SFW oleogles was reduced from 25 °C to 5 °C. Similar observation was found for the other oleogels as well due to the crystallization of the superolein at low temperature. At 15 °C, the oleogels derived from SFW and MGHO showed increasing trends in the enthalpy of melting from  $4.8 \text{ Jg}^{-1}$  to  $7.7 \text{ Jg}^{-1}$  and  $9.4 \text{ Jg}^{-1}$  for SFW oleogels and from 7.1 Jg<sup>-1</sup> to 12.1 Jg<sup>-1</sup> and 14.7 Jg<sup>-1</sup> for MGHO oleogels upon storage (from day 1 to day 3) due to the slow crystallization behavior of superolein. PBA oleogels delayed the crystallization of superolein, as no significant changes in properties were observed during the three days of storage. SFW oleogels formed uniform and

continuous crystalline structures that efficiently trapped superolein within their structures. Therefore, SFW oleogels were the most stable compared to the other oleogels. In contrast, despite their high hardness (23.1 g) and solid fat content (7.6%), MGHO oleogels were the least stable due to the formation of irregularly sized crystals with loose entanglement. Therefore, MGHO was removed from further investigation due to its poor performance in organogelation.

The effects of gelator dosage and liquid oil types on the characteristics of PBA and SFW oleogels were very complicated. The gelator dosage showed positive linear effects on the rheological, thermal and physical properties of PBA and SFW oleogels. However, the gelator dosage effect became less significant when POoIV56 and SBO:PMF (7:3) were used due to their higher saturation content. POP has been identified as a possible key compound in POoIV56 and SBO:PMF (7:3) contributes to differences in the oleogels' characteristics. The POP in SBO:PMF (7:3) had a higher degree of freedom compared to that in POoIV56 due to its incompatibility with the low-melting TAGs in SBO. Therefore, the POP in the SBO blend had a greater interaction affinity with the PBA and SFW gelators, thus improving the rheological, thermal and physical properties of the oleogels. According to microstructural analysis by XRD, the SFW oleogels derived from SBO and PMF blends exhibited a more complex crystalline system, in which crystals with lamellae sizes of 42.8 Å and 68.9 Å were concurrently present in the oleogel system. This result show that the PMF in the SBO formed cocrystals within the SFW gel structure, and therefore improved the gel strength and stability. The oleogels formed with other liquid oils showed insignificant differences in affecting the oleogels properties. Their G'LVR, G"LVR, critical stress, and AH values were much lower than those of oleogels formed with POoIV56 and SBO:PMF (7:3). These findings showed that the TAG components in the oils such as POoIV64, POoIV72, SBO, SBO:IV64 (1:1), SBO:PMF (9:1) and SBO:PMF (4:1), did not interfere with the formation of a gel structure; thus, their rheological and thermal profiles were mainly dependent on gelator dosage.

In conclusion, the stability of oleogels is attributed to microstructural factors and intermolecular interactions in oleogel formation but is less dependent on the hardness and SFC. This study also showed that PMF could be used to enhance the strength and characteristics of oleogels, especially those of oleogels formed with soft vegetable oils. This study also showed that palm liquid fractions have the potential to be used to form oleogels with satisfactory strength and stability. This new finding could be extended to real food products in the future, whereby palm liquid fractions and blends of PMF with soft vegetable oils could be used as major ingredients in solid fat production to make margarine, shortening replacements and meat products. Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Doktor Falsafah

# MIKROSTRUKTUR, SIFAT RHEOLOGI DAN KESTABILAN OLEOGEL DARIPADA ADUNAN MINYAK SAWIT OLEIN, PECAHAN SEPARA SAWIT (PMF) DAN MINYAK SOYA

Oleh

#### SAW MEI HUEY

Jun 2020

# Pengerusi: Profesor Tan Chin Ping, PhDFakulti: Sains dan Teknologi Makanan

Organogelasi merupakan cara alternatif untuk penstrukturan minyak dalam penghasilan produk lemak yang mengandungi ketepuan yang rendah. Kebanyakan penyelidikan berkenaan dengan penghasilan oleogel melibatkan penggunaan minyak sayuran lembut. Tetapi, minyak-minyak ini mengandungi ketaktepuan yang tinggi dan kurang stabil dari segi terma dan fizikal. Maka, minyak berasaskan sawit boleh menjadi pilihan yang lebih baik dalam penghasilan oleogel disebabkan oleh komposisi asid lemak yang lebih seimbang. Dalam sistem oleogel, rheologi, kestabilan, sifat-sifat fizikal dan mikrostruktur amat dipengaruhi oleh suhu penghasilan, jenis gelator dan dos gelator yang digunakan, serta jenis minyak yang digunakan. Oleh itu, kajian untuk tesis ini tertumpu kepada kesan faktor-faktor tersebut dalam pencirian oleogel serta penggunaan minyak sawit dalam pembentukan oleogel.

Pada mulanya, pemilihan gelator dijalankan berdasarkan cara menerbalikkan botol. Ester poligliserol asid behenik (PBA), wax bunga matahari (SFW) dan 'fully hydrogenated palm-based monoacylglycerol with high stearic' (MGHO) telah diuji, manakala 'fully hydrogenated palm stearin' dengan bernilai iodin 2 (PSIV2), 'hard stearin' bernilai iodin 14 (PSIV14) dan 'fully hydrogenated palm-based monoacylglycerol with high palmitic' (MGHP) telah disingkirkan daripada penyiasiatan lebih lanjut. Keputusan menunjukkan bahawa suhu dan tempoh simpanan telah menjejaskan ciri-ciri oleogel superolein yang dihasilkan. Penghabluran minyak superolein berlaku pada suhu 5 °C, dan mengakibatkan peningkatan kekerasan dari 1.6 g kepada 340 g apabila suhu penyimpanan oleogel SFW diturunkan dari 25 °C kepada 5 °C. Permerhatian yang serupa telah dikesan bagi oleogels yang lain disebabkan oleh penghabluran minyak superolein pada suhu yang rendah. Pada 15 °C, oleogel yang dihasilkan daripada SFW dan MGHO menunjukkan tren peningkatan dalam entalpi peleburan iaitu dari 4.8 Jg<sup>-1</sup> kepada 7.7 Jg<sup>-1</sup> dan 9.4 Jg<sup>-1</sup> bagi oleogel SFW dan 7.1 Jg<sup>-1</sup> kepada 12.1 Jg<sup>-1</sup> dan 14.7 Jg<sup>-1</sup> bagi oleogel MGHO, semasa simpanan dari hari pertama kepada hari ketiga. In adalah disebabkan oleh sifat superolein yang menghablur secara perlahan pada suhu tersebut. Oleogel PBA tidak menunjukkan tren ini kerana molekul PBA melambatkan process penghabluran ini. Oleogel SFW

adalah antara yang paling stabil kerana ia membentuk hablur yang seragam dengan struktur hablur berterusan yang dapat memegang minyak superolein dengan lebih cekap. Sebaliknya, oleogel MGHO adalah antara yang paling tidak stabil walaupun ia menunjukkan sifat kekerasan (23.1 g) dan kandungan lemak pepejal (7.6%) yang paling tinggi. In adalah kerana MGHO membentuk hablur yang tidak bersaiz seragam dengan susunan yang longgar yang menyebabkan minyak senang dikeluarkan daripada strukturnya. Maka, MGHO telah disingkirkan daripada eksperimen seterusnya.

Kesan dos gelator dan jenis minyak pada sifat-sifat oleogels PBA dan SFW adalah agak rumit. Secara umumnya, kuantiti gelator yang digunakan telah menunjukkan kesan linear positif pada sifat rheologi, kesan terma dan sifat fizikal. Akan tetapi, kesan kuantiti gelator ini menjadi kurang ketara apabila minyak POoIV56 dan SBO:PMF (7:3) digunakan untuk penghasilan oleogel. POP telah dikenalpasti sebagai kompaun utama yang menyebabkan perbezaan dalam sifat-sifat oleogels tersebut. POP dalam SBO:PMF (7:3) mempunyai darjah kebebasan yang lebih tinggi berbanding dengan POoIV56 kerana POP mempunyai keserasian yang rendah dengan trigliserida minyak SBO yang bertakat lebur rendah. Maka, POP dalam adunan SBO mempunyai afiniti yang lebih tinggi terhadap gelator-gelator PBA dan SFW yang boleh membentuk struktur yang lebih kuat, seterusnya meningkatkan sifat rheologi, terma dan fizikal bagi oleogel-oleogel tersebut. Berdasarkan analisis-analisis mikrostruktur, oleogel SFW yang dihasilkan daripada adunan SBO dan PMF mununjukkan sistem penghabluran yang lebih rumit. Hablur dengan saiz lamellae 42.8 Å dan 68.9 Å didapati muncul dalam sistem oleogel tersebut dengan serentak. Ini menunjukkan bahawa PMF dalam SBO membentuk kokristal dalam struktur SFW dan seterusnya meningkatkan kekuatan dan kestabilan oleogel tersebut. Oleogel-oleogel yang dihasilkan daripada minyak-minyak yang lain pula tidak menunjukkan perbezaan yang ketara dalam sifat-sifat oleogel. Ini menunjukkan bahawa komponen-komponen TAG dalam POoIV64, POoIV72, SBO, SBO:IV64 (1:1), SBO:PMF (9:1) dan SBO:PMF (4:1) tidak menjejaskan pembentukan struktur gel, maka sifat-sifat oleogelnya adalah hanya bergantung kepada kuantiti gelator yang digunakan sahaja.

Kesimpulannya, kestabilan oleogel adalah amat bergantung kepada faktor mikrostruktur dan interaksi antara molekul-molekul yang berada dalam sesuatu sistem oleogel. Kestabilan adalah kurang bergantung kepada sifat kekerasan dan SFC. Penyelidikan ini juga telah menunjukkan bahawa PMF boleh digunakan untuk menambahbaikkan kekuatan dan ciri-ciri oleogel, terutamanya oleogel yang dibentukkan daripada minyak sayuran lembut. Penyelidikan ini juga menunjukkan minyak berasaskan sawit adalah berpotensi tinggi untuk menghasilkan oleogel yang mempunyai kestabilan dan kekuatan yang agak memuaskan. Penyelidikan ini boleh dilanjutkan kepada penggunaan dalam produk makanan, di mana oleogel daripada minyak olein dan adunan PMF dengan minyak sayuran lembut boleh digunakan sebagai bahan utama dalam pembuatan marjerin, pengganti shortening dan produk daging.

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This is to confirm that:

- the research conducted and the writing of this thesis was under our supervision;
- supervision responsibilities as stated in the Universiti Putra Malaysia (Graduate Studies) Rules 2003 (Revision 2012-2013) are adhered to.

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# LIST OF ABBREVIATIONS

ANOVA	Analysis of Variance
BE	Beeswax
BEW	Berry Wax
CLW	Candelilia Wax
CRBW	Carnauba Brazilian Wax
Cryo-SEM	Cryo-scanning Electron Microscopy
DAG	Diacylglycerol
DSC	Differential Scanning Calorimeter
FA	Fatty Acid
FAL	Fatty Alcohol
FAME	Fatty Acid Methyl Esther
FFA	Free Fatty Acid
FID	Flame-ionization Detector
GRAS	Generally Regarded as Safe
$\Delta H$	Enthalpy of Melting
НС	Hydrocarbon
IV	Iodine Value
LDL	Low-density Lipoprotein
LVR	Linear Visco-elastic Region
МСТ	Medium-chain Triacylglycerols
MG	Monoglyceride
MGHO	Fully Hydrogenated Palm-based Monoacylglycerol with High Stearic
MGHP	Fully Hydrogenated Palm-based
MUFA	Monounsaturated Fatty Acid

RBW	Rice Brans Wax
PBA	Polyglycerol Behenic Acid Ester
PLM	Polarized Light Microscope
PMF	Palm Mid Fraction
pNMR	Pulsed Nuclear Magnetic Resonance
POoIV64	Superolein with Iodine Value of 64
POoIV72	Top Olein with Iodine Value of 72
PSIV2	Fully Hydrogenated Palm Stearin Iodine Value of 2
PSIV14	Hard Palm Stearin Iodine Value of 14
SAXS	Small Angle Diffraction
SAFin	Self-assembly Fibriliar Network
SBO	Soybean oil
SFA	Saturated Fatty Acid
SFC	Solid Fat Content
SFW	Sunflower Wax
TAG	Triacylglycerol
Tfm	Fully Melted Temperature
Tm	Peak of Melting
U-HPLC	Ultra High-Performance Liquid Chromatography
WAXS	Wide Angle Diffraction
w/w	Weight/Weight
WE	Wax Ester
XRD	X-ray Diffraction

#### **CHAPTER 1**

#### **INTRODUCTION**

#### 1.1 Background and Problem Statement

Oils and fats are generally composed of triacylglycerols (TAGs), in which their physical appearance depends on the chemical nature and physical properties of the constituent fatty acids attached to the glycerol backbone. For centuries, oils and fats have been well-known as some of the most important materials for food applications. Applications of fats before the 19<sup>th</sup> century mainly relied on empirical knowledge mainly resulting from observations (O'Brien, 2000). Today, fats and oils applications are mostly based on the understanding of their chemistry through scientific research.

For many edible purposes, it is desirable to produce solid fats. Traditionally, fat products are structured of high melting TAGs containing trans and saturated fatty acids. These fatty acids are crucial in food applications because they provide several functionalities to food products, such as shortening power, plasticity and elasticity (Edmund and Marangoni, 2012). However, trans and saturated fats have shown negative impacts on human cardiovascular health (Tavernier et al., 2017; Zetzl and Marangoni, 2011). According to the World Health Organization (WHO), cardiovascular disease (CVD) is one of the major causes of death globally (Voon et al., 2019). Numerous clinical studies and meta-analyses have shown that the intake of *trans* fatty acids increases serum LDL ("bad cholesterol") and decreases serum HDL ("good cholesterol") (Katan et al., 1995; Kodali, 2014; Marangoni and Garti, 2011). On the other hand, the intake of saturated fat increases serum lipid concentrations (both LDL and HDL), which could also contribute to CVD (Voon et al., 2019). The overall impact of *trans* fat on CVD is approximately double that of saturated fat due to the higher LDL:HDL ratio (Kodali, 2014). Therefore, recently, the USA Food and Drug Administration (FDA) proposed the complete removal of partially hydrogenated oils (*trans* fats) from human food (Kushairi *et al.*, 2018).

Therefore, a new strategy for structuring edible oils is required to reduce the usage of *trans* and saturated fats. However, the reduction of saturated and *trans* fatty acids in the diet has become a major challenge to food manufacturers because these fatty acids play an important role in structuring fats to provide functionality in food products (Edmund and Marangoni, 2012). In the food industry, there have been many attempts to find alternative components that can provide the desired features of texture, structure, stability and taste that are normally found in animal and vegetable fats or hydrogenated oils (Marangoni and Garti, 2011). Organogelation has become a possible alternative to replace these conventional fats, as it reduces the *trans* and saturated fats for food purposes. The purpose of organogelation is to produce low-saturation solid fat products using lower amounts of saturated components and higher amounts of liquid oil components. The process involves soft matter systems with liquid oil as the continuous phase, entrapped in a three-dimensional network structure formed by self-assembled gelator molecules.

Many trials have been conducted by researchers to apply oleogels in various food products. Hwang et al. (2013) studied the use of sunflower wax, rice bran wax and candelilla wax in gelling soybean oil. The gels were tested for their suitability for incorporation into margarine. Jang et al. (2015) investigated the use of candelilla wax for structuring canola oil and the gel was then used as an alternative to shortening in baked products such as cookies. Yılmaz and Öğütcü (2015a) produced olive oil oleogels from beeswax and sunflower wax and applied the oleogels as spreadable fat and butter alternatives. Most of the studies on oleogel preparation involve the use of soft vegetable oils such as sunflower oil, soybean oil, safflower oil, olive oil, canola oil and rice bran oil (Doan et al., 2015; Jang et al., 2015; Toro-Vazquez et al., 2007; Yılmaz and Öğütcü, 2015a). These highly unsaturated oils have disadvantages for use as the main ingredients for oil structuring, as they are thermally unstable and exhibit poor physical properties, especially when used in food processing applications that requires high processing temperatures. Furthermore, Sacks et al. (2017) reported that excessive consumption of polyunsaturated fatty acids (PUFA) may be detrimental to antioxidant-compromised individuals, although polyunsaturated fatty acids have shown a positive effect in reducing CVD risk when replacing saturated fat.

Therefore, palm olein could be a better choice for the preparation of oleogels due to its balanced fatty acid composition that contains moderate amounts of saturation as compared to conventional fats and other soft vegetable oils. According to Ahmad Tarmizi and Siew (2008), palm oleins showed much higher stability than high-oleic sunflower oil during prolonged frying (80 hours) at 180 °C, in which frying using palm oleins only produced minimal breakdown products, such as free fatty acids, and polar and polymer compounds. The high stability of palm olein against oxidative deterioration during food processing is due to its low linoleic acid content (Voon et al., 2019). Although palm olein contains higher saturated fatty acids than other soft vegetable oils, it shows no significant differences in affecting lipoprotein markers compared to other dietary oils such as canola oil, high-oleic sunflower oil, olive oil, coconut oil *etc.* as reported by Voon et al. (2019) in their most recent meta-analysis. Moreover, the authors concluded that saturated fatty acid-rich palm olein diet did not show any significant adverse effect on established surrogate lipid markers of CVD risk.

As previously mentioned, these liquid fractions from palm oil contain higher saturated contents than other vegetable oils. The role of palm olein in organogelation could be different from that of other vegetable oils, in which the saturation content of olein may interfere positively or negatively with the formation of gel network. Few studies discussed the use of palm-based products such as palm oil, palm olein, superolein or top olein for the preparation of oleogels (Baran et al., 2014; Pradhan et al., 2014). Therefore, this thesis was conducted to investigate the possibility of using palm-based oleins in the preparation of oleogels. The replacement of these highly unsaturated soft vegetable oils with palm-based oleins is expected to improve the chemical and physical stability of oleogels, which can then be applied as a potential material in food products.

A few organogelators were selected in this study including polyglycerol behenic acid ester (PBA), sunflower wax (SFW), fully hydrogenated palm-based monoacylglycerols (MGHP and MGHO), hard palm stearin (PSIV14), and fully hydrogenated palm stearin (PSIV2). Of these gelators, SFW is the most popular gelator and has shown great

potential in gelling various vegetable oils (Blake et al., 2014; Hwang et al., 2015; Hwang et al., 2011, 2012; Patel et al., 2015). There are also numerous studies that have investigated the use of monoglyceride (MG) as a gelling material, in either oil or oil-inwater systems (Bin Sintang et al., 2017a; Da Pieve et al., 2011). Regarding the other materials, their usage as gelling agents has still not been well studied.

## 1.2 Objectives of the Study

In concordance with the research background and justifications presented above, the overall objectives of the study were to investigate the effects of gelator types, gelator dosages, liquid oil type, and preparation temperature on the rheological and physicochemical characteristics of palm-based oleogels and their relation to the stability of the oleogels. To be more specific, the research was conducted to achieve the following objectives:

- 1. To screen suitable gelators (polyglycerol esters, sunflower wax, fully hydrogenated palm-based monoacylglycerols, hard palm stearin IV of 14 and fully hydrogenated palm stearin IV of 2) for the formation of palm superolein oleogels, and to investigate the effect of storage temperature and duration on the rheological and thermal characteristics of the superolein oleogels.
- 2. To study the effect of storage temperature (5 °C, 15 °C and 25 °C) and duration (day 1 to day 3) on the physical and microstructure properties of various superolein oleogels and their relationship to oleogel stability.
- 3. To evaluate the effect of liquid oil type (palm olein fractions, palm mid fraction with soybean oil blends) and gelator dosage (1% w/w to 9% w/w) on the rheological and thermal properties of oleogels made from polyglycerol esters and sunflower wax.
- 4. To investigate the effect of liquid oil type (palm olein fractions, palm mid fraction with soybean oil blends) and gelator dosage (1% w/w to 9% w/w) on the structural and physical properties of polyglycerol esters and sunflower wax oleogels and their relationship to oleogel stability.

#### REFERENCES

- Abdallah, D. J. and Weiss, R. G. (2000). Organogels and Low Molecular Mass Organic Gelators. Advanced Materials 12(17): 1237-1247.
- Ahmad Tarmizi, A. H. and Siew, W. L. (2008). Quality Assessment of Palm Products upon Prolonged Heat Treatment. *Journal of Oleo Science* 57(12): 639-648.
- AOCS (Reapproved 2017a). AOCS Official Method Ce 5c-93: Individual Triglycerides in Oils and Fats by HPLC. In AOCS Official Method, Urbana: AOCS.
- AOCS (Reapproved 2017b). AOCS Official Method Cj 2-95: X-Ray Diffraction Analysis of Fats. In AOCS Official Method, Urbana: AOCS.
- AOCS (Revised 2017). AOCS Official Method Ce 5b-89: Triglycerides in Vegetable Oils by HPLC. In AOCS Official Method, Urbana: AOCS.
- Augusto, P. E. D., Soares, B. M. C., Chiu, M. C. and Gonçalves, L. A. G. (2012). Modelling the effect of temperature on the lipid solid fat content (SFC). *Food Research International* 45(1): 132-135.
- Baran, N., Singh, V. K., Pal, K., Anis, A., Pradhan, D. K. and Pramanik, K. (2014). Development and Characterization of Soy Lecithin and Palm Oil-based Organogels. *Polymer-Plastics Technology and Engineering* 53(9): 865-879.
- Barbut, S., Wood, J. and Marangoni, A. G. (2016). Effects of Organogel Hardness and Formulation on Acceptance of Frankfurters. *Journal of Food Science* 81(9): C2183-C2188.
- Beers, A., Ariaansz, R. and Okonek, D. (2008). Trans Isomer Control in Hydrogenation of Edible Oils. 147-180.
- Bin Sintang, M. D., Danthine, S., Brown, A., Van de Walle, D., Patel, A. R., Tavernier, I., Rimaux, T. and Dewettinck, K. (2017a). Phytosterols-induced viscoelasticity of oleogels prepared by using monoglycerides. *Food Research International* 100: 832-840.
- Bin Sintang, M. D., Danthine, S., Patel, A. R., Rimaux, T., Van De Walle, D. and Dewettinck, K. (2017b). Mixed surfactant systems of sucrose esters and lecithin as a synergistic approach for oil structuring. *Journal of Colloid and Interface Science* 504: 387-396.
- Birker, P. J. M. W. L. and Padley, F. B. (1987). Physical properties of fats and oils. In A. B. R. J. Hamilton, ed. Recent Advances in Chemistry and Techonology of Fats and Oils, pp. 1-11. New York: Elsevier.
- Blake, A. I., Co, E. D. and Marangoni, A. G. (2014). Structure and Physical Properties of Plant Wax Crystal Networks and Their Relationship to Oil Binding Capacity. *Journal of the American Oil Chemists' Society* 91(6): 885-903.

- Blake, A. I. and Marangoni, A. G. (2015). Plant wax crystals display platelet-like morphology. *Food Structure* 3: 30-34.
- Bodennec, M., Guo, Q. and Rousseau, D. (2016). Molecular and microstructural characterization of lecithin-based oleogels made with vegetable oil. *RSC Advances* 6(53): 47373-47381.
- Bot, A. and Agterof, W. G. M. (2006). Structuring of edible oils by mixtures of γoryzanol with β-sitosterol or related phytosterols. *Journal of the American Oil Chemists' Society* 83(6): 513-521.
- Bot, A., den Adel, R. and Roijers, E. C. (2008). Fibrils of  $\gamma$ -Oryzanol +  $\beta$ -Sitosterol in Edible Oil Organogels. *Journal of the American Oil Chemists' Society* 85(12): 1127-1134.
- Bot, A., den Adel, R., Roijers, E. C. and Regkos, C. (2009a). Effect of Sterol Type on Structure of Tubules in Sterol + γ-Oryzanol-Based Organogels. Food Biophysics 4(4): 266-272.
- Bot, A., Veldhuizen, Y. S. J., den Adel, R. and Roijers, E. C. (2009b). Non-TAG structuring of edible oils and emulsions. *Food Hydrocolloids* 23(4): 1184-1189.
- Carelli, A. A., Frizzera, L. M., Forbito, P. R. and Crapiste, G. H. (2002). Wax composition of sunflower seed oils. *Journal of the American Oil Chemists'* Society 79(8): 763-768.
- Cegla-Nemirovsky, Y., Aserin, A. and Garti, N. (2015). Oleogels from Glycerol-Based Lyotropic Liquid Crystals: Phase Diagrams and Structural Characterization. Journal of the American Oil Chemists' Society 92(3): 439-447.
- Cerqueira, M. A., Fasolin, L. H., Picone, C. S. F., Pastrana, L. M., Cunha, R. L. and Vicente, A. A. (2017). Structural and mechanical properties of organogels: Role of oil and gelator molecular structure. *Food Research International* 96: 161-170.
- Chemical Book (a). Polyglyceryl-10 Heptastearate. Retrieved 1 Mac 2019 from https://www.chemicalbook.com/ProductChemicalPropertiesCB1963517\_EN.h tm
- Chemical Book (b). Polyglyceryl-10 Tristearate. Retrieved 1 Mac 2019 from https://www.chemicalbook.com/ProductChemicalPropertiesCB4965653\_EN.h tm
- Chen, C. H. and Terentjev, E. M. (2009). Aging and Metastability of Monoglycerides in Hydrophobic Solutions. *Langmuir* 25(12): 6717-6724.
- Chen, C. H. and Terentjev, E. M. (2010). Effects of Water on Aggregation and Stability of Monoglycerides in Hydrophobic Solutions. *Langmuir* 26(5): 3095-3105.

- Chen, C. H., Van Damme, I. and Terentjev, E. M. (2009). Phase behavior of C18 monoglyceride in hydrophobic solutions. *Soft Matter* 5(2): 432-439.
- Criado, M., Hernández-Martín, E. and Otero, C. (2007). Optimized interesterification of virgin olive oil with a fully hydrogenated fat in a batch reactor: Effect of mass transfer limitations. *European Journal of Lipid Science and Technology* 109(5): 474-485.
- D'Souza, V., deMan, J. M. and deMan, L. (1990). Short spacings and polymorphic forms of natural and commercial solid fats: A review. *Journal of the American Oil Chemists' Society* 67(11): 835-843.
- Da Pieve, S., Calligaris, S., Co, E., Nicoli, M. C. and Marangoni, A. G. (2010). Shear Nanostructuring of Monoglyceride Organogels. *Food Biophysics* 5(3): 211-217.
- Da Pieve, S., Calligaris, S., Panozzo, A., Arrighetti, G. and Nicoli, M. C. (2011). Effect of monoglyceride organogel structure on cod liver oil stability. *Food Research International* 44(9): 2978-2983.
- da Silva, T. L. T., Chaves, K. F., Fernandes, G. D., Rodrigues, J. B., Bolini, H. M. A. and Arellano, D. B. (2018). Sensory and Technological Evaluation of Margarines With Reduced Saturated Fatty Acid Contents Using Oleogel Technology. *Journal of the American Oil Chemists' Society* 95(6): 673-685.
- Daniel, J. and Rajasekharan, R. (2003). Organogelation of plant oils and hydrocarbons by long-chain saturated FA, fatty alcohols, wax esters, and dicarboxylic acids. *Journal of the American Oil Chemists' Society* 80(5): 417-421.
- Dassanayake, L., Kodali, D., Ueno, S. and Sato, K. (2012). Crystallization Kinetics of Organogels Prepared by Rice Bran Wax and Vegetable Oils. *Journal of Oleo Science* 61: 1-9.
- Dassanayake, L., R. Kodali, D. and Ueno, S. (2011). Formation of oleogels based on edible lipid materials. *Current Opinion in Colloid & Interface Science CURR OPIN COLLOID INTERFACE S* 16: 432-439.
- Dassanayake, L. S. K., Kodali, D. R., Ueno, S. and Sato, K. (2009). Physical Properties of Rice Bran Wax in Bulk and Organogels. *Journal of the American Oil Chemists' Society* 86(12): 1163.
- Davidovich-Pinhas, M., Barbut, S. and Marangoni, A. (2015a). The gelation of oil using ethyl cellulose. *Carbohydrate polymers* 117C: 869-878.
- Davidovich-Pinhas, M., Barbut, S. and Marangoni, A. G. (2014). Physical structure and thermal behavior of ethylcellulose. *Cellulose* 21(5): 3243-3255.
- Davidovich-Pinhas, M., Gravelle, A. J., Barbut, S. and Marangoni, A. G. (2015b). Temperature effects on the gelation of ethylcellulose oleogels. *Food Hydrocolloids* 46: 76-83.

- deMan, J. M. (1992). X-ray diffraction spectroscopy in the study of fat polymorphism. *Food Research International* 25(6): 471-476.
- deMan, L., deMan, J. M. and Blackman, B. (1989). Polymorphic behavior of some fully hydrogenated oils and their mixtures with liquid oil. *Journal of the American Oil Chemists' Society* 66(12): 1777-1780.
- Dijkstra, A. J. (2006). Revisiting the formation of trans isomers during partial hydrogenation of triacylglycerol oils. *European Journal of Lipid Science and Technology* 108(3): 249-264.
- Dijkstra, A. J. (2007). Modification processes and food uses. In F. D. Gunstone, J. L. Harwood and A. J. Dijkstra, ed. The Lipid Handbook with CD-ROM, Third Edition, pp. 263-333. Boca Raton: CRC Press.
- Doan, C. D., Patel, A. R., Tavernier, I., De Clercq, N., Van Raemdonck, K., Van de Walle, D., Delbaere, C. and Dewettinck, K. (2016). The feasibility of waxbased oleogel as a potential co-structurant with palm oil in low-saturated fat confectionery fillings. *European Journal of Lipid Science and Technology* 118(12): 1903-1914.
- Doan, C. D., To, C. M., De Vrieze, M., Lynen, F., Danthine, S., Brown, A., Dewettinck, K. and Patel, A. R. (2017). Chemical profiling of the major components in natural waxes to elucidate their role in liquid oil structuring. *Food Chemistry* 214: 717-725.
- Doan, C. D., Van de Walle, D., Dewettinck, K. and Patel, A. R. (2015). Evaluating the Oil-Gelling Properties of Natural Waxes in Rice Bran Oil: Rheological, Thermal, and Microstructural Study. *Journal of the American Oil Chemists'* Society 92(6): 801-811.
- Beers, A. and Mangnus, G. (2004). Hydrogenation of edible oils for reduced trans-fatty acid content. *INFORM International News on Fats, Oils and Related Materials* 15: 404-405.
- Edmund, D. C. and Marangoni, A. G. (2012). Organogels: An Alternative Edible Oil-Structuring Method. *Journal of the American Oil Chemists' Society* 89(5): 749-780.
- El-Fiqi, A., Lee, J. H., Lee, E.-J. and Kim, H.-W. (2013). Collagen hydrogels incorporated with surface-aminated mesoporous nanobioactive glass: Improvement of physicochemical stability and mechanical properties is effective for hard tissue engineering. *Acta Biomaterialia* 9(12): 9508-9521.
- Fahmi Daman Huri, M., Ng, S.-F. and Hanif Zulfakar, M. (2013). Fish Oil-Based Oleogels : Physicochemicals Characterisation And In Vitro Release of Betamethasone Dipropionate. *International Journal of Pharmacy and Pharmaceutical Sciences* 5: 458-467.

- Farfán, M., Álvarez, A., Gárate, A. and Bouchon, P. (2015). Comparison of Chemical and Enzymatic Interesterification of Fully Hydrogenated Soybean Oil and Walnut Oil to Produce a Fat Base with Adequate Nutritional and Physical Characteristics. *Food technology and biotechnology* 53(3): 361-366.
- Farmani, J., Hamedi, M., Safari, M. and Madadlou, A. (2007). Trans-free Iranian vanaspati through enzymatic and chemical transesterification of triple blends of fully hydrogenated soybean, rapeseed and sunflower oils. *Food Chemistry* 102(3): 827-833.
- Faur, L. (1996). Transformation of fat for use in food products. In A. Karleskind, ed. Oils and Fats Manual: A Comprehensive Treatise (Volume 2), pp. 897-1024. Paris: Lavoisier Publishing.
- Fayaz, G., Goli, S. A. H., Kadivar, M., Valoppi, F., Barba, L., Calligaris, S. and Nicoli, M. C. (2017). Potential application of pomegranate seed oil oleogels based on monoglycerides, beeswax and propolis wax as partial substitutes of palm oil in functional chocolate spread. *LWT* 86: 523-529.
- Fredrick, E., Foubert, I., Van De Sype, J. and Dewettinck, K. (2008). Influence of Monoglycerides on the Crystallization Behavior of Palm Oil. Crystal Growth & Design 8(6): 1833-1839.
- Gallego, R., Arteaga, J. F., Valencia, C. and Franco, J. M. (2013). Rheology and thermal degradation of isocyanate-functionalized methyl cellulose-based oleogels. *Carbohydrate polymers* 98(1): 152-160.
- George, M. and Weiss, R. G. (2006). Low molecular-mass organic gelators. In R. G. Weiss and P. Terech, ed. Molecular Gels: Materials with self-asembled fibrillar networks, pp. 449-453. The Netherlands: Springer.
- Ghazali, H. M., Hamidah, S. and Che Man, Y. B. (1995). Enzymatic transesterification of palm olein with nonspecific and 1,3-specific lipases. *Journal of the American Oil Chemists' Society* 72(6): 633-639.
- Gravelle, A. J., Barbut, S. and Marangoni, A. G. (2012). Ethylcellulose oleogels: Manufacturing considerations and effects of oil oxidation. *Food Research International* 48(2): 578-583.
- Gunstone, F. D. (2001a). Procedures used for lipid modification. In *F. D. Gunstone*, ed. Structured and Modified Lipids, pp. 11-35. New York: Marcel Dekker.
- Gunstone, F. D. (2001b). Why are structured lipids and new lipid sources required? In *F. D. Gunstone*, ed. Structured and Modified Lipids, pp. 1-9. New York: Marcel Dekker.
- Han, L.-J., Li, L., Zhao, L., Li, B., Liu, G.-Q., Liu, X.-Q. and Wang, X.-D. (2013). Rheological properties of organogels developed by sitosterol and lecithin. *Food Research International* 53(1): 42-48.

- Haryati, T., Che Man, Y. B., Ghazali, H. M., Asbi, B. A. and Buana, L. (1998). Determination of iodine value of palm oil based on triglyceride composition. *Journal of the American Oil Chemists' Society* 75(7): 789-792.
- Horn, M. (2018). Fat Crystallization Fractionation by Entrainment and Characterization using Refractometry. Technical University of Berlin, Berlin.
- Hwang, H.-S., Kim, S., Evans, K. O., Koga, C. and Lee, Y. (2015). Morphology and networks of sunflower wax crystals in soybean oil organogel. *Food Structure* 5: 10-20.
- Hwang, H.-S., Kim, S., Singh, M., Winkler-Moser, J. K. and Liu, S. X. (2011). Organogel Formation of Soybean Oil with Waxes. *Journal of the American Oil Chemists' Society* 89(4): 639-647.
- Hwang, H.-S., Kim, S., Singh, M., Winkler-Moser, J. K. and Liu, S. X. (2012). Organogel Formation of Soybean Oil with Waxes. *Journal of the American Oil Chemists' Society* 89(4): 639-647.
- Hwang, H.-S., Singh, M., Bakota, E. L., Winkler-Moser, J. K., Kim, S. and Liu, S. X. (2013). Margarine from Organogels of Plant Wax and Soybean Oil. *Journal of the American Oil Chemists' Society* 90(11): 1705-1712.
- Idris, N. A. and Mat Dian, N. L. H. (2005). Interesterified palm oil as alternatives to hydrogenation. *Asia Pacific Journal of Clinical Nutrition* 14: 396-401.
- Imai, T., Nakamura, K. and Shibata, M. (2001). Relationship between the hardness of an oil-wax gel and the surface structure of the wax crystals. *Colloids and Surfaces* A: Physicochemical and Engineering Aspects 194(1): 233-237.
- Jahurul, M. H. A., Zaidul, I. S. M., Norulaini, N. A. N., Sahena, F., Abedin, M. Z., Ghafoor, K. and Mohd Omar, A. K. (2014). Characterization of crystallization and melting profiles of blends of mango seed fat and palm oil mid-fraction as cocoa butter replacers using differential scanning calorimetry and pulse nuclear magnetic resonance. *Food Research International* 55: 103-109.
- Jana, S. and Martini, S. (2016). Physical characterization of crystalline networks formed by binary blends of waxes in soybean oil. *Food Research International* 89: 245-253.
- Jang, A., Bae, W., Hwang, H.-S., Lee, H. G. and Lee, S. (2015). Evaluation of canola oil oleogels with candelilla wax as an alternative to shortening in baked goods. *Food Chemistry* 187: 525-529.
- Jimenez-Colmenero, F., Salcedo-Sandoval, L., Bou, R., Cofrades, S., Herrero, A. M. and Ruiz-Capillas, C. (2015). Novel applications of oil-structuring methods as a strategy to improve the fat content of meat products. *Trends in Food Science & Technology* 44(2): 177-188.

- Jin, J., Jie, L., Zheng, L., Cheng, M., Xie, D., Jin, Q. and Wang, X. (2018). Characteristics of palm mid-fractions produced from different fractionation paths and their potential usages. *International Journal of Food Properties* 21(1): 58-69.
- Kanagaratnam, S., Enamul Hoque, M., Mat Sahri, M. and Spowage, A. (2013). Investigating the effect of deforming temperature on the oil-binding capacity of palm oil based shortening. *Journal of Food Engineering* 118(1): 90-99.
- Katan, M. B., Zock, P. L. and Mensink, R. P. (1995). Trans Fatty Acids and Their Effects on Lipoproteins in Humans. *Annual Review of Nutrition* 15(1): 473-493.
- Kellens, M., Gibon, V., Hendrix, M. and De Greyt, W. (2007). Palm oil fractionation. *European Journal of Lipid Science and Technology* 109(4): 336-349.
- Kesselman, E. and Shimoni, E. (2007). Imaging of Oil/Monoglyceride Networks by Polarizing Near-Field Scanning Optical Microscopy. *Food Biophysics* 2(2): 117-123.
- Kodali, D. R. (2014). Trans Fats: Health, Chemistry, Functionality, and Potential Replacement Solutions. In D. R. Kodali, ed. Trans Fats Replacement Solutions, pp. 1-39. Urbana: AOCS Press.
- Kouzounis, D., Lazaridou, A. and Katsanidis, E. (2017). Partial replacement of animal fat by oleogels structured with monoglycerides and phytosterols in frankfurter sausages. *Meat Science* 130: 38-46.
- Kushairi, A., Loh, S. K., Azman, I., Elina, H., Meilina, O.-A., Zanal, B. M. N. I., Razmah, G., Shamala, S. and Parveez, G. K. A. (2018). Oil palm economic performance in Malaysia and R&D progress in 2017– Review Article. *Journal of Oil Palm Research* 30: 163-195.
- Lampert, D. (2000). Process and products of interesterification. In E. F. Walter and J. W. Peter, ed. Introduction to Fats and Oils Technology (Second Edition), pp. 208-234. Champaign: AOCS Press.
- Lan, Y. and Rogers, M. A. (2015). 12-Hydroxystearic acid SAFiNs in aliphatic diols a molecular oddity. *CrystEngComm* 17(42): 8031-8038.
- Libster, D., Aserin, A. and Garti, N. (2011). Oleogels Based on Non-lamellar Lyotropic Liquid Crystalline Structures for Food Applications. In A. G. Marangoni and N. Garti, ed. Edible Oleogels (Second Edition), pp. 235-269. Urbana: AOCS Press.
- Lim, J., Jeong, S., Oh, I. K. and Lee, S. (2017). Evaluation of soybean oil-carnauba wax oleogels as an alternative to high saturated fat frying media for instant fried noodles. *LWT* 84: 788-794.
- List, G. (2014). Trans Fats Replacement Solutions for Frying and Baking Applications, Shortenings, Margarines, and Spreads. In *D. R. Kodali*, ed. Trans Fats Replacement Solutions, pp. 245-273. Urbana: AOCS Press

- List, G. R. and Jackson, M. A. (2011). Low Trans Hydrogenation. In *G. R. List and J. W. King*, ed. Hydrogenation of Fats and Oils (Second Edition), pp. 305-313. AOCS Press.
- Lopez-Martínez, A., Charó-Alonso, M. A., Marangoni, A. G. and Toro-Vazquez, J. F. (2015). Monoglyceride organogels developed in vegetable oil with and without ethylcellulose. *Food Research International* 72: 37-46.
- Lowe, B. (1937). Experimental cookery: From the chemical and physical standpoint. By
  B. Lowe. 2nd ed. Pp. xi + Coo. New York: J. Wiley & Sons, Inc.; London: Chapman & Hall, Ltd., 1937. 22s. Gd. *Journal of the Society of Chemical Industry* 56(44): 969-970.
- Lupi, F., De Santo, M., Ciuchi, F., Baldino, N. and Gabriele, D. (2018). The role of edible oils in low molecular weight organogels rheology and structure. *Food Research International* 111.
- Lupi, F., Gabriele, D., Baldino, N., Mijovic, P., I Parisi, O. and Puoci, F. (2013a). Olive oil/policosanol organogels for nutraceutical and drug delivery purposes. *Food & Function* 4.
- Lupi, F., Gabriele, D., Facciolo, D., Baldino, N., Seta, L. and De Cindio, B. (2012). Effect of organogelator and fat source on rheological properties of olive oilbased organogels. *Food Research International* 46: 177–184.
- Lupi, F., Gabriele, D., Greco, V., Baldino, N., Seta, L. and De Cindio, B. (2013b). A rheological characterisation of an olive oil/fatty alcohols organogel. *Food Research International* 51: 510–517.
- Lupi, F. R., Greco, V., Baldino, N., de Cindio, B., Fischer, P. and Gabriele, D. (2016). The effects of intermolecular interactions on the physical properties of organogels in edible oils. *Journal of Colloid and Interface Science* 483: 154-164.
- Lupi, F. R., Shakeel, A., Greco, V., Baldino, N., Calabrò, V. and Gabriele, D. (2017). Organogelation of extra virgin olive oil with fatty alcohols, glyceryl stearate and their mixture. *LWT* 77: 422-429.
- Marangoni, A. G. and Garti, N. (2011). An overview of the past, present, and future of organogels. In A. G. Marangoni and N. Garti, ed. Edible Oleogels: Structure and Health Implications, pp. 1-18. Urbana: AOCS Press.
- Mattice, K. D. and Marangoni, A. G. (2018a). Edible Applications of Ethylcellulose Oleogels. In *A. R. Patel*, ed. Edible Oil Structuring: Concepts, Methods and Applications, pp. 250-274. Cambridge: The Royal Society of Chemistry.
- Mattice, K. D. and Marangoni, A. G. (2018b). New Insights into Wax Crystal Networks in Oleogels. In *A. R. Patel*, ed. Edible Oil Structuring: Concepts, Methods and Applications, pp. 69-94. Cambridge: The Royal Society of Chemistry.

- McClements, D. J. (2010). Emulsion Design to Improve the Delivery of Functional Lipophilic Components. *Annual Review of Food Science and Technology* 1(1): 241-269.
- McNeill, G. P. (2014). Processing Solutions: Fractionation and Blended Oils. In, pp. 123-138.
- Mert, B. and Demirkesen, I. (2016a). Evaluation of highly unsaturated oleogels as shortening replacer in a short dough product. *LWT Food Science and Technology* 68: 477-484.
- Mert, B. and Demirkesen, I. (2016b). Reducing saturated fat with oleogel/shortening blends in a baked product. *Food Chemistry* 199: 809-816.
- Microscopy, M. (2013). What are the differences between brightfield, darkfield and phase contrast? In, vol. 2019).
- Miskandar, M. S., Che Man, Y. B., Abdul Rahman, R., Nor Aini, I. and Yusoff, M. S. A. (2004). Palm oil crystallization: effects of cooling time and oil content. *Journal of Food Lipids* 11(3): 190-207.
- Miskandar, M. S. and Nor Aini, I. (2010). Palm stearin as low trans hard stock for margarine. *Sains Malaysiana* 39: 821-827.
- Moghtadaei, M., Soltanizadeh, N. and Goli, S. A. H. (2018). Production of sesame oil oleogels based on beeswax and application as partial substitutes of animal fat in beef burger. *Food Research International* 108: 368-377.
- Morales-Rueda, J. A., Dibildox-Alvarado, E., Charó-Alonso, M. A. and Toro-Vazquez, J. F. (2009). Rheological Properties of Candelilla Wax and Dotriacontane Organogels Measured with a True-Gap System. *Journal of the American Oil Chemists' Society* 86(8): 765-772.
- Moriano, M. E. and Alamprese, C. (2017). Organogels as novel ingredients for low saturated fat ice creams. *LWT* 86: 371-376.
- Mossoba, M. M. M. and Kramer, J. K. G. (2003). Official Methods for the Determination of Trans Fat, Second Edition. In Structure and Occurence of Trans Fatty Acids, Urbana: AOCS Press.
- MPOB. (2005). MPOB Test Method P3.4-Part 4. In *Methods of test for palm oil and palm oil products: Preparation of methyl esters of fatty acids-part 4: Rapid method*, (pp. 308-309). Kuala Lumpur: Malaysian Palm Oil Board.
- Naudet, M. (1996). Main chemical constituents of fats. In *H. Karlheinz*, ed. Oils and Fats Manual: A Comprehensive Treatise (Volume 1), pp. 67-116. Paris: Lavoisier Publishing.
- Nikiforidis, C. V. and Scholten, E. (2014). Self-assemblies of lecithin and α-tocopherol as gelators of lipid material. *RSC Adv*. 4(5): 2466-2473.

- Nor Aini, I. and Miskandar, M. S. (2007). Utilization of palm oil and palm products in shortenings and margarines. *European Journal of Lipid Science and Technology* 109(4): 422-432.
- Norizzah, A. R., Chong, C. L., Cheow, C. S. and Zaliha, O. (2004). Effects of chemical interesterification on physicochemical properties of palm stearin and palm kernel olein blends. *Food Chemistry* 86(2): 229-235.
- Nur Haqim, I., Miskandar, M. S. and Rafidah, A. H. (2018). Influence of Palm-Based Fluid Shortening on the Physical and Textural Properties of Biscuits. *Journal* of Oil Palm Research 30: 299-305.
- O'Brien, R. D. (2000). Fats and Oil: An Overview. In *R. D. O'Brien, W. E. Farr and P. J. Wan,* ed. Introduction to Fats and Oils Technology, Second Edition, Champaign, Illinois: AOCS Press.
- O'Keefe, S. F. and Sarnoski, P. J. (2017). Nomenclature and classification of lipids. In *C. C. Akoh*, ed. Food Lipids: Chemistry, Nutrition, and Biotechnology, Fourth Edition, pp. 3-36. Boca Raton: CRC Press.
- Öğütcü, M., Arifoğlu, N. and Yılmaz, E. (2015). Preparation and Characterization of Virgin Olive Oil-Beeswax Oleogel Emulsion Products. *Journal of the American Oil Chemists' Society* 92(4): 459-471.
- Öğütcü, M., Temizkan, R., Arifoğlu, N. and Yılmaz, E. (2015). Structure and Stability of Fish Oil Organogels Prepared with Sunflower Wax and Monoglyceride. *Journal of Oleo Science* 64(7): 713-720.
- Öğütcü, M. and Yılmaz, E. (2014). Oleogels of virgin olive oil with carnauba wax and monoglyceride as spreadable products. *Grasas y Aceites* 65(3): e040.
- Öğütcü, M. and Yılmaz, E. (2015). Characterization of Hazelnut Oil Oleogels Prepared with Sunflower and Carnauba Waxes. *International Journal of Food Properties* 18(8): 1741-1755.
- Öğütcü, M. and Yilmaz, E. (2014). Oleogels of virgin olive oil with carnauba wax and monoglyceride as spreadable products. *Grasas Aceites* 63(3): e040.
- Oh, I. K., Amoah, C., Lim, J., Jeong, S. and Lee, S. (2017). Assessing the effectiveness of wax-based sunflower oil oleogels in cakes as a shortening replacer. *LWT* 86: 430-437.
- Oh, I. K. and Lee, S. (2018). Utilization of foam structured hydroxypropyl methylcellulose for oleogels and their application as a solid fat replacer in muffins. *Food Hydrocolloids* 77: 796-802.
- Ojijo, N., Kesselman, E., Shuster, V., Eichler, S., Eger, S., Neeman, I. and Shimoni, E. (2004a). Changes in microstructural, thermal, and rheological properties of olive oil/monoglyceride networks during storage. *Food Research International* 37: 385-393.

- Ojijo, N. K. O., Neeman, I., Eger, S. and Shimoni, E. (2004b). Effects of monoglyceride content, cooling rate and shear on the rheological properties of olive oil/monoglyceride gel networks. *Journal of the Science of Food and Agriculture* 84(12): 1585-1593.
- Okuro, P. K., Malfatti-Gasperini, A. A., Vicente, A. A. and Cunha, R. L. (2018). Lecithin and phytosterols-based mixtures as hybrid structuring agents in different organic phases. *Food Research International* 111: 168-177.
- Omar, Z., Rashid, N. A., Fauzi, S. H. M., Shahrim, Z. and Marangoni, A. G. (2015). Fractal dimension in palm oil crystal networks during storage by image analysis and rheological measurements. *LWT - Food Science and Technology* 64(1): 483-489.
- Patel, A., Cludts, N., Sintang, M. D., Lesaffer, A. and Dewettinck, K. (2014a). Edible oleogels based on water soluble food polymers: Preparation, characterization and potential application. *Food Funct.* 5: 2833-2841.
- Patel, A., Rajarethinem, P., Cludts, N., Lewille, B., DeVos, W., Lesaffer, A. and Dewettinck, K. (2014b). Biopolymer-Based Structuring of Liquid Oil into Soft Solids and Oleogels Using Water-Continuous Emulsions as Templates. Langmuir : the ACS journal of surfaces and colloids 31.
- Patel, A., Schatteman, D., De Vos, W. and Dewettinck, K. (2013a). Shellac as a natural material to structure a liquid oil-based thermo reversible soft matter system. *RSC Advances*.
- Patel, A. R. (2018). Oil Structuring: Concepts, Overview and Future Perspectives. In A. R. Patel, ed. Edible Oil Structuring: Concepts, Methods and Applications, pp. 1-22. Cambridge: The Royal Society of Chemistry.
- Patel, A. R., Babaahmadi, M., Lesaffer, A. and Dewettinck, K. (2015). Rheological Profiling of Organogels Prepared at Critical Gelling Concentrations of Natural Waxes in a Triacylglycerol Solvent. *Journal of Agricultural and Food Chemistry* 63(19): 4862-4869.
- Patel, A. R., Rajarethinem, P. S., Grędowska, A., Turhan, O., Lesaffer, A., De Vos, W. H., Van de Walle, D. and Dewettinck, K. (2014c). Edible applications of shellac oleogels: spreads, chocolate paste and cakes. *Food & Function* 5(4): 645-652.
- Patel, A. R., Schatteman, D., De Vos, W. H., Lesaffer, A. and Dewettinck, K. (2013b). Preparation and rheological characterization of shellac oleogels and oleogelbased emulsions. *Journal of Colloid and Interface Science* 411: 114-121.
- Pehlivanoğlu, H., Demirci, M., Toker, O. S., Konar, N., Karasu, S. and Sagdic, O. (2018). Oleogels, a promising structured oil for decreasing saturated fatty acid concentrations: Production and food-based applications. *Critical Reviews in Food Science and Nutrition* 58(8): 1330-1341.

- Pembe, W. M., Ramadhan, A. H., Omar, K. A., Jin, J., Jianhua Huang, Liyou, Z. and Jin, Q. (2017). Blending of Mango Kernal Fat Stearine with Palm Oil Mid-fraction to Obtain Cocoa Butter Equivalent. *American Journal of Food Science and Nutrition Research* 4(2): 71-78.
- Pernetti, M., van Malssen, K., Kalnin, D. and Flöter, E. (2007a). Structuring edible oil with lecithin and sorbitan tri-stearate. *Food Hydrocolloids* 21(5): 855-861.
- Pernetti, M., van Malssen, K. F., Flöter, E. and Bot, A. (2007b). Structuring of edible oils by alternatives to crystalline fat. *Current Opinion in Colloid & Interface Science* 12(4): 221-231.
- Petrauskaité, V., De Greyt, W. F., Kellens, M. J. and Huyghebaert, A. D. (1998). Chemical interesterification of vegetable oil blends: optimization of process parameters. *OCL* 5: 65-69.
- Peyronel, M. F. and Marangoni, A. G. (2013). X-Ray Powder Diffractometry. In, vol. 2019): Lipid Library AOCS.
- Pradhan, S., Sagiri, S. S., Singh, V. K., Pal, K., Ray, S. S. and Pradhan, D. K. (2014). Palm oil-based organogels and microemulsions for delivery of antimicrobial drugs. *Journal of Applied Polymer Science* 131(6).
- Razul, M. S. G., MacDougall, C. J., Hanna, C. B., Marangoni, A. G., Peyronel, F., Papp-Szabo, E. and Pink, D. A. (2014). Oil binding capacities of triacylglycerol crystalline nanoplatelets: nanoscale models of tristearin solids in liquid triolein. *Food & Function* 5(10): 2501-2508.
- Ribeiro, A. P. B., Grimaldi, R., Gioielli, L. A. and Gonçalves, L. A. G. (2009). Zero trans fats from soybean oil and fully hydrogenated soybean oil: Physico-chemical properties and food applications. *Food Research International* 42(3): 401-410.
- Rogers, M. A. (2009). Novel structuring strategies for unsaturated fats Meeting the zero-trans, zero-saturated fat challenge: A review. *Food Research International* 42(7): 747-753.
- Rogers, M. A. (2018). Biomimicry: An Approach for Oil Structuring. In A. R. Patel, ed. Edible Oil Structuring: Concepts, Methods and Applications, pp. 53-68. Cambridge: The Royal Society of Chemistry.
- Rogers, M. A. and Kim, J. H. J. (2011). Rheological assessment of the sol-gel transition for self-assembling low molecular weight gelators. *Food Research International* 44(5): 1447-1451.
- Rogers, M. A. and Marangoni, A. G. (2008). Non-Isothermal Nucleation and Crystallization of 12-Hydroxystearic Acid in Vegetable Oils. *Crystal Growth & Design* 8(12): 4596-4601.

- Rogers, M. A., Tang, D., Ahmadi, L. and Marangoni, A. G. (2008a). Fat Crystal Networks. In J. M. Aguilera and P. J. Lillford, ed. Food Materials Science, pp. 369-414. New Yok: Springer, New York.
- Rogers, M. A., Wright, A. J. and Marangoni, A. G. (2008b). Crystalline stability of selfassembled fibrillar networks of 12-hydroxystearic acid in edible oils. *Food Research International* 41(10): 1026-1034.
- Rousseau, D. and Marangoni, A. (2008). Chemical Interesterification of Food Lipids: Theory and Practice. *Food Sci. Technol.* (*N.Y.*) 88: 251-281.
- Sacks, F. M., Lichtenstein, A. H., Wu, J. H. Y., Appel, L. J., Creager, M. A., Kris-Etherton, P. M., Miller, M., Rimm, E. B., Rudel, L. L., Robinson, J. G., Stone, N. J. and Horn, L. V. V. (2017). Dietary Fats and Cardiovascular Disease: A Presidential Advisory From the American Heart Association. *Circulation* 136(3): e1-e23.
- Sagiri, S. S., Samateh, M. and John, G. (2018). Biobased Molecular Structuring Agents. In A. R. Patel, ed. Edible Oil Structuring: Concepts, Methods and Applications, pp. 23-52. Cambridge: The Royal Society of Chemistry.
- Sagiri, S. S., Singh, V. K., Pal, K., Banerjee, I. and Basak, P. (2015). Stearic acid based oleogels: A study on the molecular, thermal and mechanical properties. *Materials Science and Engineering: C* 48: 688-699.
- Sato, K. (2018a). Introduction: Relationships of Structures, Properties and Functionality. In K. Sato, ed. Crystallization of Lipids: Fundamentals and Applications in Food, Cosmetics, and Pharmaceuticals, pp. 1-15. West Sussex: John Wiley & Sons Ltd.
- Sato, K. (2018b). Polymorphism of Lipid Crystals. In K. Sato, ed. Crystallization of Lipids: Fundamental and Applications in Food, Cosmetics, and Pharmaceuticals, pp. 17-60. West Sussex: John Wiley & Sons Ltd.
- Saw, M. H. (2010). New Palm Oil Products by Enzymatic Interesterification and Dry Fractionation. University of Malaya, Kuala Lumpur.
- Saw, M. H., Chong, C. L. and Yeoh, C. B. (2015). New Development in Palm Oil Fractionation. *Palm Oil Development* 62: 1-14.
- Saw, M. H. and Siew, W. L. (2014). The Effectiveness of Immobilized Lipase Thermomyces lanuginosa in Catalyzing Interesterification of Palm Olein in Batch Reaction. *Journal of Oleo Science* 63(3): 295-302.
- Sawalha, H., den Adel, R., Venema, P., Bot, A., Flöter, E. and van der Linden, E. (2012). Organogel-Emulsions with Mixtures of β-Sitosterol and γ-Oryzanol: Influence of Water Activity and Type of Oil Phase on Gelling Capability. *Journal of Agricultural and Food Chemistry* 60(13): 3462-3470.

- Sawalha, H., Venema, P., Bot, A., Flöter, E. and van der Linden, E. (2011). The Influence of Concentration and Temperature on the Formation of  $\gamma$ -Oryzanol+ $\beta$ -Sitosterol Tubules in Edible Oil Organogels. *Food Biophysics* 6(1): 20-25.
- Schaink, H. M., van Malssen, K. F., Morgado-Alves, S., Kalnin, D. and van der Linden, E. (2007). Crystal network for edible oil organogels: Possibilities and limitations of the fatty acid and fatty alcohol systems. *Food Research International* 40(9): 1185-1193.
- Shah, D. K., Sagiri, S. S., Behera, B., Pal, K. and Pramanik, K. (2013). Development of olive oil based organogels using sorbitan monopalmitate and sorbitan monostearate: A comparative study. *Journal of Applied Polymer Science* 129(2): 793-805.
- Shakeel, A., Farooq, U., Iqbal, T., Yasin, S., Lupi, F. and Gabriele, D. (2018). Key characteristics and modelling of bigels systems: A review. *Materials Science and Engineering:* C 97.
- Siew, W. L. (2001). Understanding the Interactions of Diacylglycerols with Oils for Better Product Performance. *Palm Oil Development* 36: 6-12.
- Siew, W. L. (2011). Palm Oil In F. D. Gunstone, ed. Vegetable Oils in Food Technology Composition, Properties and Uses, Second Edition, pp. 25-58. West Sussex: Wiley-Blackwell.
- Singh, V. K., Pramanik, K., Ray, S. S. and Pal, K. (2015). Development and Characterization of Sorbitan Monostearate and Sesame Oil-Based Organogels for Topical Delivery of Antimicrobials. AAPS PharmSciTech 16(2): 293-305.
- Sreenivasan, B. (1978). Interesterification of fats. *Journal of the American Oil Chemists'* Society 55(11): 796-805.
- Sulaiman, M. Z., Sulaiman, N. M. and Kanagaratnam, S. (1997). Triacylglycerols responsible for the onset of nucleation during clouding of palm olein. *Journal* of the American Oil Chemists' Society 74(12): 1553-1558.
- Szydłowska-Czerniak, A., Karlovits, G., Lach, M. and Szłyk, E. (2005). X-ray diffraction and differential scanning calorimetry studies of  $\beta' \rightarrow \beta$  transitions in fat mixtures. *Food Chemistry* 92(1): 133-141.
- Tan, C. P. and Che Man, Y. B. (2002). Differential scanning calorimetric analysis of palm oil, palm oil based products and coconut oil: effects of scanning rate variation. *Food Chemistry* 76(1): 89-102.
- Tanti, R., Barbut, S. and Marangoni, A. G. (2016). Hydroxypropyl methylcellulose and methylcellulose structured oil as a replacement for shortening in sandwich cookie creams. *Food Hydrocolloids* 61: 329-337.

- Tavernier, I., Doan, C. D., Van de Walle, D., Danthine, S., Rimaux, T. and Dewettinck, K. (2017). Sequential crystallization of high and low melting waxes to improve oil structuring in wax-based oleogels. *RSC Advances* 7(20): 12113-12125.
- Timms, R. E. (1984). Phase behaviour of fats and their mixtures. *Progress in Lipid Research* 23(1): 1-38.
- Toro-Vazquez, J. F., Charó-Alonso, M. A. and Alvarez-Mitre, F. M. (2018). Gelation Properties of Gelator Molecules Derived from 12-Hydroxystearic Acid. In A. R. Patel, ed. Edible Oil Structuring: Concepts, Methods and Applications, pp. 106-132. Cambridge: The Royal Society of Chemistry.
- Toro-Vazquez, J. F., Morales-Rueda, J. A., Dibildox-Alvarado, E., Charó-Alonso, M., Alonzo-Macias, M. and González-Chávez, M. M. (2007). Thermal and Textural Properties of Organogels Developed by Candelilla Wax in Safflower Oil. Journal of the American Oil Chemists' Society 84(11): 989-1000.
- Trappe, V. and Weitz, D. A. (2000). Scaling of the Viscoelasticity of Weakly Attractive Particles. *Physical Review Letters* 85(2): 449-452.
- Uvanesh, K., Sagiri, S. S., Banerjee, I., Shaikh, H., Pramanik, K., Anis, A. and Pal, K. (2016). Effect of Tween 20 on the Properties of Stearate Oleogels: an in-Depth Analysis. *Journal of the American Oil Chemists' Society* 93(5): 711-719.
- Vintiloiu, A., Lafleur, M., Bastiat, G. and Leroux, J.-C. (2008). In Situ-Forming Oleogel Implant for Rivastigmine Delivery. *Pharmaceutical Research* 25(4): 845-852.
- Voon, P. T., Lee, S. T., Ng, T. K. W., Ng, Y. T., Yong, X. S., Lee, V. K. M. and Ong, A. S. H. (2019). Intake of Palm Olein and Lipid Status in Healthy Adults: A Meta-Analysis. *Advances in Nutrition* 10(4): 647-659.
- Wang, T. (2011). Soybean Oil. In F. D. Gunstone, ed. Vegetable Oils in Food Technology Composition, Properties and Uses, Second Edition, pp. 59-105. West Sussex: Wiley-Blackwell.
- Willis, W. M. and Marangoni, A. (2002). Enzymatic Interesterification: Chemistry, Nutrition, and Biotechnology, Second Edition. In Food Lipids, pp. 839-875. New York: Marcel Dekker Inc. .
- Yılmaz, E. and Öğütcü, M. (2015a). Oleogels as spreadable fat and butter alternatives: sensory description and consumer perception. *RSC Advances* 5(62): 50259-50267.
- Yılmaz, E. and Öğütcü, M. (2015b). The texture, sensory properties and stability of cookies prepared with wax oleogels. *Food & Function* 6(4): 1194-1204.
- Zeitoun, M. A. M., Neff, W. E., List, G. R. and Mounts, T. L. (1993). Physical properties of interesterified fat blends. *Journal of the American Oil Chemists' Society* 70(5): 467-471.

- Zetzl, A. K., Gravelle, A. J., Kurylowicz, M., Dutcher, J., Barbut, S. and Marangoni, A. G. (2014). Microstructure of ethylcellulose oleogels and its relationship to mechanical properties. *Food Structure* 2(1): 27-40.
- Zetzl, A. K. and Marangoni, A. G. (2011). Novel strategies for nanostructuring liquid oils into functional fats. In A. G. Marangoni and N. Garti, ed. Edible Oleogels: Structure and Health Implications, pp. 19-47. Urbana: AOCS Press.
- Zetzl, A. K., Marangoni, A. G. and Barbut, S. (2012). Mechanical properties of ethylcellulose oleogels and their potential for saturated fat reduction in frankfurters. *Food & Function* 3(3): 327-337.
- Zulim Botega, D. C., Marangoni, A. G., Smith, A. K. and Goff, H. D. (2013a). Development of Formulations and Processes to Incorporate Wax Oleogels in Ice Cream. *Journal of Food Science* 78(12): C1845-C1851.
- Zulim Botega, D. C., Marangoni, A. G., Smith, A. K. and Goff, H. D. (2013b). The Potential Application of Rice Bran Wax Oleogel to Replace Solid Fat and Enhance Unsaturated Fat Content in Ice Cream. *Journal of Food Science* 78(9): C1334-C1339.

# APPENDICES

# **Appendix A-1:**

# (A) Melting and (B) Cooling Thermograms of Top Olein Oleogels Produced with 10% w/w to 100% w/w of PBA Organogelator



## Appendix A-2:



(A) Melting and (B) Cooling Thermograms of Top Olein Oleogels Produced with 10% w/w to 100% w/w of SFW Gelator











# Comparison of Stickiness of Oleogels Formed with Combinations of Different Liquid Oils and 1 to 9% w/w SFW Gelator at 15 °C

### **BIODATA OF STUDENT**

Saw Mei Huey was born in April 1983 in Taiping, Perak. She completed her primary and secondary educations at the schools in Taiping before continuing her high school education at Sekolah Menengah King Edward VII, Taiping. She received a Bachelor of Science degree (with Distinction) in Applied Chemistry in August 2006. In December 2007, she got married and subsequently pursued her master's degree program at the same university, where she researched the palm new products from enzymatic interesterification and fractionation. She received her Master of Science degree in August 2010 with publication of two referred scientific journals from her master work. She has been working as a research officer at Malaysian Palm Oil Board (MPOB) since 2007, under Analytical and Quality Development Unit. She had authored a total of five referred scientific journals scientific journals, resulting from her research work in MPOB. She is currently in the doctoral program at University of Putra Malaysia with full sponsorship from MPOB.

## LIST OF PUBLICATIONS

#### **Publication Resulting from this Thesis:**

## A. Referred Scientific Journals

- Saw, M. H., Lim, W. H., Yeoh, C. B., Badlishah, S. B. and Tan, C. P. (2020). Screening of Organogelators for Structuring Palm Superolein. *Journal of Oil Palm Research* 32: 152-158.
- Saw, M. H., Lim, W. H., Yeoh, C. B., and Tan, C. P. Effect of Storage Temperature and Duration on Rheological and Thermal Characteristics of Superolein Oleogels. *Food Research International* FOODRES-D-20-02537. Under review.

#### **B.** Proceedings of Conferences/Seminars

- Saw, M.H., Zaliha, O., Lim, W.H. and Tan, C.P. Effect of temperature on physical and morphological properties of palm-based and soybean oil-based oleogels. Presented at National Seminar on *Palm Oil Milling, Refining, Environment and Quality 2016*, 29-30 November 2016, Kuala Lumpur, Malaysia. (Poster).
- Saw, M.H., Zaliha, O., Lim, W.H. and Tan, C.P. Effect of preparation conditions on stability and characteristics of different types of superolein oleogels. Presented at *International Palm Oil Congress & Exhibition 2017*, 14-16 November 2017, Kuala Lumpur, Malaysia. (Poster).
- Saw, M.H., Yeoh, C.B., Lim, W.H. and Tan, C.P. Effect of Preparation Conditions on Rheological Properties of Superolein Oleogels. Presented at National Seminar on Palm Oil Milling, Refining, Environment and Quality 2018, 27-28 November 2018, Kuala Lumpur, Malaysia. (Poster).