



Effect of fully hydrogenated coconut oil on the physical properties of non-hydrogenated coconut oil

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Abbreviations

AOCS	American Oil Chemist Society
CCLa	dicapricmonolaurin
CLaLa	Dilauricmonocaprin
CNO/CO	Coconut oil
CVD	Cardiovascular Disease
DSC	Differential scanning calorimetry
FAC	Fatty Acid Composition
FAMEs	Fatty acid methyl esters
FHCO	Fully Hydrogenated Coconut Oil
FHSO	Fully Hydrogenated Soybean Oil
G'	Storage Modulus
GC	Gas Chromatography
HDL	High Density Lipoprotein
HPLC	High-performance Liquid Chromatography
HRS	Hours
IE	Interesterified
IV	Iodine Value
k	Avrami constant (min-n)
KHO	Potassium Hydroxide
LaLaLa	Trilaurin
LaLaM	dilauricmonomyristin
LaMM	Dimyristicmonolaurin
LDL	Low Density Lipoprotein
LFRA	Leatherhead Food Research Association
MCFA	Medium Chain Fatty Acids
MCT	Medium Chain Tryglycerol
MUFA	Monounsaturated Fatty Acids
n	Avrami exponent
NHCO	Non - Hydrogenated Coconut Oil
PH-SBO	Partially Hydrogenated Soybean Oil
PLM	Polarised light Microscope
pNMR	Nuclear Magnetic Resonance Spectroscopy

PS	Palm Stearin
PUFA	Polyunsaturated Fatty Acids
PV	Peroxide Value (PV)
SBO	Soybean Oil
SFA	Saturated Fatty Acid
SFC	Solid fat content
SFC(∞)	limit of the solid fat content when time tends to infinity
SFC(t)	Solid fat content (%) as a function of time
SFCmax	Maximum Solid Fat Content
SMP	Slip melting point
SV	Saponification Value
TAG	Triacylglycerol
tcs	crystallization stability time
Te	Endset Transition Temperatures
To	Onset Temperature
Tp	Peak Temperature
VCO	Virgin coconut oil
ΔT	Degree of Undercooling
τ SFC	Induction Time
$^{\circ}\text{C}$	Degree Celsius

1. INTRODUCTION

Food is an essential aspect of human function, existence, and experience and often, diverse and distinct social problems come together around food (Thompson, 2015). Food industries are looking for how they will secure and provide plentiful, healthy and nutritious food for all while addressing the multiple burdens of undernutrition, overweight and obesity and micronutrient deficiencies. Fat is an important part of a healthy diet as it is a great source of energy, and supplies essential fatty acids and fat-soluble vitamins. An estimated 80% of the total fat produced is used for food; this highlights the importance of fats in food products.

Fats and oils are very important raw materials and functional ingredients for several food products such as confectionery, bakery, ice creams, emulsions, and sauces, shortenings, margarine, and other specially tailored products. Lipids also hugely contribute to the desired texture of end products, impart a characteristic flavour and act as a delivery system for fat soluble ingredients and vitamins. They confer desirable characteristics on several foods, contribute to tenderness to shortened cake, and by aerating batter, fats aid in establishing texture in cakes; they also add flavour to foods and influence the order in which components of flavour are released when foods are eaten, besides having a lubricating effect and producing a sensation of moistness in the mouth. Many fat-based food products require solid fats to interact with other ingredients in order to provide the desired structure and to offer oxidative stability.

Most natural oils and fats have only limited application in their original state, due to their particular fatty acid and triacylglycerol composition (Chiu, et al., 2008). The best-known modification processes applied today in the edible oil industry are hydrogenation,

interesterification (chemical or enzymatic) and fractionation. The main purpose of these processes is to change the physicochemical properties of the oil or fat, by reducing the degree of unsaturation of the acyl groups (hydrogenation), by redistributing the fatty acids chains (interesterification) or by a physical separation of the triacylglycerol's through selective crystallization and fractionation. The partial hydrogenation method results in a substantial formation of trans fatty acids, compounds that act as coronary artery disease risk factors by modulating the synthesis of cholesterol and its fractions and acting on the eicosanoids. However, the development of the hydrogenation technique transformed the shortening industry and promoted the use of fully hydrogenated vegetable oil for its increased stability, health benefit and no-trans configuration. The interesterified fats can be used in various applications by replacing the partially hydrogenated fats; consequently, interesterification can successfully substitute the partial hydrogenation process. Saturated fats are the only viable sources of the required high-melting (solid) fats as a use of its alternative, trans fats has been phased out or banned in some cases such as in Denmark, and New York City.

In the food industry, physical properties of fat play a significant role in two major areas: (a) optimization and controlling the processing of end products such as chocolate, butter, margarine, ice-cream, whipped cream among others and (b) purification of oils and fats into fractions with specific properties and functionalities. Also, the crystal network of fat plays a key role in the development of specific structure with desired physical, textural and sensorial properties of most lipid-based food products that are consumed on a regular basis. Therefore, a fundamental understanding of this phenomenon is necessary to assist food researchers to

characterize the properties of food products and optimize the processing parameters in order to control the characteristics of final products as well as to lay a platform for future development of newer food products with added functionality. In previous research, some group studied the thermal and rheological properties of ternary blends of coconut oil (CO) and palm stearin (PS), with either partially hydrogenated soybean oil (PH-SBO) or refined soybean oil (trans-free-SBO) crystallized under quiescent conditions. Recent research showed that, compared to other fats, the composition and the phase behaviour of coconut oil are relatively simple which is widely used in various food application because of physiological properties of lauric acid in the metabolism and in health issues such as cholesterol and fat accumulation and storage. Miscibility of coconut oil with different oils is hardly limited. In this study, we used fully hydrogenated coconut fat to find the appropriate melting and solidification properties as well as texture profile of fat blends. Fully hydrogenated oil does not contain trans isomers, therefore, its suitable substitute of the partly hydrogenated oil. The several studies have focused on the influence of blending, enzyme-catalysed transesterification and hydrogenation of oils on their chemical composition, thermal and structural properties. [Baltork et al., 2001 Kovács et al., 2008., Solymosi, et al., 2011]. Also determination of solid fat content and melting point of blends of coconut oil and anhydrous milk fat gave scientific results to food industry [Soos et al., 2014].

In European countries, coconut fats are one of the major ingredients in snacks and confectionary industries. Due to its melting and crystallization characteristics, margarine and shortening production, as well as the confectionary industry, consider coconut oil as a basic material in product formulations. Coconut oil is extensively used in the food industries as a

confectionary fat particularly in the preparation of ice creams. Coconut oil (CNO) contains about 90% saturated fatty acid (SFA), that do not get oxidized, including medium chain fatty acids (60–66%) which are nutritionally important (Mensink and Katan 1990). MCFA have several desired features such as high oxidative stability (due to their saturation), low viscosity and melting points and high solubility in water. Coconut oil is one of the widely used edible oils in the diet because it contains lauric acid (C12) as its major fatty acid, accounting for 45– 53 % of the overall fatty acid composition. MCT are digested more easily and absorbed rapidly by the body than other fats. When non-hydrogenated coconut oil supplements have been provided, studies often find evidence for modest benefits of coconut oil consumption on lipid profiles. Animal studies have shown that coconut oil in particular lowered total cholesterol, lipoproteins, and phospholipids. It has been reported that despite the high consumption of coconut as saturated fats, the ratios of total cholesterol to HDL-cholesterol, and LDL-cholesterol to HDL-cholesterol were lower, thus lowering cardiovascular disease (CVD) risk in rural males with a high degree of physical activity, subsisting on a diet consisting mainly of plant food. Coconut oil which is rich in lauric acid has less effect on total cholesterol and LDL-c and is a better alternative to butter and hydrogenated vegetable fats.

2. OBJECTIVES OF THIS RESEARCH WORK

5. To study the effect of fully hydrogenated coconut oil on physical properties (crystallization and melting) of non-hydrogenated coconut oil by using Nuclear Magnetic Resonance Spectroscopy(pNMR) and Differential scanning calorimetry (DSC).
5. To study the effect of fully hydrogenated coconut oil on rheological and textural properties of non-hydrogenated coconut oil.
5. To study microstructural changes in crystal of coconut blends by using polarized light microscopy.

3. LITERATURE REVIEW

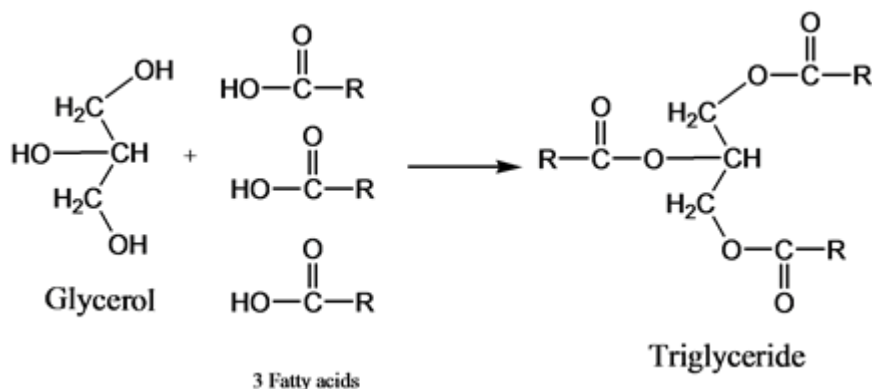
Considering the past decade, interest in fats and oils as very important raw materials and functional ingredients has increased in food, cosmetics, and pharmaceuticals industries. (Gunstone & Padley, 1997). Fats and oils have many physical and chemical characteristics, such as the melting point, crystallization behaviour and the crystalline form. The studies on different properties of fats and oil and blends have been carried out in various parts of the world to explore an important role in food quality control and food processing. Blending vegetable fats/oils with different compositions and properties is one of the simplest methods to create new specific products with desired textural, oxidative, and nutritional properties which lead to improved industrial applications. To improve the characters of the oil and fat food, acquire some special products, making some studies about the effect of blending fully hydrogenated coconut oil on physical and chemical characteristics, and their crystalline form of non-hydrogenated coconut oil is important in recent year.

This chapter describes coconut oil, its composition, physicochemical properties, rheology, crystal microstructure and health's benefits.

3.1 Fats & Oil

The term “lipid” has been loosely defined as any of a group of organic compounds that are insoluble in water but soluble in organic solvents. These chemical features are present in a broad range of molecules such as fatty acids, phospholipids, sterols, sphingolipids, terpenes and others. Fats & oil are made up of three elements carbon, oxygen and hydrogen. Fats and oils are called

triglycerides (or triacylglycerols) because they are esters composed of three fatty acid units joined to glycerol, a trihydroxy alcohol:



A triglyceride is called fat if it is a solid at room temperature (25°C); it is called an oil if it is a liquid at that temperature. These differences in melting points reflect differences in the degree of unsaturation and the number of carbon atoms in the constituent fatty acids. Triglycerides obtained from animal sources are usually solid, while those of plant origin are generally liquid. They are insoluble in water but soluble in most organic solvents. They have lower densities than water, and may have consistencies at ambient temperature of solid, semisolid, or clear liquid.

The main components of edible fats and oils are triglycerides. The minor components include Monoacylglycerol (MAG) and Diacylglycerol (DAG), free fatty acids, phosphatides, sterols, fat-soluble vitamins, tocopherols, pigments, waxes, and fatty alcohols. The free fatty acid content of crude oil varies widely based on the source. Other than the free fatty acids, crude vegetable oils contain approximately 1.5 to 2 % of these minor components.

3.2 Coconut oil

Coconut palm is productively grown within 20° north and south of the equator, especially along with coastal areas. There are two types of coconut palm: the tall and the dwarf. The coconut is an

important fruit tree in the world, providing food for millions of people and many health benefits beyond its nutritional content that it is called "The Tree of Life". It is a unique source of various natural products for the development of medicines against various diseases and also for the development of industrial products. Fresh coconut kernel contains: moisture (50%), oil (34%), ash (2.2%), fibre (3.0%), protein (3.5%) and carbohydrate (7.3%) (Canapi et al. 2005). The shell is split open and allowed to dry. The meat on the inside of the shell is called copra and it is the source of coconut oil in a yield of ~65%. The oil is extracted by pressing, usually followed by solvent extraction. Coconut oil is derived from the dried fruit (endosperm) which undergoes refining steps of alkali treatment, bleaching and deodorization. As shown in figure 3.1, coconut oil is produced mainly in the Philippines, Indonesia, India, Vietnam and Mexico. The production record of coconut oil is uneven because of the climatic and political instabilities of countries. The Philippines and Indonesia are major exporters, while EU-15 and the US are major importers.

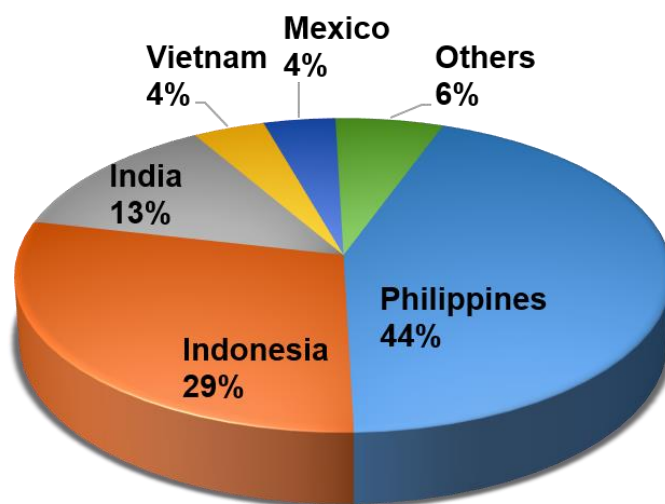


Figure 3. 1 Top countries involved in coconut oil production in 2015

3.3 Chemical composition

Coconut oil is an edible oil classified under the lauric acid group of plant oils, and over 90% of its fatty acids are saturated. Coconut oil has been extensively used for edible and non-edible purposes all over the world. The respective acid fraction of coconut oil contains lauric acid at the level of approximately 50% on which detergent industries mainly depend. It has the lowest percentage of unsaturated fatty acids (oleic, linoleic and linolenic) with a reported range of values from 3.7% (Banzon and Velasco, 1982) to 8.3% (Levitt, 1967) compared to palm, peanut, corn, soybean and linseed oils which contain 53, 82, 83.6, 86.1 and 90.5%, respectively (Banzon and Velasco, 1982).

The pleasant odour and taste of coconut oil when the oil is extracted from fresh material is mainly due to γ - and δ lactones, which are in trace amounts (Gunstone 2006). Table 2.1 shows the fatty acid composition (FAC) of coconut oil (Pantzaris and Basiron 2002 and Codex Alimentarius 2009). The major fatty acids are lauric (12:0) and myristic acids (14:0), at about 48% and 18% respectively.

Table 3. 1 Fatty acid composition (% weight) of coconut oil

Fatty acid	Mean	Range	Codex 2009
C6:0	0.4	0-0.6	ND-0.7
C8:0	7.3	4.6-9.4	4.60–10.0
C10:0	6.6	5.5-7.8	5.0–8.0
C12:0	47.8	45.1–50.3	45.10–53.20
C14:0	18.1	16.8–20.6	16.8–21.0
C16:0	8.9	7.7–10.2	7.5–10.2
C18:0	2.7	2.5–3.5	2.0–4.0
C18:1	6.4	5.4–8.1	5.0–10.0
C18:2	1.6	1.0–2.1	1.0–2.5
C18:3	-	-	ND–0.2
C20:0	0.1	0–0.2	ND–0.2
C20:1	-	-	ND–0.2

According to the study, medium-chain fatty acids ranged from 60 to 63%. The major triglycerides (TAGs) in coconut oil contain approximately 50% lauric acid and more than 15% of C6, C8, and C10 fatty acids (Canapi et al., 2005). The medium-chain fatty acids have some specific functional and nutritional properties which include antiviral, antibacterial, antiplaque, antiprotozoal, healing, anti-inflammatory and anti-obesity effects (Gopala Krishna et al., 2010, German and Dillard, 2004). Because of the nutritional and medicinal benefits of MCFA, it has been recognized as a multipurpose nutrient supplement. Takayoshi and Hirosuke, 1995 reported medium-chain fatty acids promote human health and reduce the risk of atherogenic or heart diseases unlike the long-chain fatty acids (Beermann et al., 2003). (Fig.3.2)

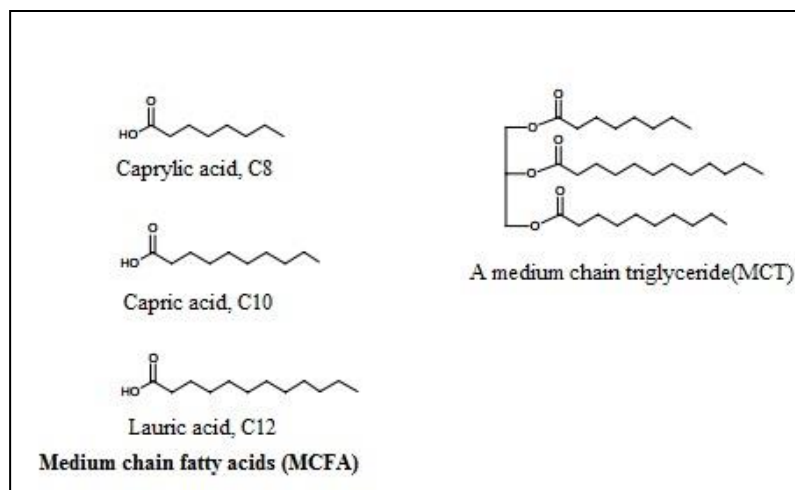


Figure 3. 2 Examples of medium-chain fatty acids (MCFA) and medium chain triglycerides (MCT)

TAG can be separated and quantified by high-performance liquid chromatography (HPLC) or by high-temperature programmed gas chromatography and reported as the ‘equivalent carbon number’ or as the sum of carbon atoms of the three fatty acids attached to the glycerol moiety respectively. Table 3.2 shows the Triacylglycerol of Coconut oil based on the Leatherhead Food Research Association survey (1989) of 34 specimens, with C₃₂ to C₄₂ as the major TAG groups. The TAG molecular species dicapricmonolaurin (CCLa), dilauricmonocaprin (CLaLa), trilaurin (LaLaLa), dilauricmonomyristin (LaLaM), dimyristicmonolaurin (LaMM) were the major TAG present in the coconut oil (Kumar and Krishna, 2015) (Fig. 3.3).

Table 3. 2 Triacylglycerol composition by carbon number (% weight) of coconut oil (Pantzaris and Basiron, 2002).

TG species	Mean	Range
CCLa	0.8	0.5–1.0
CLaLa	3.5	2.6–5.0
CaLaLa	13.4	10.8–17.5
CaCaM	17.1	15.6–20.1
LaLaLa	19.1	18.3–20.6
LaLaM	16.5	15.1–18.0
LaMM	10.2	8.4–11.9
LaPP	7.3	5.5–8.8
LaMP	4.1	2.8–4.7
MOO	2.5	1.6–3.0
MPO	2.1	1.2–2.6
POP	1.5	0.7–2.0
POO	1.2	0–2.0
OOO	0.8	0–1.7

Dayrit (2015) reviewed that the most dominant regiospecific TAG species in coconut oil were (with assigned sn-positions): 1,2,3-trilauryl glyceride (C12-C12-C12), 1-capro,2,3-dilauryl glyceride (C10-C12-C12), and 1-capro,2-lauryl,3-myristyl glyceride (C10-C12-C14). Freshly pressed coconut oil is a mixture of triglycerides, diglycerides, monoglycerides, and free fatty acids. Some researcher estimated the composition to be approximately 85 % triglycerides, 7 % diglycerides, and 3 % monoglycerides by using thin-layer chromatography. Dayrit and co-workers' results shown non-TAG components to be 1.5 % diglycerides, 0.01 % 1-monoglycerides, and 0.13 % free fatty acids. Marina et. al., (2009) analysed TAG composition of coconut oil samples by using reversed-phase liquid chromatography. They reported that 21.95% of LaLaLa, 13.15% of CCLa, 17.33% of CLaLa, 17.18% of LaLaM and 10.19% of LaMM with

La, C and M are lauric, capric and myristic acids, respectively present in refined, bleached and deodorized coconut oil.

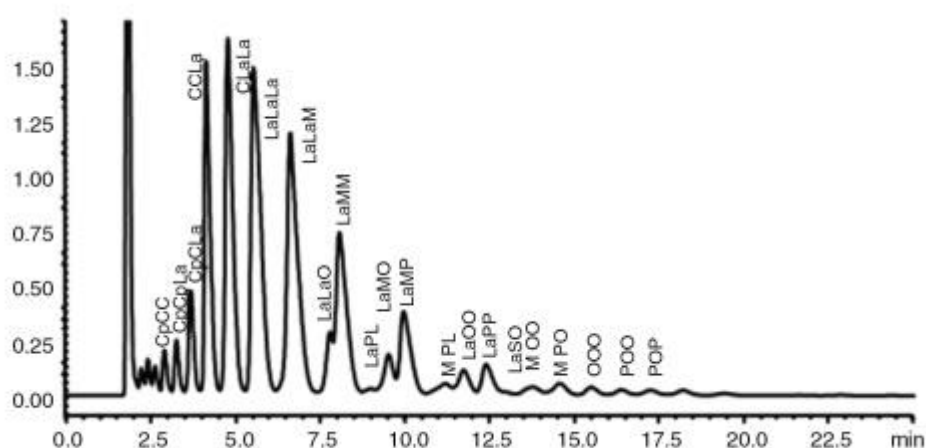


Figure 3. 3 Triacylglycerol profile of coconut oil

In a comparative study of various vegetable oils, Karupaiah and Sundram (2007) determined the triacylglycerol profiles and fatty acid compositions of coconut and palm kernel oil. They reported that fatty acid analysis of the TG shows that the TG of coconut oil has a low degree of unsaturation (9%) and contains high levels of the two saturated fatty acids, lauric (C12:0) and myristic (C14:0). These two saturated fatty acids make up 51 and 21% of the fatty acid content, respectively. A Bhatnagar et al. (2009) study has shown that coconut oil is rich in MCFA (59.7%) while other vegetable oils like sunflower oil, safflower oil, soybean oil, palm oil, rice bran oil, groundnut oil, mustard oil, and sesame oil are deficient in MCFA (0%) Whereas its deficient in PUFA (1.2%) and MUFA (6.1%). Dauqan et al., (2011) evaluated the fatty acids composition of four different vegetable oils by Gas chromatography. The results showed that the predominant component of red palm olein and palm olein was oleic acid (44.616% and 49.482%, respectively) and palmitic acid (42.465% and 36.768%, respectively) whilst the corn oil was

rich in linoleic acid (18:0) 47.189% but coconut oil was rich in lauric acid (12:0) 46.458% compared to the other oil samples. Mansor et al.; (2012) studied Virgin Coconut Oils (VCO) which were prepared from fresh-dry (grated coconut route), chilling and thawing, enzymatic and fermentation method. The physicochemical, FA and TAG analyses of the VCO extracted from different methods showed some significant differences, while the tocopherol content does not differ significantly among the different types of extraction methods used.

3.4 Modification of coconut oil

Coconut oil is used extensively for food and industrial purposes and is one of the major ingredients for food production. Quality, stability and nutritional features of oils are the most important factors in food technology. There is no pure oil with good functional and nutritional properties and appropriate oxidative stability. The rearrangement or structural alteration (modification) of the fatty acids in native oils and fats is commonly used in food industries to meet product-specific demands. Coconut oil is primarily used in the bakery industry as shortenings, as cocoa butter substitutes in the confectionery industry, in margarine preparation, and as a butter substitute. The modification can be accomplished by different processes such as hydrogenation, interesterification, fractionation and blending, etc. (Nor Aini & Noor Lida, 2005) and these can also be used for improving the stability of fat and fat products (De & Patel 2010). The modification of fats enhances their commercial applications by improving the product's taste, texture, and other characteristics such as modified (desirable) melting point and crystal behaviour, increased shelf life etc.

Hydrogenation of vegetable oils reduces the unsaturated fatty acids content of triglycerides by hydrogen addition to the double bonds of unsaturated fatty acids. Oils are allowed to react with hydrogen gas under pressure, at high temperature (120 to 210 °C) in the presence of metal catalysts such as nickel/platinum/copper for 6 to 8 hrs. Hydrogenation not only affects the functionality of oils, but also enhances the oxidative stability (shelf life) of the food product (O'Brien 2009). Hydrogenation raises the melting point of fats and retards rancidity. Unfortunately, during hydrogenation some double bonds can be isomerized and converted from cis state to trans state. Trans fatty acids are known as a risk factor for coronary vascular diseases, insulin resistance and obesity, complemented by systemic inflammation; the features of metabolic syndrome (Iqbal, 2014). Fully hydrogenated products are almost completely saturated and do not contain trans fats. Full hydrogenation of the oils makes them too solid, not having the desired functionality of partially hydrogenated oils (O'Brien 2009), which makes them difficult to use for cooking. Fully hydrogenated fats, considered as containing zero trans fatty acids have been proposed as a viable substitute for partially hydrogenated fats (Abdullina et al. 2012). Full hydrogenation is an alternative that produces hard fats, which may be used to prepare low to zero-trans commercial fats through interesterification. The interesterification process leads to the formation of different cis & trans combinations and yields more desirable physical properties (Strayer et al. 2006). Chemical interesterification is not more expensive than modification methods like hydrogenation and fractionation. It is more expensive than physical blending of fats (Dijkstra, 2015). The process involves blending high saturated hard fats (e.g., palm oil, palm stearin and fully hydrogenated vegetable oils) with liquid edible oils to produce fats with

intermediate characteristics. Many research studies show that the chemical interesterification of fully hydrogenated oil and vegetable oil significantly changes the composition of the TAG and the solid fat content, slip melting point, compatibility, and consistency of their blends. (Guedes et al., 2014, Farmani 2015). Vegetable oils including corn, palm, peanut, cottonseed, canola, and sunflower can be randomly interesterified with fully hydrogenated soybean oil or fully hydrogenated cottonseed hard fats to produce desirable fat compositions for margarines and shortenings (List et al. 1995). Chemical and enzymatic interesterification has been specially employed in the formulation of margarines and shortenings with no trans FAs while still maintaining physical properties, taste and stability (List et al.1997).

Oil blending is a technological method that is used to produce specific products with desired textural and oxidative properties. There are many reports where blending is used in the edible oil industry. Combining sunflower oil with canola oil or palm oil (De Marco et al., 2007; Farag, El-Agaimy, & Abd El Hakeem, 2010), and mixing soybean oil with hydrogenated soybean oil or corn oil with high-oleic sunflower oil (Abdulkarim, Myat, & Ghazali, 2010; Naghshineh, Ariffin, Ghazali, Mirhosseini, & Mohammad, 2010) have seen extensive use.

3.5 Physical and chemical properties

Edible oils are vital constituents of our daily diet, which provide energy, essential fatty acids and serve as a carrier of fat-soluble vitamins. Different physical and chemical parameters of edible oil were used to monitor the compositional quality of oils (Ceriani et al., 2008 and Mousavi et al., 2012). These physicochemical parameters including iodine value (IV),

saponification value (SV), viscosity, density and peroxide value (PV) are used to assess the quality and functionality of the oil (Zahir et al., 2014). The physical and chemical properties of oil depend upon its chemical composition. Even today these values play a vital role when utilising different oils in the production of industrial products. Coconut oil has unique characteristics such as having bland flavour, pleasant odour, high resistance to rancidity, narrow temperature ranges of melting, easy digestibility and absorbability, high gross for spray oil use and superior foam retention capacity for whip-topping use (Che Man and Marina 2006). It is colourless to pale brownish-yellow.

According to the Codex standard (2009), iodine value of edible coconut oil is in between 6.3 to 10.6, saponification value 248-265 mg KOH/g oil, peroxide value up to 10 mg of KHO/kg of oil, relative density 0.908-0.921 and refractive index 1.448-1.450. According to O' Brien (1998), the normal range of iodine value for coconut oil is 6 -11, while the saponification value is 248-265. The iodine value was used to measure the degree of unsaturation of fats and oils. The low content of iodine value indicates that coconut oil has a high degree of saturation as compared to other vegetable oils. Therefore, coconut is very stable to oxidative deterioration when exposed to atmospheric oxygen (Onyeike and Acheru, 2002). The IV affects quality parameters such as the shelf life of VCO, appearance, as well as taste and scent. The peroxide value is the number of peroxides present in vegetable oils. The amount of peroxides present in vegetable oils reflect its respective oxidative level and thus its tendency to become rancid. Coconut oils generally exhibit high oxidative stability due to the presence of large amounts of saturated fatty acids (>91%). Unsaturated fatty acids easily react with oxygen to form peroxides. Oils with high peroxide value

are unstable and easily become rancid. The saponification value is a measure of the average molecular weight of all the fatty acids present. The higher the saponification value, the shorter the fatty acids on the glyceryl backbone. Some comparative vegetable oil research studies reported that coconut oil has a very high saponification value, which indicates coconut oil contains a higher amount of short-chain fatty acids.

3.6 Melting Point

Melting point is a parameter of significant importance for characterizing and developing interesterified fats. Some scientists report that fat moves in the capillary tube when there is approximately 4–5% of solid fat, making it possible to determine the melting point at which the SFC is in this range. Solid fat content (SFC) and melting point are of the most important physical properties determining special applications of margarines and shortenings (Narine, Ghotra, & Dyal, 2002). The melting range of fat has a direct relationship with its degree of hardness and it can be used as criterion of purity. LFRA survey reported that coconut oil has a melting point of 24.1-24.5 °C (Table 3.3). The melting points of oils increase with increasing fatty acids' chain length and decrease as the acids become more unsaturated. The low melting point of coconut oil is not caused by a relatively high degree of unsaturation, as is the case with ordinary oils, but rather by the low average molecular weight of its glycerides. Completely hydrogenated coconut oil has a melting point of ~45.1°C compared to 23.5-26°C for unhydrogenated coconut oil.

Table 3. 3 Melting point (°C) and SFC values of natural fats (Weiss, 1983)

Fat	Melting point (°C)	SFC value (%) at different temperatures (°C)				
		10	21.1	26.7	33.3	37.8
Butter	36	32	12	9	3	0
Cocoa butter	29	62	48	8	0	0
Coconut oil	26	55	27	0	0	0
Lard	43	25	20	12	4	2
Palm oil	39	34	12	9	6	4
Palm kernel oil	29	49	33	13	0	0
Tallow	48	39	30	28	23	18

3.7 Thermal Properties

The melting and crystallization behaviour of vegetable oils and fats is very important for functionality in many prepared food products. These thermal properties are counterparts of the triacylglycerol (TAG) profile in vegetable oils and fats (Breitschuh & Windhab., 1996), and can therefore be used in qualitative and quantitative ways for identification of vegetable oils and fats (Yap & DeMan., 1989). The thermal behaviour of some of these vegetable fats, such as cocoa butter, milk fat and hydrogenated fats, has received much attention owing to their valuable properties in food formulations and their widespread use in the confectionery, dairy and margarine industries (Chaiseri & Dimick., 1995). Nevertheless, the analysis of the thermal behaviour of liquid oils is still in its early stages.

3.8 Crystallization

Lipid crystallization behaviour has very important implications, mainly for industrial processing of products whose physical properties depend largely on the presence of fat crystals, such as chocolates, margarines, and shortenings. Crystallization refers to the formation of solid crystals from a homogenous solution. Differences in crystal shapes result from different molecular packings. Crystallization in fat systems refers to the phase transition from liquid oil, in which molecules are in chaotic motion, to solid crystalline fat characterised by closely packed, ordered molecules. According to Foubert et al., 2009, Crystallization of fats determines important properties of foods, including: (i) the consistency and plasticity of fat-rich products such as butter, margarine and chocolate during the stages of production and storage; (ii) sensory properties such as the melting sensation in the mouth; (iii) physical stability with respect to the formation and settling of crystals, oil exudation and coalescence of particles and emulsions; and (iv) visual appearance, for example the shininess of chocolates and toppings (Jang et al.2005)

The crystallization process is divided into undercooling of molten fat, nucleation and crystal growth phases. A fat that is cooled to the point of supersaturation is undercooled or supercooled (Marangoni 2005). The degree of undercooling (ΔT) is defined as the difference between the temperature at which a liquid fat is crystallized (T_c) and the average melting temperature of its constituent lipid species. At low degrees of undercooling ($\Delta T = 5\text{--}10\text{ }^\circ\text{C}$) and thus minimal supersaturation, the melt will exist in a metastable state. In this state, the higher melting TAG molecules will begin to aggregate in crystal embryos that continually form, break, and re-form. In this state, the molecules from the unstable solid phase (embryos) are in

equilibrium with the molecules from the liquid phase (Toro-Vazquez and Gallegos-Infante 1996).

According to Boistelle (1988), nucleation involves the spontaneous formation of nuclei which results in a decrease in the free energy level of the system accompanied by a release of latent heat. Nucleation is thus the formation of small TAG clusters (stable nuclei) large enough to speed up the formation of a crystalline lattice structure. (Fig. 3.4) The crystalline network is developed by subsequent growth of the nuclei by incorporating TAGs from the melt. The number of nuclei formed per unit time and per unit volume is defined as the nucleation rate (Walstra 2003). Fat's tendency to crystallize is of fundamental concern to processing techniques. Knowledge of the crystal network formed by TAGs is necessary for understanding and modifying the various functional properties of fats. For example, prevention of bloom formation in chocolate requires an understanding of how the liquid phase migrates in the fat crystal network while modifying the texture of butter requires an understanding of the TAG crystal size and how these crystals bind oil (Sonwai & Rousseau., 2010, Rousseau et al., 1996).

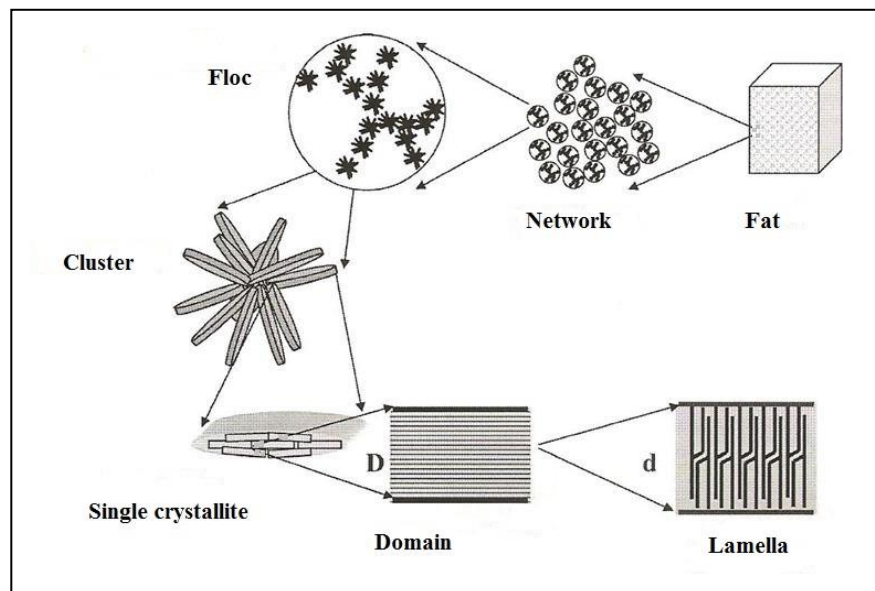


Figure 3. 4 Structural hierarchy in fat crystal networks (Marangoni 2010)

Triacylglycerols (TAG) generally crystallize initially into the α and β' polymorphic forms, although the β form is more stable. The polymorphic transformation is an irreversible process from the less stable to the more stable form, and depends on the temperature and time involved [Ribeiro et al., 2009]. Fats with crystals in the β' form offer greater functionality, because they are softer, support aeration better, and offer creaming properties. Thus, generally β' form is the polymorph of greatest interest for producing high-fat foods. However, as long as proper processing methods are adopted, suitable products can be obtained even using fats with a high propensity towards the β form [Oh et al., 2005].

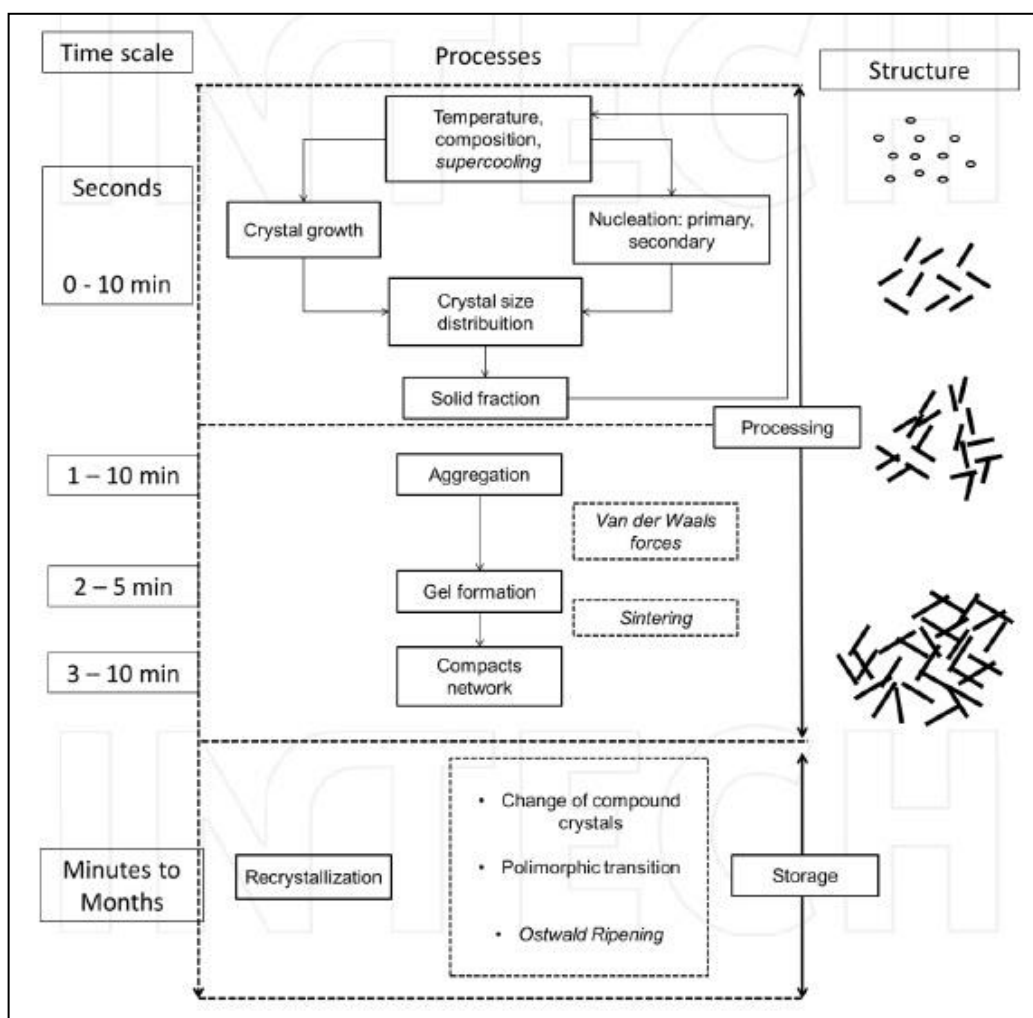


Figure 3.5 Process schematic of the process involving crystallization and storage of fats.

3.9 Crystallization kinetics

Crystallization kinetics intensively influences the final structure of fats and has been shown to be closely related to their rheological and plasticity properties. When monitoring the formation of the solid crystalline material with respect to time, it is possible to verify the nature of the crystallization process. Characterization of crystallization kinetics can be performed according to the induction time (τ_{SFC}) or the nucleation period (relative to the beginning of crystal formation) and the maximum solid fat content- SFC_{max} . SFC is the percentage of solid fat particles in liquid oil at various temperatures. The study of fat content (in particular solid, saturated and trans-fat content) and of the nature of food fats is becoming increasingly important

due to health considerations. The induction time reflects the time required for the formation of a stable nucleus of critical size in the liquid phase (Himawan et al., 2006). As a definition, the τ SFC is the time required to obtain one crystalline nucleus per unit volume. The τ SFC generally increases with increasing isothermal crystallization temperature and decreasing sample melting point. Another useful parameter for evaluating isothermal crystallization is the crystallization stability time defined as the total time for stabilization of the solid fat content at a given temperature. This parameter consists of the sum of the time characteristics for nucleation and crystal growth (Hachiya et al., 1989).

The model most widely used to describe the kinetics of isothermal phase transformation is the Avrami model, developed in 1940, which relates the kinetics determined experimentally with the form of growth and final structure of the crystal lattice (Narine, Humphrey, and Bouzidi., 2006). The Avrami equation gives an indication of the nature of the crystal growth process and is given by

$$\frac{SFC(t)}{SFC(\infty)} = 1 - e^{-kt^n} \quad (1)$$

where $SFC(t)$ describes the solid fat content (%) as a function of time, $SFC(\infty)$ is the limit of the solid fat content when time tends to infinity, k is the Avrami constant (min^{-n}) which considers both the nucleation and growth rate of the crystals, and n is the Avrami exponent, which indicates the mechanism of crystal growth (Wright et al, 2000). The crystallization half-life ($t_{1/2}$) reflects the magnitude k and n according to the relationship

$$t_{1/2} = \left(\frac{0.693}{k} \right)^{1/n} \dots \dots \dots (2)$$

The Solid Fat Content (SFC) of a vegetable oil blend is responsible for many fundamental characteristics of fatty foods, such as physical appearance, organoleptic properties and spreadability, while also influencing plasticity of an edible oil product (Rao et al., 2001). The directional crystallization kinetics of coconut oil was studied under the temperature gradient from 13°C to 15°C. Peng et al., 2012 reported that during the crystallization of coconut oil, the overall crystal growth rate decreased over time, but it increased with the growth of temperature difference. Also, they find variation trend of crystallization yield with temperature difference was the same with crystal growth rate. Some research has reported effects of ultrasonic treatment on the crystallization behaviour of Virgin coconut oil (VCO) under a temperature gradient field.

3.10 Microstructure of Fat crystal

Crystals occur in a wide variety of shapes and sizes in a fat crystal network. The physical properties of fat products depend in part on crystal morphologies, which lead to the different textures in the finished product. The shape of the final crystals with their individual surfaces depends on the conditions under which the crystals were formed. Thus, a variety of crystal shapes exist although differences are small in some cases. Changes in a crystal's shape are related to the growth rate of the different faces. Crystal growth can occur in one, two or three dimensions, characterizing the formation of needle, disk, and spherulite-shaped crystals respectively. These shapes can be predicted from the results shown by the value of the Avrami exponent (n) (Sharples., 1966) (Table). Different forms of crystals are produced when the growth parameters are different. These parameters can be temperature, speed of crystal growth, and the presence of minor components and impurities. Systems that have a high latent heat of fusion and

low thermal conductivity are likely to form dendrites. Different lipid polymorphs have different shapes: spherulitic crystals are common for the β' polymorph and plate-shaped crystals for the β form. Plate-shaped crystals of the β -polymorph can produce the perception of a grainy texture in fat. The morphology of crystals is influenced by polymorphism; however, it can be less dependent on the polymorphic form.

Table 3. 4 Values of the Avrami exponent (n) for different types of crystal nucleation and growth.

Avrami exponent (n)	Type of crystal growth	Expected nucleation
$3+1 = 4$	growth of spherulites	sporadic nucleation
$3+0 = 3$	growth of spherulites	instantaneous nucleation
$2+1 = 3$	growth of disks	sporadic nucleation
$2+0 = 2$	growth of disks	instantaneous nucleation
$1+1 = 2$	growth of rods	sporadic nucleation
$1+0 = 1$	growth of rods	instantaneous nucleation

Lee and others (2008) studied the microstructure of a blend of fully hydrogenated soybean oil (FHSO) and palm stearin (PS) blends before and after lipase-catalysed interesterification. They observed large, rod-like spherulitic crystals in PS while long needle-like crystals were densely packed in FHSO. Both physical blending and interesterification changed the crystal morphology of the crystals. The physical blends produced needle-shaped crystals, whereas the crystals in the interesterified (IE) fat had a different shape compared to those in the physical blends. They suggested that the amount of PS influenced the structure and network of

crystals, thus increasing the amount of PS induced the formation of smaller and more densely packed crystals.

Shi and others (2005) investigated the crystal morphology of model lipid systems containing low-melting and high-melting lipid classes. The high-melting lipid class or its TAG saturation level mainly dominated the morphology of crystal elements and their aggregation. For mixtures containing trisaturated long-chain FA, fat crystals were flake-shaped, and grain-like aggregates were formed. For systems containing mixed long chains, fat crystals were needle-shaped, and typical and regular spherulites were formed. For a system containing disaturated long chains, although the elementary crystals were still needle-shaped, irregular spherulites and flocs of these spherulites were created from these elementary crystals.

3.11 Rheology of fats

The rheological properties of crystal networks formed by fat crystals are important in food products containing a significant amount of fats and oils. Determination of rheological properties of fats is important, especially for the design of devices for transportation, pumping, and storing of these substances. Rheological properties identification also plays an important role in food rheology, where rheology relates to quality control or sensory properties. Viscosity measurements are commonly used to monitor changes in fat rheology due to crystallisation, but the application of shear can destroy some of the delicate interactions present in fat systems. There are two principal models of rheology, which are Newtonian and non-Newtonian systems. Marangoni and Tang (2008) showed that the shear elastic modulus obtained from small deformation rheological measurements is a suitable indicator of the hardness of the material, as

well as being sensitive to the native, intact microstructure of fats. The storage modulus, G' , or other rheological measures, however, cannot be simply related to the molecular structure of the triacylglycerol molecules, which make up the network. The rheological properties of fats are the result of a combined effect of the SFC and the microstructure of the fat crystal networks, including the shape, size, and spatial distribution pattern of the fat crystals. many foods (such as ice creams, cheese, baking and confectionery applications) are characterised by the presence of hard fats, able to give the proper texture (Ghotra, Dyal, & Narine, 2002; Marangoni, 2009).

4. MATERIALS AND METHODS

4.1 Materials

In this study, we used Barco coconut oil as the initial non-hydrogenated coconut oil (NHCO) which was kindly provided by Mayer's Kft from Budapest. The fully hydrogenated coconut oil (FHCO) was obtained from a local industry in Hungary. The oils and fats were stored at 0°C before use. All the chemicals used were either analytical or high-performance liquid chromatography (HPLC) grade.

1. Sodium hydroxide solution 50%
2. Sodium acetate, For HPLC, $\geq 99.0\%$,

4.2 Methods

4.2.1 Preparation of oil blends

The blends were prepared for study in the proportions of 25:75 (Blend 1), 50:50 (Blend 2), 75:25 (Blend 3) (w/w%) non-hydrogenated coconut oil: fully hydrogenated coconut oil (Fig 4.1). The total volume of blend were 200 gram. Materials were melted at 100 °C and homogenized for 10 min in order to destroy the crystal structure completely. All blends and pure fat samples were stored in a refrigerator at 10 °C until use.



Figure 4. 1 Non-hydrogenated coconut oil and Fully hydrogenated coconut oil and their blends.

4.2.2 Fatty acid composition

Fatty acid methyl esters (FAMES) were prepared by the method described in the French standard (NF T 60-233, 1977) and analysed by capillary gas chromatography (Shimadzu GC – 2010, Barcelona, Spain) using a fused-silica capillary column (SP-2380, 30m × 0.25mm × 0.2 µm film thickness; Supelco Inc., USA). Injector and detector temperatures were kept at 220 °C and 250 °C respectively. The initial temperature of the column was 180 °C and was programmed to increase to 250 °C at a rate of +5 °C/min. Nitrogen was used as a carrier gas at a flow rate of 1.0 ml/min. The fatty acid composition of pure fats was determined as the relative percentage. Based on these results, the fatty acid composition of the blends was calculated.

4.2.3 Slip melting point (SMP)

SMP was measured according to AOCS Method Cc.3.25 (1993). Capillary tubes were filled with a 1-cm height of melted fat. The capillary tubes were kept in a refrigerator for 24 h to solidify the fat. The tubes were subsequently attached with a rubber band to a thermometer and suspended in a 600 ml beaker of boiled distilled water. The bath temperature was adjusted to 8–

10 °C below the SMP of the sample and heat was applied using a heating coil element to increase the bath temperature at a rate of ± 1 °C/min. The temperature at which the fat column rises was reported as the SMP. For the measurements of SMP of samples, the experiment was repeated three times to obtain results of higher accuracy.

4.2.4 Solid fat content (SFC) analysis by pNMR

Solid fat content analysis was carried out in two ways: as a function of time and as a function of temperature, to get solid fat profiles of oils by using pulsed Nuclear Magnetic Resonance spectrometer (pNMR). Samples were melted (100°C/ 15min) and kept in a high precision dry bath at 80°C for the complete destruction of their crystal history (Campos, 2005). The solid fat content directly proportional to crystallization time, which was monitored by pNMR Brucker pc 120 Minispec. Solid fat content (SFC) was measured at 10°C, 15°C and 18°C. Each sample tube was placed in the sample holder in the NMR equipment, with the reading compartment stabilized at 10 $\pm$ 1°C, 15 $\pm$ 1°C and 18 $\pm$ 1°C. The analyses of samples were performed in triplicate for each temperature. The data acquisition was automatic, with measurements taken every 3 min for 180 minutes. The quantification of the crystallization kinetics was performed according to the Avrami model. The equation (1) in this model is widely used for the description of isothermal phase transformation kinetics (Narine et al., 2006, Toro-Vazqu et al., 2002)

$$\frac{SFC(t)}{SFC(\infty)} = 1 - e^{-kt^n} \dots\dots\dots(1)$$

In equation (1) SFC (t) denotes solid fat content (%) as time function, SFC (∞) is the solid fat content limit as time tends to infinity, k is the Avrami constant (min⁻¹) which considers both

nucleation and growth rate, and n is the Avrami exponent which indicates the crystal growth mechanism (Marina et al 2009). The equation was linearized and after substituting the results of the measurements, linear regression analysis was performed in order to calculate the values of k and n .

The melting profile of the fats was studied by measuring the solid fat content (%) at $5\pm1^{\circ}\text{C}$, $10\pm1^{\circ}\text{C}$, $15\pm1^{\circ}\text{C}$, $20\pm1^{\circ}\text{C}$, $25\pm1^{\circ}\text{C}$ and $30\pm1^{\circ}\text{C}$ respectively by the same NMR Analyzer. The fat was melted at 80°C by using a water bath and placed in a refrigerator (0°C) for 60 min before the first SFC measurement. Afterward, the SFC was determined at temperature ranges of 5 to 30°C (with 5°C intervals) through equilibrating the NMR tubes in these temperatures for 30 min before measurement. Determinations were done in triplicate.



Figure 4. 2 Nuclear Magnetic Resonance spectrometer (NMR) Bruker pc 120 Minispec

4.2.5 Crystallization and melting characteristics by DSC

For DSC analysis, a Perkin–Elmer differential scanning calorimeter, DSC-7 equipped with a thermal analysis data station (Perkin–Elmer Corp., Norwalk, CT, USA) was used. This

DSC was available at Department of Refrigeration and Livestock Products' Technology for measurement. Nitrogen (99.999% purity) was the pure gas and flowed at approximately 20 ml/min. The calorimeter was calibrated according to standard procedures established in the manufacturer user manual.



Figure 4. 3 Differential scanning calorimeter

The data processing software used was Pyris Series Thermal Analysis System. The DSC instrument was calibrated using indium (m.p. 156.6 °C, $\Delta H_f = 28.45$ J/g) and n-dodecane (m.p. -9.65 °C, $\Delta H_f = 216.73$ J/g). Samples of ~20 mg were loaded to the middle of the aluminium pans using a small spatula and hermetically sealed with an empty pan serving as a reference. Samples were subjected to the following temperature programme as follows: Fat sample were heated to 80 °C to remove crystallization history. Then samples were cooled to 0 °C and kept at this temperature for 10 min. Heating was performed from 0 °C up to 80 °C. Samples were kept at this temperature for 30 min, and then the cooling program was applied at 1 °C min⁻¹ to -20 °C and

kept under this condition for 10 min. Finally, the samples were heated up to ambient temperature. Measurements were done during the constant speed heating and cooling processes. In the present study, the samples were cooled and/or heated at 1°C/min predetermined scanning rate. Each DSC scan was collected on a new sample to ensure that all of the samples started with the same thermal history and “standard” state.

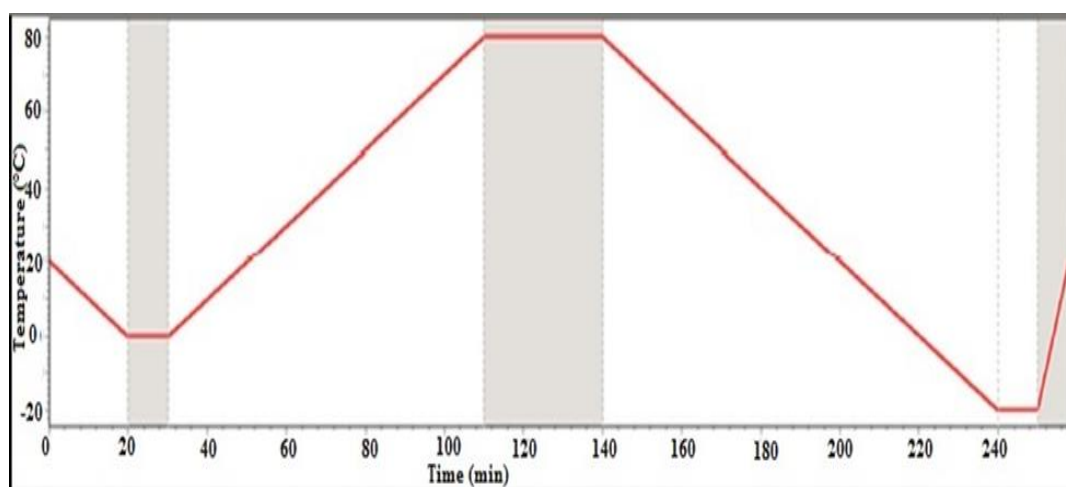


Figure 4. 4 Differential scanning calorimetry (DSC) heating and cooling curves

The thermal melting and crystallisation characteristics of each sample in a DSC scan can be indicated by various temperatures. The melting transition temperatures were assigned to each thermal curve, based on the temperature at which the greatest value for the heat flow occurred. The crystallising transition temperatures were assigned to each thermal curve, based on the temperature at which the lowest value for the heat flow occurred.

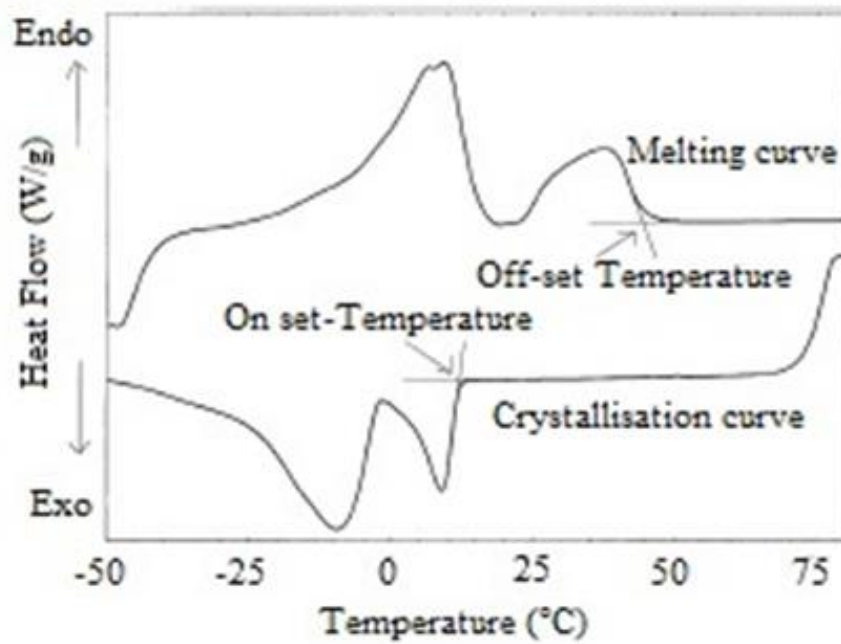


Figure 4. 5 DSC heating or cooling curve

For the melting curve, the offset-temperature (T_{off} ; point where the extrapolated leading edge of the last endotherm intersects with the baseline) was also determined (Fig. 4.4). The start of crystallisation transition, T_{on} , for all studies, was taken as the onset point of the transition, that is the point at which the extrapolated baseline intersects the extrapolated slop in the transition state (Fig. 4.5). The onset- and offset-temperatures could not be determined from the melting and crystallisation curves, respectively, because no final baseline was observed. In the study, peak enthalpies (in joule per gram), Max peak temperature ($^{\circ}\text{C}$) and On set temperature ($^{\circ}\text{C}$) at $1^{\circ}\text{C}/\text{min}$, were determined (Biliaderis., 1983). All DSC values reported are the average of three scans.

4.2.6 Texture profile analysis

Spreadability of margarine and butter is an important aspect of the consumer acceptability of these products. A spreadability test was performed to determine the textural

properties of the formulations using a Texture analyser (TA-TX Plus, Stable Micro System, UK) equipped with a 2 kg load cell.



Figure 4. 6 Texture analyser (TA-TX Plus, Stable Micro System, UK)

The samples were heated in a microwave oven at 80°C for complete melting of the crystals, and placed in 50 mL beakers. The conditioning was performed in an incubator for 24 hours at 5°C for the pre-crystallization of the fat and then for 24 hours at the 25°C temperature. Fat samples were initially transferred into TMS spreadability jig and pressed down in order to eliminate air pockets. An analytical probe was twice penetrated into each fat sample to a defined depth (15 mm) and at a defined rate (2 mm/s) (Campos, 2005). Any excess of sample was scraped off with a knife. Experiments were carried out at least five times. As a result of this

study, a force-time curve was obtained. Hardness is the force required to attain a given deformation and the altitude of the first peak gives the hardness value. The areas under the curves were also determined and they represented the amount of work required to perform the shearing process; that is, to spread the samples along the surfaces of the female cone.

4.2.7 Rheology measurements

This study is divided into two sections where the first section discusses the effect of temperature on viscoelastic properties and the second section discusses the effect of shear rate and shear stress on oil viscosity.

Oscillatory rheology

Rheological measurements were performed by a controlled stress-strain rheometer (MCR 301, Physica/Anton Paar, Ostfildern Germany–Europe) connected to a circulating water bath for the temperature control. This anton par rheometer was available at Department of Refrigeration and Livestock Products Technology.



Figure 4. 7 Rheometer (MCR 301, Physica/Anton Paar, Ostfildern Germany–Europe)

The small-amplitude oscillatory shear test were performed. The viscoelastic behaviour of the samples was evaluated from 10°C to 25°C by using a parallel plate (diameter: 50 mm) and a gap distance of 2 mm. Excess sample protruding from the edge of the sensor was trimmed off carefully with a thin blade. In our measurement, an oscillatory shear strain was applied to the sample at constant frequency of 10 rad/sec and a constant strain amount of 0.1 %, which satisfies the linear viscoelastic condition. The values of shear storage modulus (G') and shear loss modulus (G'') were obtained from Rheoplus software.

Dynamic viscosity tests

Dynamic viscosity tests were conducted by using a rotational rheometer with a coaxial cylindrical measurement system. The tests were carried out at different temperatures respectively 30°C, 40°C, 50°C, 60°C, 70°C and 80°C respectively. This test consists on transferring the oil to a measuring cup until it reaches a predefined mark designed inside the cup, then this cup containing the sample is inserted to a temperature jacket that is fixed to a measuring head with a cylindrical spindle connected. The spindle rotates inside the measuring cup with the oil and the rheological information is monitored by the measuring head. A total of 31 readings were obtained varying the shear rate from 100 s^{-1} to 1500 s^{-1} . As most of the oils and the mixtures presented a Newtonian behaviour, the average value of all the readings was reported as the shear stress at respective temperature.

4.2.8 Polarized light microscopy measurements (PLM):

Crystal morphology was recorded during crystallization. Polarised light microscopy was used to visualise the microstructure of the fat crystal networks. This analysis was done in Energy research centre, Institute of Technical Physics and Materials Science, Budapest. A drop of sample was taken and placed between a slide and a cover-slide to evaluate crystals microstructure. Images were taken using a Canon 1000D DSLR camera mounted on an SP300F polarised light microscope obtained from Brunel Microscopes Ltd., Chippenham, UK. A minimum of six images were taken of each sample. A photomicrograph was obtained at 100× magnification.

4.2.9 Statistical Analysis

All samples oil were submitted to one-way analysis of variance (ANOVA). This analysis of the data from the NHCO & FHCO was used to study the differences between 3 blends. The significances of all terms in the polynomial were judged statistically by computing the F-value at probability (p) of 0.05. The statistical analysis was performed using Statgraphics Plus V5.1 software (Statpoint Technologies, Warrenton, VA)

5. RESULTS AND DISCUSSION

5.1 Fatty acid composition

The fatty acid composition of non-hydrogenated coconut oil (NHCO), fully hydrogenated coconut oil (FHCO) and its blends used for the experimental study are shown in Table 5.1. Our study shows for non-hydrogenated coconut oil (NHCO) the predominant fatty acids were lauric acid (45.8%), myristic acid (18.8%), palmitic acid (10.1%) and oleic acid (7.1%). The fully hydrogenated coconut oil (FHCO) was high in lauric acid (53.3%), followed by myristic acid (21.3%) but low in unsaturated fatty acid e.g. oleic acid and linoleic acid. Dayrit (2008) studied that the primary fatty acid of coconut is lauric acid, which is present in the range of 45-53%. Due to a high percentage of saturated fatty acids, coconut oil has much better thermal stability and oxidative stability, compared with several other edible oils (Jayadas & Nair, 2006). The percentage of unsaturated fatty acid in NHCO was around 9%. Bhatnagar et al; (2009) found that coconut oil is rich in MCFA (59.7%) while deficient in PUFA (1.2%) and MUFA (6.1%). As expected, hydrogenation had reduced the level of unsaturation of the oils compared to the natural oils reported in the literature. The addition of FHCO to NHCO had shown some diversity in fatty acid composition. The increment and decrement of fatty acids can lead to changes in physicochemical and functional properties of the fat blends. The results from this study, showed that the percentage of the total saturated fatty acid (SFA) ranged from 92.90% for FHCO:NHCO (75:25) to 97.25% for blend of FHCO:NHCO (25:75), with the predominant presence of lauric

acid (C12:0) and myristic acid (C14:0). These fat blends showed a significant difference in fatty acid composition, in comparison to non-hydrogenated coconut oil.

Table 5. 1 Fatty acid composition (%) of non- hydrogenated coconut fat, fully hydrogenated coconut fat and its blends.

Fatty acid %	FHCO	FHCO: NHCO (w/w)			NHCO
		75:25	50:50	25:75	
C6:0	0.10 ± 0.01 ^a	0.22 ± 0.01 ^b	0.34 ± 0.02 ^c	0.47 ± 0.02 ^d	0.60 ± 0.10 ^e
C8:0	2.0 ± 0.10 ^a	3.18 ± 0.02 ^b	4.45 ± 0.04 ^c	5.71 ± 0.05 ^d	7.0 ± 0.10 ^e
C10:0	2.7 ± 0.02 ^a	3.4 ± 0.01 ^b	4.1 ± 0.02 ^c	4.76 ± 0.25 ^d	5.56 ± 0.20 ^e
C12:0	53.33 ± 0.01 ^d	51.40 ± 0.40 ^{cd}	49.51 ± 0.50 ^{bc}	47.65 ± 0.04 ^b	45.8 ± 0.03 ^a
C12:1	0.1 ± 0.02 ^c	0.078 ± 0.10 ^c	0.05 ± 0.02 ^b	0.025 ± 0.02 ^{ab}	0 ^a
C14:0	21.3 ± 0.30 ^e	20.68 ± 0.20 ^c	20.05 ± 0.01 ^c	19.43 ± 0.15 ^b	18.76 ± 0.25 ^a
C16:0	10 ± 1.00 ^a	10.03 ± 0.35 ^a	10.05 ± 0.05 ^a	10.08 ± 0.01 ^a	10.1 ± 0.40 ^a
C18:0	10 ± 2.00 ^e	8.25 ± 0.10 ^d	6.46 ± 0.25 ^c	4.75 ± 0.10 ^b	3 ± 0.01 ^a
C18:1 trans	0.03 ± 0.10 ^a	0.058 ± 0.01 ^{ab}	0.085 ± 0.10 ^{bc}	0.11 ± 0.01 ^c	0.14 ± 0.03 ^d
C18:1 cis	0.30 ± 0.10 ^a	2.00 ± 1.0 ^b	3.63 ± 0.11 ^c	5.46 ± 0.20 ^d	7.11 ± 0.15 ^e
C18:2 trans	0 ^a	0.02 ± 0.01 ^a	0.05 ± 0.02 ^b	0.08 ± 0.05 ^c	0.11 ± 0.01 ^c
C18:2 cis	0.10 ± 0.03 ^a	0.48 ± 0.03 ^b	0.86 ± 0.01 ^c	1.26 ± 0.05 ^d	1.7 ± 0.10 ^e
C 20	0.10 ± 0.20 ^a	0.10 ± 0.10 ^a	0.96 ± 0.05 ^a	0.11 ± 0.02 ^a	0.1 ± 0.01 ^a
Other	0.02 ± 0.05 ^a	0.03 ± 0.01 ^a	0.05 ± 0.05 ^b	0.07 ± 0.02 ^c	0.08 ± 0.01 ^d
SFA	99.40 ± 0.15 ^e	97.25 ± 0.25 ^d	95.1 ± 0.12 ^c	92.95 ± 0.20 ^b	90.8 ± 0.06 ^a

Values are means ± SD of triplicate analysis. Means with different letters in the same row indicate significant differences at p < 0.05

5.2 Solidification

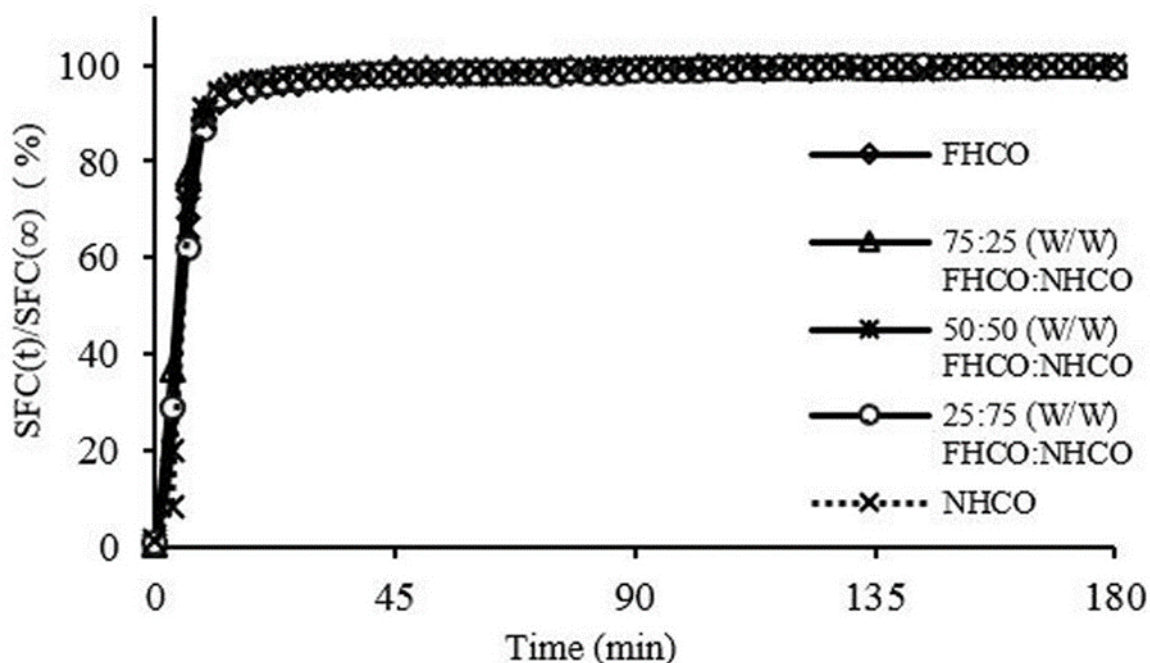


Figure 5. 1 Solidification curve at temperature 10±1 °C

The nature of the process of crystallization is determined by monitoring the formation of crystalline solid material as a function of time. The crystallization intensively influences the final structure of fats and is intrinsically linked to industrial food processing. In this study non-hydrogenated coconut oil, fully hydrogenated coconut oil and its 3 blends were crystallized at 10±1°C, 15±1 °C and 18±1 °C (See Fig. 5.1, Fig. 5.2, Fig. 5.3). Isothermal crystallization curves of original oils and blends were examined by pNMR and analysed. Fully hydrogenated coconut fat induced dramatic changes in crystallization behaviour (SFC max values) of non-hydrogenated coconut oil. All fat samples showed sigmoidal curves for temperatures of 10±1 and 15±1 °C. Crystallization was very fast and the equilibrium SFC was constant as the crystallization time

increased. As the temperature was increased to 18 ± 1 °C, all fat samples showed sigmoidal curves. Ribeiro et al., 2009 also observed a similar effect on isotherms in the blending of fully hydrogenated soybean oil and soybean oil.

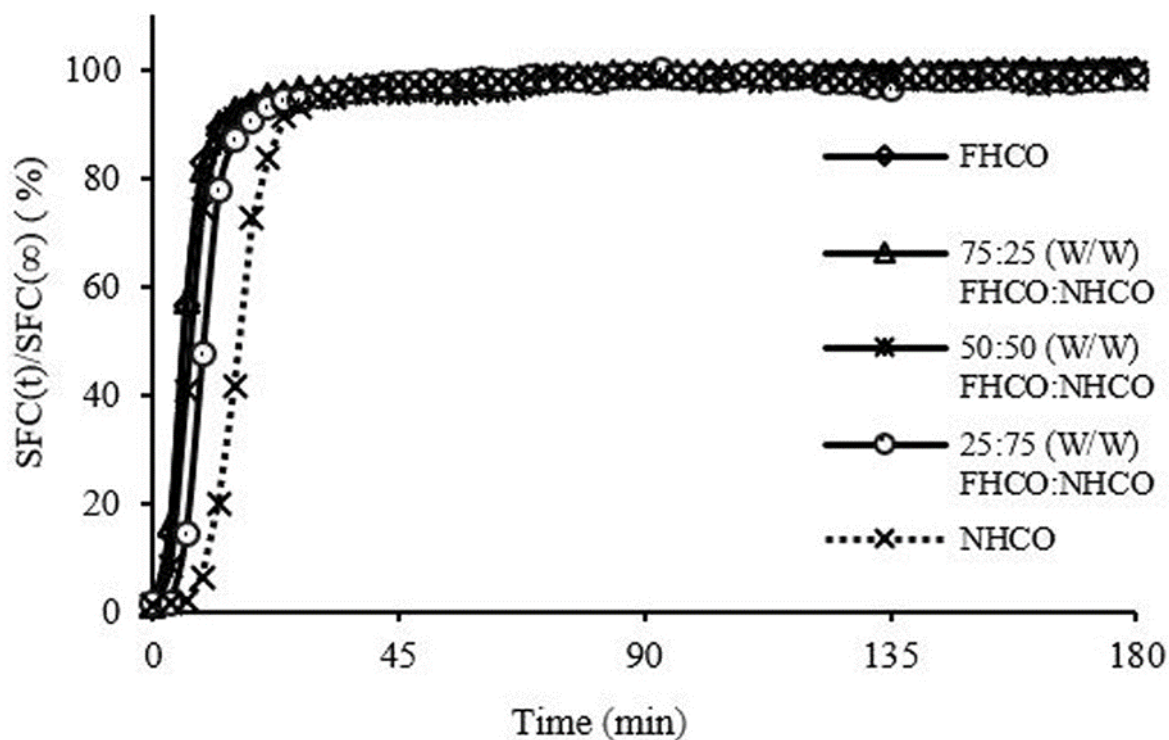


Figure 5.2 Solidification curve at temperature 15 ± 1 °C

The analysis of the curves showed that the induction time of the crystallization decreased in parallel to increases in temperature gradients from 62 ± 1 °C to 70 ± 1 °C. The equilibrium SFCmax values are modified in accordance to the blending ratio and temperature gradients. It seems that nucleation and crystal growth in the non-hydrogenated coconut oil are more retarded relative to the blended fats and FHCO. This could be a result of the increased complexity of the mix of triglycerides in the blends. Additionally, the examination of Fig. 5.1, Fig. 5.2 and Fig. 5.3 makes it apparent that at 18 ± 1 °C all evaluated samples displayed longer times to attain complete

crystallization equilibrium when compared to samples crystallized at 10 ± 1 °C. The SFC curves displayed moderate elevation of SFC values during the crystallization time.

The differences in the crystallization behaviour of fat samples at different temperatures are demonstrated by the linearized Avrami lines (Fig. 5.4, Fig. 5.5, Fig. 5.6). These straight lines were fitted to the values of $\ln[-\ln [1-\text{SFC}(t)/\text{SFC}(\infty)]]$ against $\ln(t)$. The parameters of the Avrami equations are summarized in Table 2. The Avrami exponent (n), Avrami rate constant (k), as well as the coefficient of determination (R^2) are shown in Table 5.2.

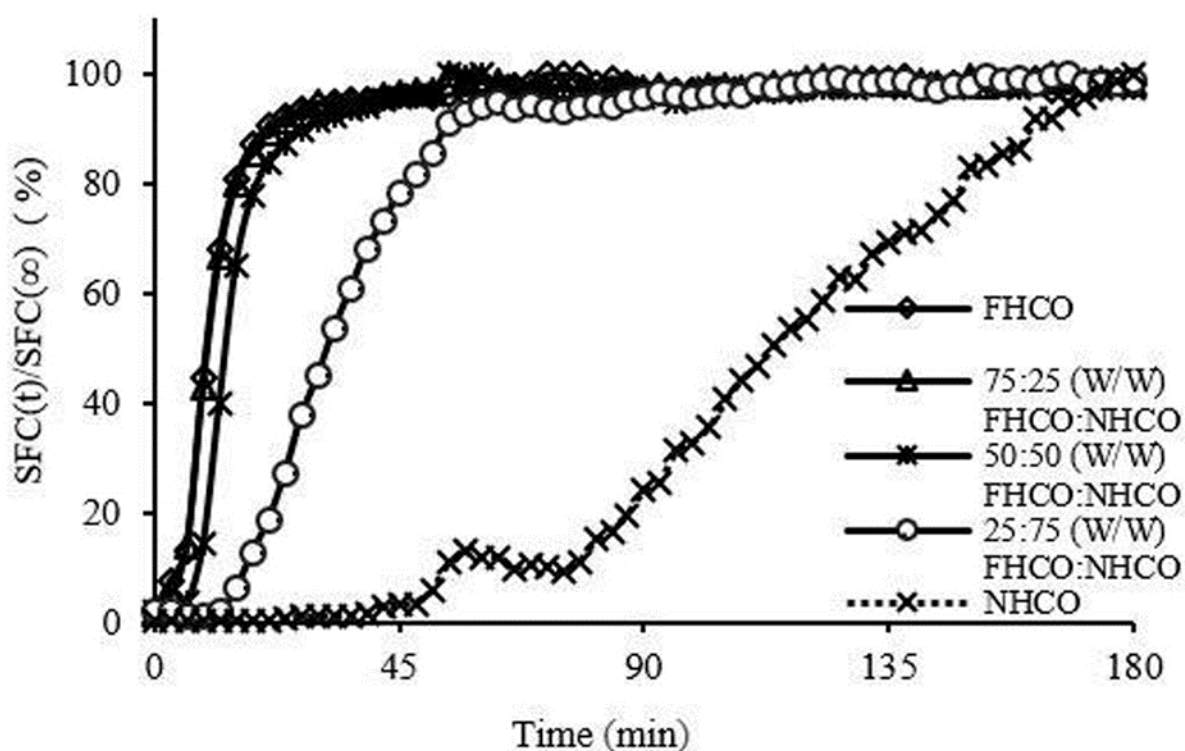


Figure 5. 3 Solidification curve at temperature 18 ± 1 °C

These parameters are to be considered when outlining the applications of fats. The addition of FHCO to non-hydrogenated coconut oil promoted proportional increases in the SFCmax value.

Similar results were obtained additionally in the blending of fully hydrogenated cottonseed oil and canola oil.

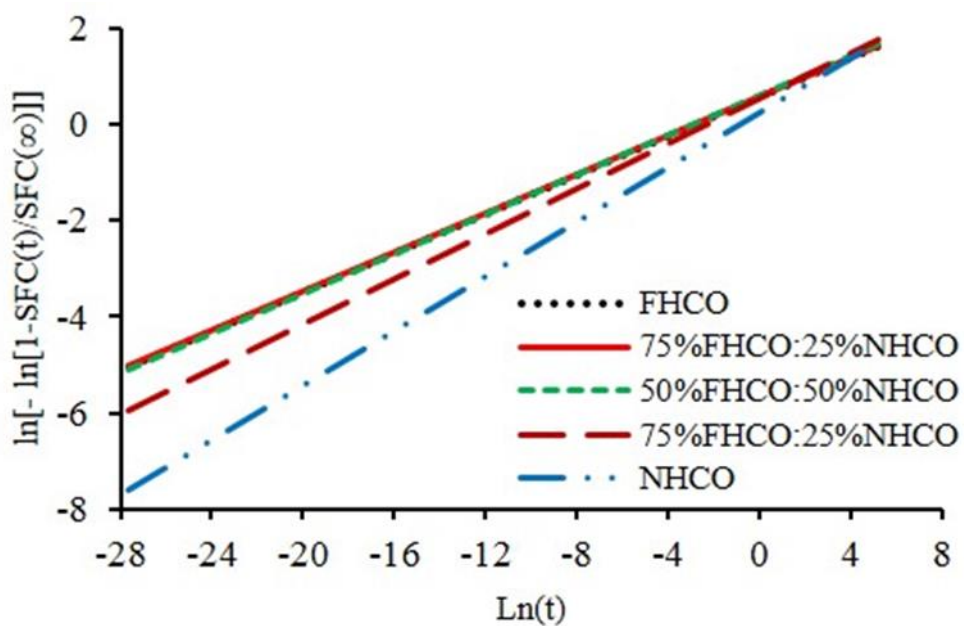


Figure 5. 4 Plots of $\ln[-\ln[1-SFC(t)/SFC(\infty)]]$ vs $\ln(t)$ at $10 \pm 1^\circ\text{C}$

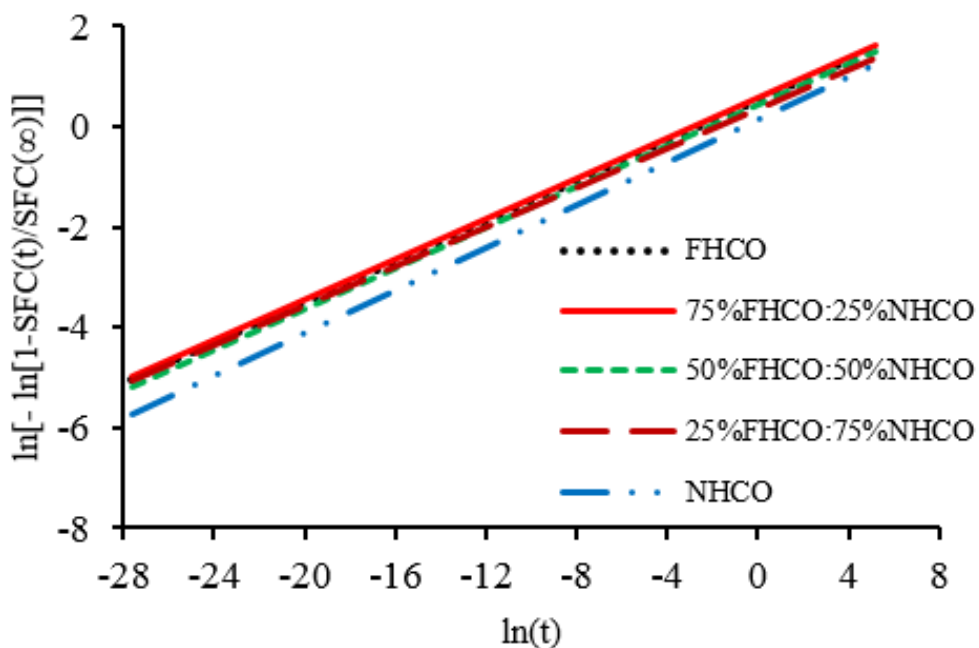


Figure 5. 5 Plots of $\ln[-\ln[1-SFC(t)/SFC(\infty)]]$ vs $\ln(t)$ at $15 \pm 1^\circ\text{C}$

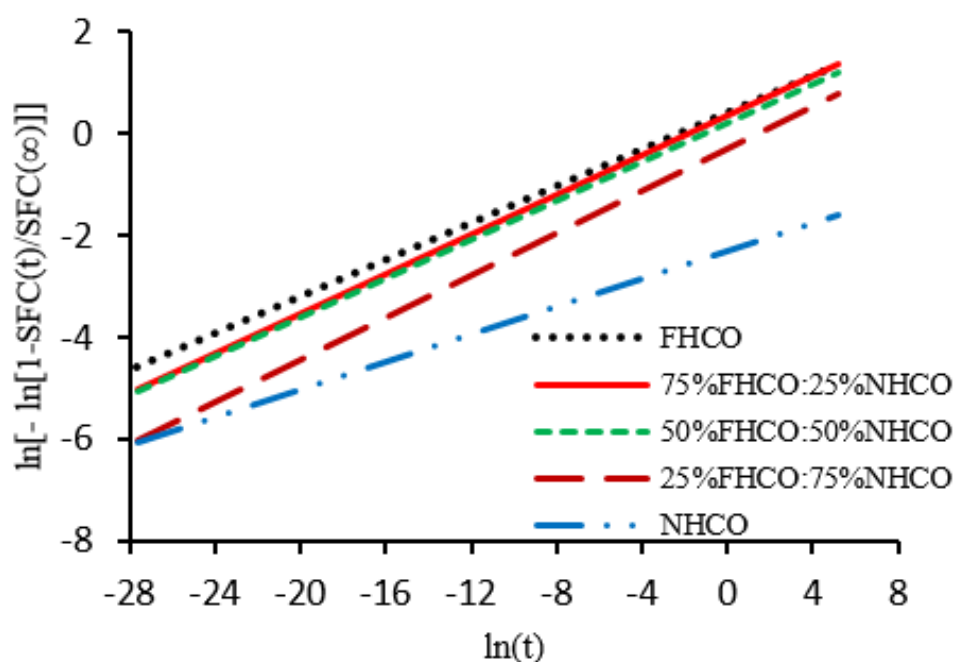


Figure 5. 6 Plots of $\ln[-\ln[1-SFC(t)/SFC(\infty)]]$ vs $\ln(t)$ at $18\pm1\text{ }^{\circ}\text{C}$

Table 5. 2 Avrami constant (k), Avrami exponent (n), and R2 for fat samples at different temperature

Samples	Temp.	Avrami constant k (min^{-1})	Avrami Exponent (n)	R ²
NHCO	10 $\pm$ 1 $^{\circ}\text{C}$	1.7751	0.20	0.8846
	15 $\pm$ 1 $^{\circ}\text{C}$	1.1467	0.21	0.8570
	18 $\pm$ 1 $^{\circ}\text{C}$	0.0989	0.13	0.7080
25% NHCO 75% FHCO	10 $\pm$ 1 $^{\circ}\text{C}$	1.7391	0.23	0.9693
	15 $\pm$ 1 $^{\circ}\text{C}$	1.8002	0.20	0.9034
	18 $\pm$ 1 $^{\circ}\text{C}$	1.4211	0.19	0.7766
50% NHCO 50% FHCO	10 $\pm$ 1 $^{\circ}\text{C}$	1.2969	0.28	0.9718
	15 $\pm$ 1 $^{\circ}\text{C}$	1.5345	0.20	0.8738
	18 $\pm$ 1 $^{\circ}\text{C}$	1.2079	0.19	0.8592
75% NHCO 25% FHCO	10 $\pm$ 1 $^{\circ}\text{C}$	1.7906	0.20	0.9441
	15 $\pm$ 1 $^{\circ}\text{C}$	1.4172	0.19	0.7453
	18 $\pm$ 1 $^{\circ}\text{C}$	0.7322	0.20	0.7592
FHCO	10 $\pm$ 1 $^{\circ}\text{C}$	1.8255	0.20	0.9433
	15 $\pm$ 1 $^{\circ}\text{C}$	1.7069	0.20	0.9070
	18 $\pm$ 1 $^{\circ}\text{C}$	1.4743	0.18	0.7703

Avrami model is good to be used for describing the crystallization kinetics of coconut oil based on changes of oil solid fat content during the crystallization process. The model has the adjustability of more than 99% with the experimental results in this study. Coconut oil

crystallization temperature has positive correlation with the crystallization-rate-constant and the Avrami index but has negative correlation with the maximum SFC that can be achieved.

5.3 Thermal study

Differential scanning calorimetry (DSC) is a thermoanalytical technique to monitor changes in physical or chemical properties of materials as a function of temperature by detecting the heat changes associated with such process. Fat melting is an endothermic process in which the energy is absorbed, whereas crystallization is an exothermic process in which the energy is released. In general, the thermal behaviour of oils and fats depends on the chemical composition and the time-temperature protocol applied in the DSC experiment (Tan and Che 2002).

The crystallization curves of non-hydrogenated coconut oil and fully hydrogenated coconut oil as well as their blends were similar, showing only one exothermic peak between 11.11 °C and 16.67 °C. (Fig. 5.7)

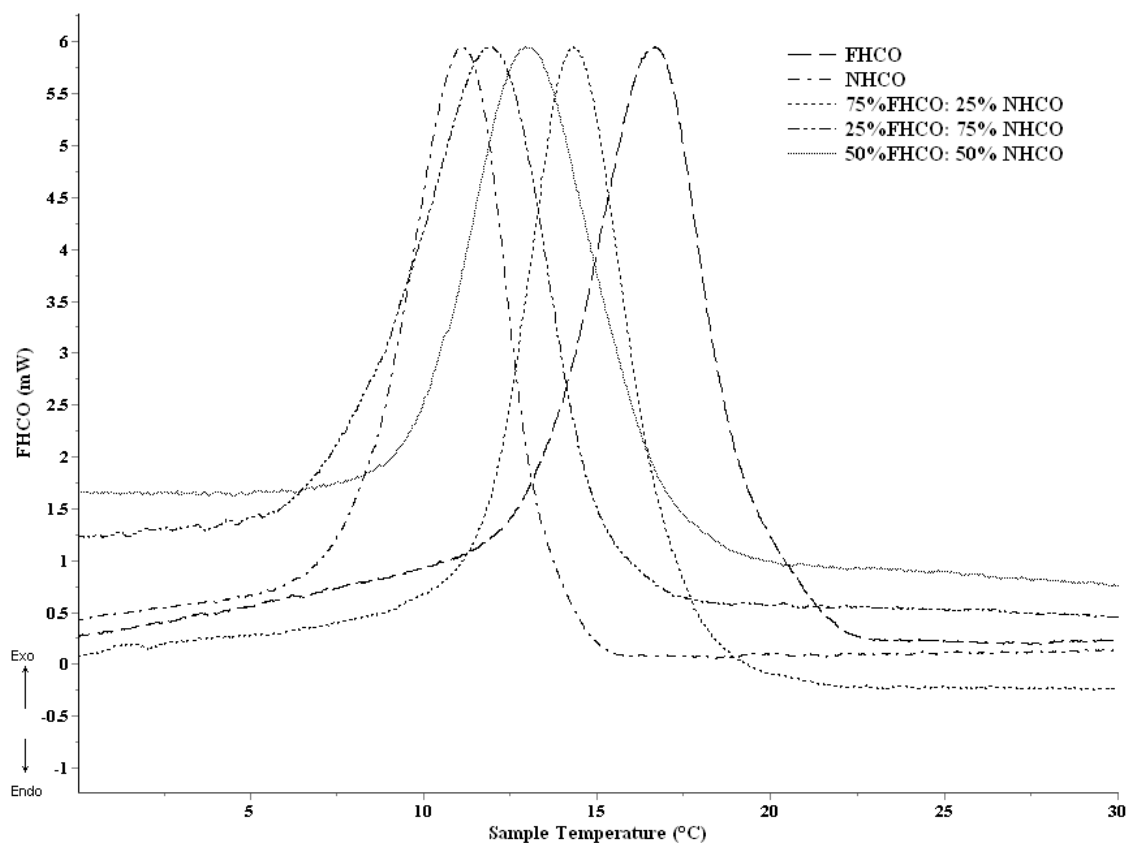


Figure 5. 7 Differential scanning calorimetry cooling curves of coconut fats and blends.

Non-hydrogenated Coconut oil had a great exothermic peak at 11.11 °C (enthalpy: -62.10 J g^{-1}). In the present study the crystallization points were determined as the end set temperature values of the crystallization peaks. Results indicated that there was a shift in the crystallization peak of coconut oil blends to lower temperature. Blending of non-hydrogenated coconut oil with fully hydrogenated coconut oil did not change the cooling profile of the oil blends to any great extent. There was no new peak emerging following the blending but small differences in peak temperature were observed as the FHCO level increased in NHCO. These differences arise from the increase of SFA content in samples with the increase of FHCO ratio.

Table 5. 3 Thermal properties of non-hydrogenated coconut fat, fully hydrogenated coconut fat and its blends.

Samples	Enthalpy (J/g)	Max. peak Temperature (°C)
FHCO	-82.94 ± 0.12^d	16.67 ± 0.34^d
75% FHCO:25% NHCO	-76.28 ± 0.34^c	14.32 ± 0.18^c
50% NHCO:50% FHCO	-67.94 ± 0.41^b	11.97 ± 0.22^b
25% FHCO:75% NHCO	-66.82 ± 0.78^b	11.55 ± 0.51^a
NHCO	-62.10 ± 0.67^a	11.11 ± 0.37^a

The thermal properties of various oil samples from the DSC melting and crystallization curves can be characterized by onset (T_o), peak temperature (T_p) and end set (T_e) transition temperatures. Table 5.3 shows the parameters of the crystallization curves for the non-hydrogenated coconut oil, fully hydrogenated coconut oil and blends. As expected, this data showed that peak crystallization temperature increased with the increase in the proportion of fully hydrogenated coconut fat in blends. The same results were reported in the case of canola oil and fully hydrogenated canola oil (Jenab et al.2013). The crystallization enthalpy values of non-hydrogenated coconut oil and hydrogenated coconut oil were between -82.94 and -62.10 J/g. All parameters evaluated in relation to the crystallization curves showed positive relation to full hydrogenation.

From the results of the chemical composition of our samples it was obvious that FHCO contained mostly saturated fatty acids that resulted in a somewhat uniform triglyceride (TAG) structure. Less TAG can form more stable crystals because the uniform TAG's form compact crystals. This may be the reason why equilibrium SFC is higher and crystallization is faster per

the amount of the FHCO in the fat mixtures. On the other hand, NHCO has more unsaturated fatty acids, and the TAG structure must be more complex as a consequence of this. This complexity results in a less-packed crystal structure and smaller equilibrium SFC, as well as less slow crystallization.

5.4 Solid fat Content

The SFC curve (Solid Fat Content vs. Temperature) determines the specific application of the edible oil/fat and thus is an important quality control parameter for manufacture as well as for product development. The SFC curve represents the ratio between the solids and the liquids in a certain fat at various temperatures. Fig.5.8 shows solid fat index profile of two coconut fat and its blends.

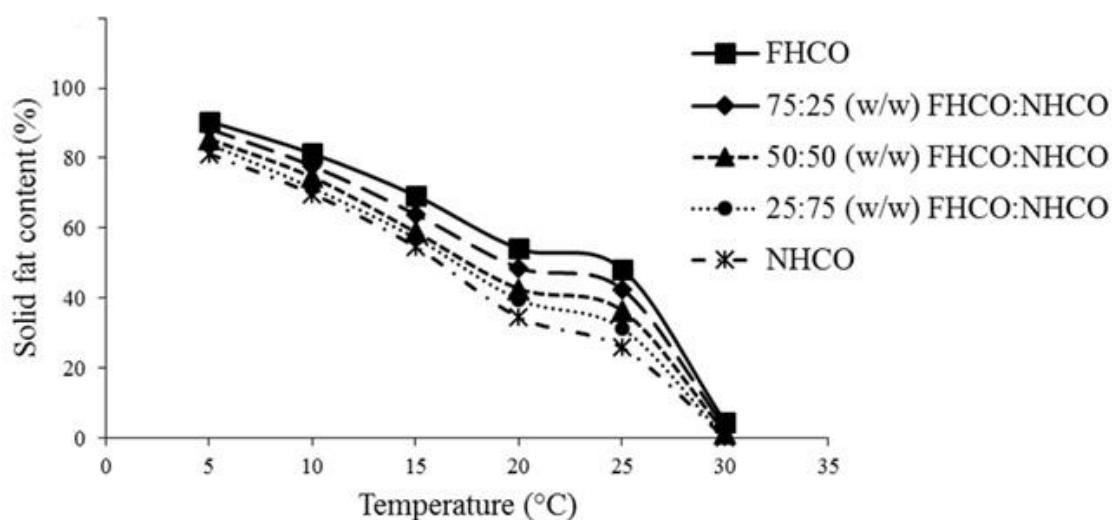


Figure 5. 8 Solid fat content profile of two coconut fat and its blends.

As shown in Fig.5.8, fully hydrogenated coconut oil (FHCO) had the highest SFC (90.49%) at $5 \pm 1^\circ\text{C}$ temperature and not melted completely (SFC=4.46%) at $30 \pm 1^\circ\text{C}$. Whereas the SFC profile of Non-hydrogenated coconut oil (NHCO) showed a lower SFC value at the temperature range $5 - 30^\circ\text{C}$ ($p < 0.05$). There were marked differences in SFC between the FHCO and NHCO.

The large variations of SFC for coconut oil samples can be mainly explained by differences in their fatty acid composition.

SFC profiles of fat blends with proportion of 75:25, 50:50 and 25:75 (w/w) FHCO:NHCO were significantly different from each other, increasing with an increasing proportion of FHCO in the blend ($p < 0.05$). The SFC values of all samples decreased with increasing temperature.

At $10 \pm 1^\circ\text{C}$, the blend showed SFC ranging from 71 % to 78 % , which decreased non-linearly until melting completely at $30 \pm 1^\circ\text{C}$. All samples were stable in SFC value at $20\text{--}25^\circ\text{C}$. The greatest decrease in SFC occurred from $25 \pm 1^\circ\text{C}$ onwards, due to the fast melting and solubization of trisaturated tryglycerols which was present in samples.

Blending of fully hydrogenated coconut oil in non-hydrogenated coconut oil resulted in an increase in SFC in blends at all temperatures. The only difference between FHCO and NHCO is the lack of Oleic and Linoleic acid in FHCO (as they were converted to stearic acid upon the hydrogenation). In other word, NHCO contains two more fatty acid types as compared to the FHCO. In tems of TAG profile, FHCO does not contain any TAGs having oleic or linoleic acid in their structure. Accordingly, FHCO has a simpler fatty acid and TAG composition. Due to the formation of mixed triglycerols or change in fatty acid composition, the blends showed a complex melting profile and the format of the curves was significantly modified by blending proportion.

These SFC results are useful in determining the suitability of oil blends for a particular purpose in developing new food products. The increased SFC of blends would provide them with enhanced texture and specific melting behaviour suitable for specific applications.

5.5 Melting characteristics

Fig.5.9 depicts the melting profiles of the initial fats and their blends. The melting behaviour of original oils and blends was characterized by only one endothermic peak. The components with the lowest melting point tend to melt first and represent the most unsaturated triglycerides, while components with the higher melting point which represent the most saturated triglycerides will melt later.

Similarly, results showed NHCO started melting first when compared to other samples due to a higher content of unsaturated triglyceride. The addition of fully hydrogenated coconut oil in non-hydrogenated coconut oil did not change the melting behaviour but as the content of FHCO was increased, the melting peaks of blend shifted towards the high temperatures (Fig.5.9). The similar DSC profile of coconut oil was reported by Adhikari et al. (2010). These melting profiles gave an indication of the amount of crystallized fat and the occurrence of polymorphic transitions.

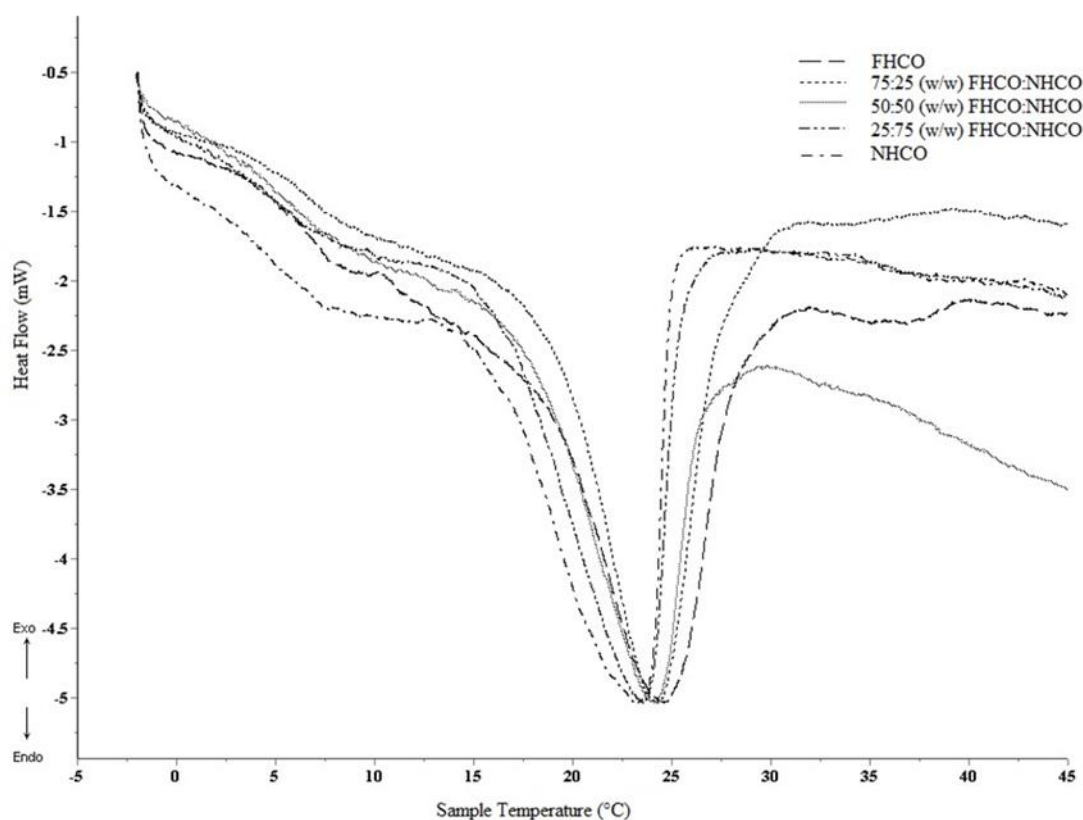


Figure 5. 9 Melting profile of two coconut fat and its blends.

Table 5.4. shows the thermal characteristics of original oils and their blends. No significant differences were observed in T_{on} or T_p values of NHCO in addition to FHCO. T_{on} values ranged from 15.60 °C to 20.50 °C while T_p values ranged from 23.27 °C and 24.61 °C. No significant

differences were observed for melting enthalpies of NHCO with the addition of FHCO with enthalpy values between 46.38 J/g and 80.24 J/g (Table.5.4).

Table 5. 4 Thermal properties of non-hydrogenated coconut fat, fully hydrogenated coconut fat and its blends

Sample	Max Peak temperature (°C)	Enthalpy (J/g)
FHCO	24.55 ± 0.27 ^c	80.24 ± 0.02 ^e
75:25 (w/w) FHCO:NHCO	24.30 ± 0.20 ^c	76.21 ± 0.11 ^d
50:50 (w/w) FHCO:NHCO	23.96 ± 0.12 ^b	63.44 ± 0.04 ^c
25:75 (w/w) FHCO:NHCO	23.52 ± 0.08 ^a	55.84 ± 0.23 ^b
NHCO	23.27 ± 0.51 ^a	46.38 ± 0.02 ^a

Values are means ± SD of triplicate analysis. Means with different letters in the same columns indicate significant differences at p<0.05

5.6 Solid Fat Index

The solid-liquid ratio in fats, expressed as solid fat content was determined from the DSC melting and solidification curves by partial integration. The heat flow to or from fat samples was measured as it is heated and cooled isothermally. The estimation of the solid fat index of samples is depending upon onset temperature and the end temperature of crystallization and melting. The all samples showed only one prominent peak in the crystallization and melting thermogram. The similar thermal behaviour of coconut oil and hydrogenated coconut oil was explored with major one peak in different studies (TAN et, al., 2002, SHEN et, al., 2001). All thermal parameters evaluated in relation to the crystallization thermogram showed a positive linear relation to fully hydrogenated coconut fat in the non-hydrogenated coconut fat. For all samples, the solid fat index values calculated by crystallization thermograms are shown in figure 5.10. The DSC showed a clear difference in values of the solid fat index of fats and its blends. This difference may be because of crystallization enthalpies of triglycerides (NASSU & GUARALDO, 1995).

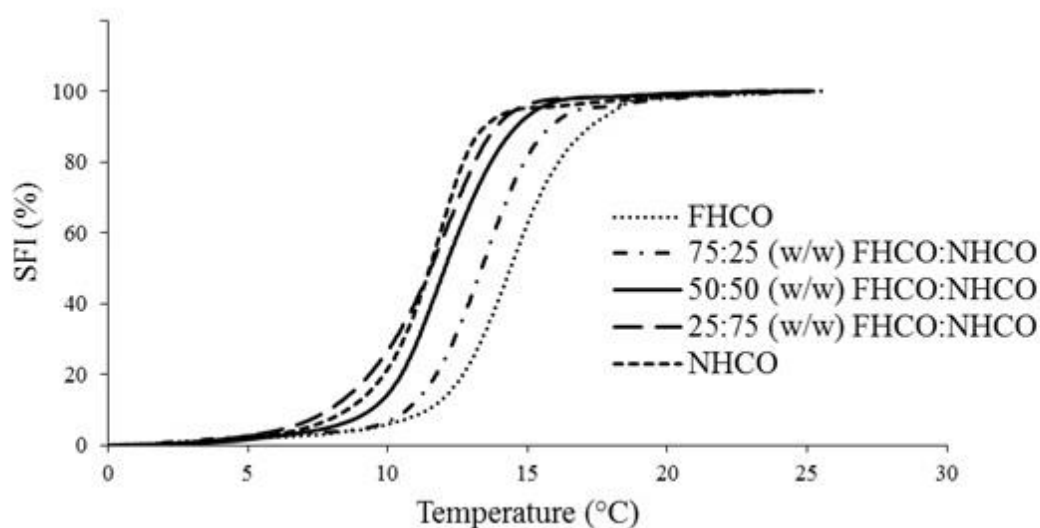


Figure 5. 10 Solid fat index vs temperature of crystallization of two coconut fats and its blends.

Figure 5.11 shows the solid fat index profile of all samples calculated from melting thermographs. The DSC results showed significant difference in melting behaviour, solid fat index, and melting range of samples. For example, as the ratio of FHCO in NHCO increased, the peak for lower melting samples shifted towards higher melting range. For the DSC method, SFI values of all samples were close to each other at low temperature. The non-hydrogenated coconut fat was melted completely at 25 ± 1 °C whereas other samples had percentage solid crystals. The range of melting temperature was modified as proportion of fully hydrogenated coconut oil increased in blends.

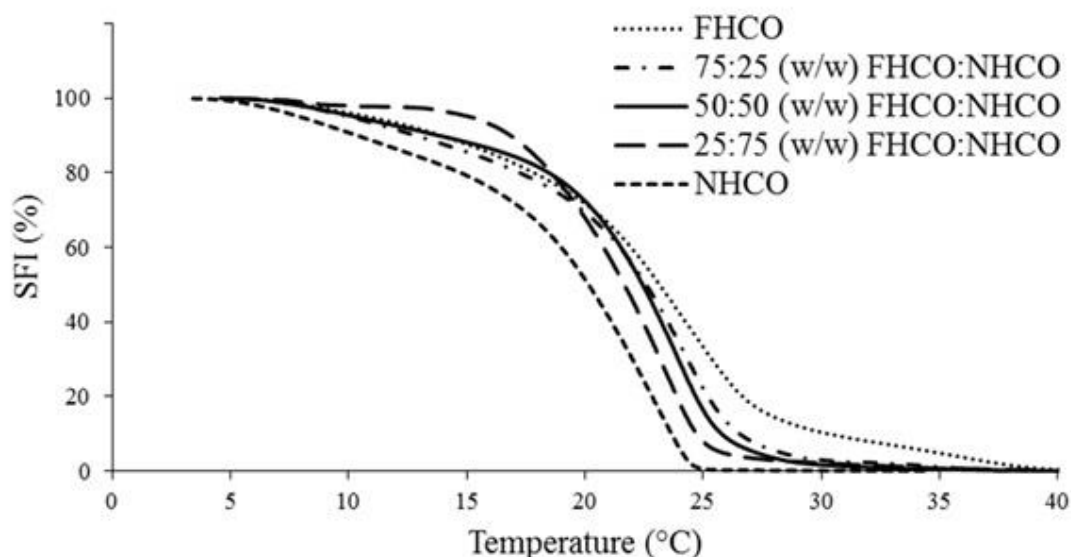


Figure 5. 11 Solid fat index profile of two coconut fat and its blends.

5.7 Comparison of SFC measured by NMR and DSC

In the NMR method, we obtained limited information because of the measurement at each required temperature whereas the DSC method gave SFI values from thermogram including the whole temperature range from one unique measurement. Generally, the values of SFI measured by DSC using a melting thermogram (Figure 5.11) were higher than the NMR method (Figure 5.8) for two coconut fats and their blends. This agreed very well with findings by Walker et al., 1971 and Tieko et al., 1995. Shen and co-worker (2001) found same the differences between the two techniques with a different rate of temperature. In this study, the average rate of temperature change in the NMR procedure was about 30 times slower than the DSC method.

5.8 Slip melting point

SMP is one of the important physical property of fats and oils which used for characterization of melting/solidification properties.

Table 5. 5 The slip melting point (SMP) of non-hydrogenated coconut fat, fully hydrogenated coconut fat and its blends.

Sample	Melting point (°C)	Melting point SFI (°C)
FHCO	30.2 ± 0.3 ^d	38.5 ± 0.7 ^d
75:25 (w/w) FHCO:NHCO	28.40± 0.2 ^c	35.18 ± 0.4 ^c
50:50 (w/w) FHCO:NHCO	25.80 ± 0.4 ^b	33.73 ± 0.7 ^c
25:75 (w/w) FHCO:NHCO	25.02 ± 0.1 ^b	31.06 ± 0.2 ^b
NHCO	22.00 ± 0.2 ^a	25.25 ± 0.4 ^a

Values are means ± SD of triplicate analysis. Means with different letters in the same column indicate significant differences at $p < 0.05$

Table 5.5 shows the slip melting point (SMP) of non-hydrogenated coconut oil, fully hydrogenated coconut oils and its blends. The highest melting point of FHCO was due to the presence of long-chain saturated fatty acids. Some research study observed SMPs of the fats and oils change with the chain length of FAs, unsaturation ratio, trans FA content, and the position of the FAs in the glycerol backbone.

5.9 Textural properties

The hardness, cohesiveness, adhesiveness, adhesive force and chewiness of fat samples at the temperature of 25 °C are presented in Table 5.6. The pure fully hydrogenated coconut fat (FHCO) has the highest value of hardness (11.22 N) and cohesiveness (33.95 g), which is not the case with the pure non-hydrogenated coconut fat. We observed that the addition of FHCO to non-hydrogenated coconut fat at different

concentrations leads to an increase in values of textural parameters, proportional to the increase in FHCO concentration. The same results were obtained after the addition of small amounts of hard fats to palm oil. (de Oliveira et al., 2015).

Table 5. 6 Textural properties of original fats and their blends

Samples	Hardness (N)	Cohesiveness (N.mm)	Adhesive ness	Adhesive force	Chewiness (N/mm)
NHCO	1.67 ^d	2.57 ^d	-0.13 ^d	-1.38 ^d	61.54 ^a
FHCO	11.22 ^a	33.95 ^a	-2.09 ^a	-9.74 ^a	19.47 ^d
25:75 (w/w) NHCO:FHCO	6.74 ^b	20.04 ^b	-0.14 ^b	-6.27 ^b	44.89 ^b
50:50 (w/w) NHCO:FHCO	3.69 ^c	10.86 ^c	-0.87 ^c	-3.53 ^c	28.36 ^c
75:25 (w/w) NHCO:FHCO	3.42 ^c	11.17 ^c	-0.73 ^c	-3.29 ^c	26.18 ^{cd}

Results are expressed as mean values. Means in a column with different superscripts are significantly different. (P < 0.05)

5.10 Rheological measurements

Viscoelasticity studies provide valuable data that can be correlated to fat crystal network structure. The parameter derived from small-amplitude oscillatory shear tests includes storage modulus (solid-like or elastic, G') and loss (liquid-like or viscous, G'') moduli.

Figures 5.12-5.17 show amplitude test graphs for all samples. In our study, we observed that during the heating process, crystallized coconut fat showed a viscoelastic crystalline structure with $G' > G''$. But above a certain temperature, the coconut fat melted quickly to a liquid state and the value of G' and G'' decreased drastically (Fig. 5.12). On the other hand, G' and G'' of fully hydrogenated coconut fat decreases linearly with increasing temperature until it reaches 22 °C and it showed a viscoelastic solid structure as a

result (Fig. 5.13). Higaki et al. (2004) found that G' and G'' values typical of the gel-like state changed to those typical of the liquid-like state with fully hydrogenated rapeseed oil and sal fat olein. In Fig 5.14, 5.15, 5.16 and 5.17, blends containing higher FHCO contents had higher G' and G'' as a function of temperature. The non-hydrogenated coconut fats showed a linear viscoelastic region up to 18 °C whereas fully hydrogenated coconut oil showed up to 21 °C. As the concentration of fully hydrogenated coconut oil increased in non-hydrogenated coconut fat, the linear viscoelastic region increased slightly with an increase in relative temperature.

Viscosity of coconut oil

All fat samples were investigated in the temperature range of 30 °C to 80 °C. From Fig 5.18 to Fig. 5.21, it was clear that fluidized fat samples are subjected to Newtonian behaviour at high temperatures, which is independent of the shear rate. It was found that the viscosity of all oils investigated had shown shear rate and temperature dependence where the viscosity of the oils reduces as the temperature and shear rate increase. The fat samples exhibiting gel-like behaviour are shown as Bingham plastic fluid curve with the apparent yield value at 30 °C, 40 °C, and 50 °C. This rheological behaviour is similar to the results observed by Santos et al. (2004) for some vegetable oils on heating at a different temperature. The Herschel-Bulkley model was fitted to flow curves of non-hydrogenated coconut fat, fully hydrogenated coconut fat, and their three blends with R^2 values 0.9999.

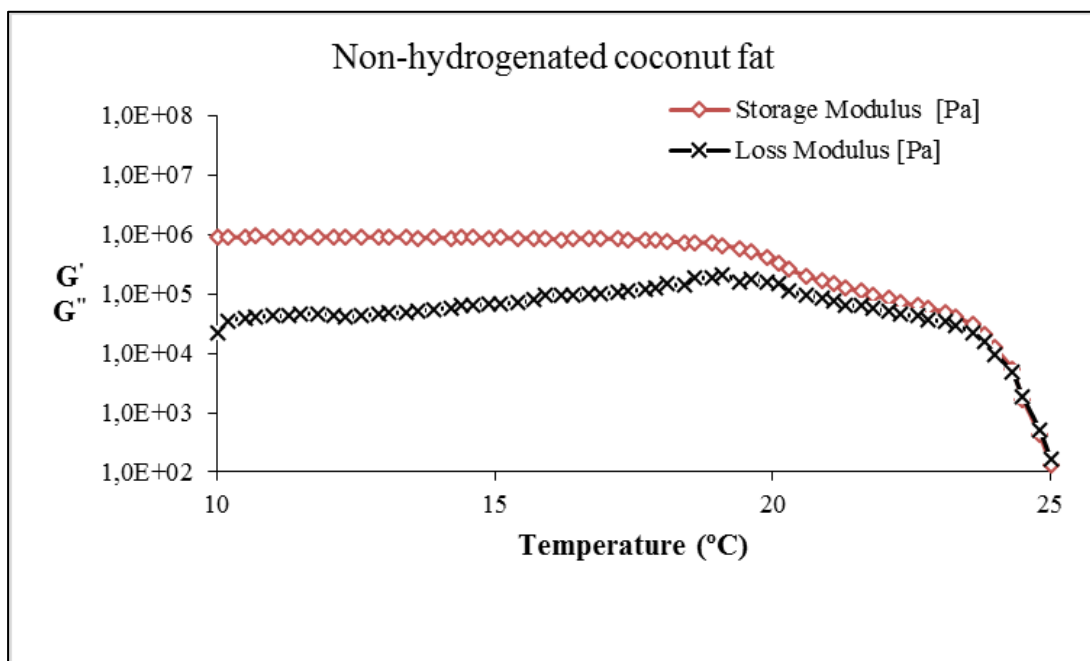


Figure 5. 12 Rheological properties in terms of storage modulus (G') and loss modulus (G'') of non-hydrogenated coconut fat as a function of temperature.

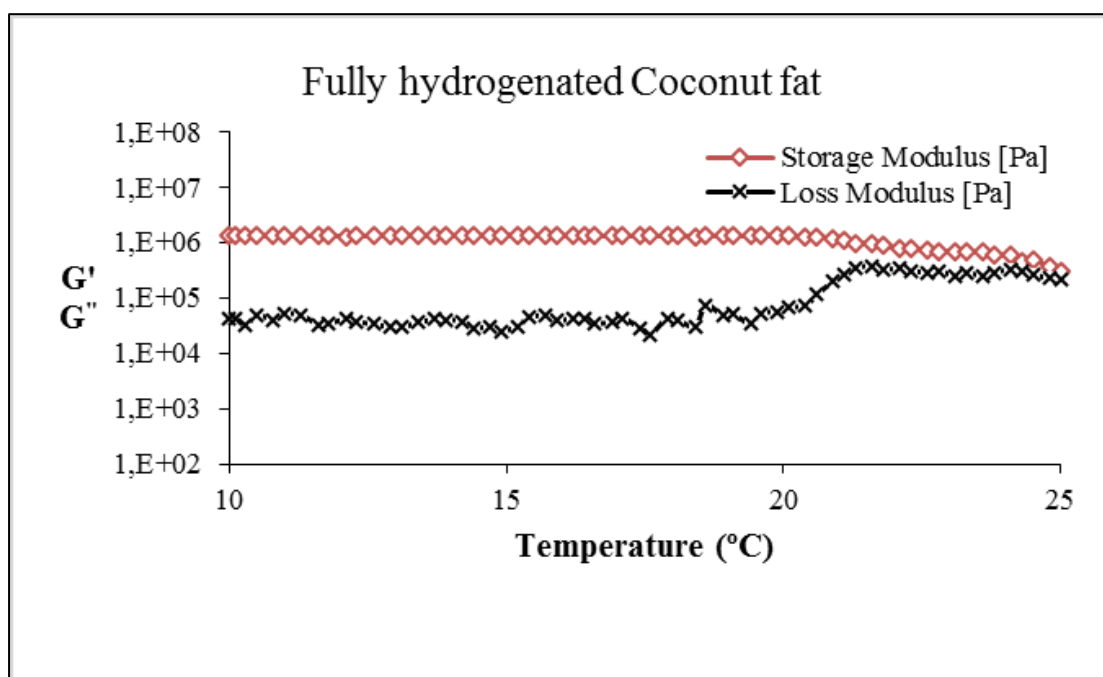


Figure 5. 13 Rheological properties in terms of storage modulus (G') and loss modulus (G'') of fully hydrogenated coconut fat as a function of temperature.

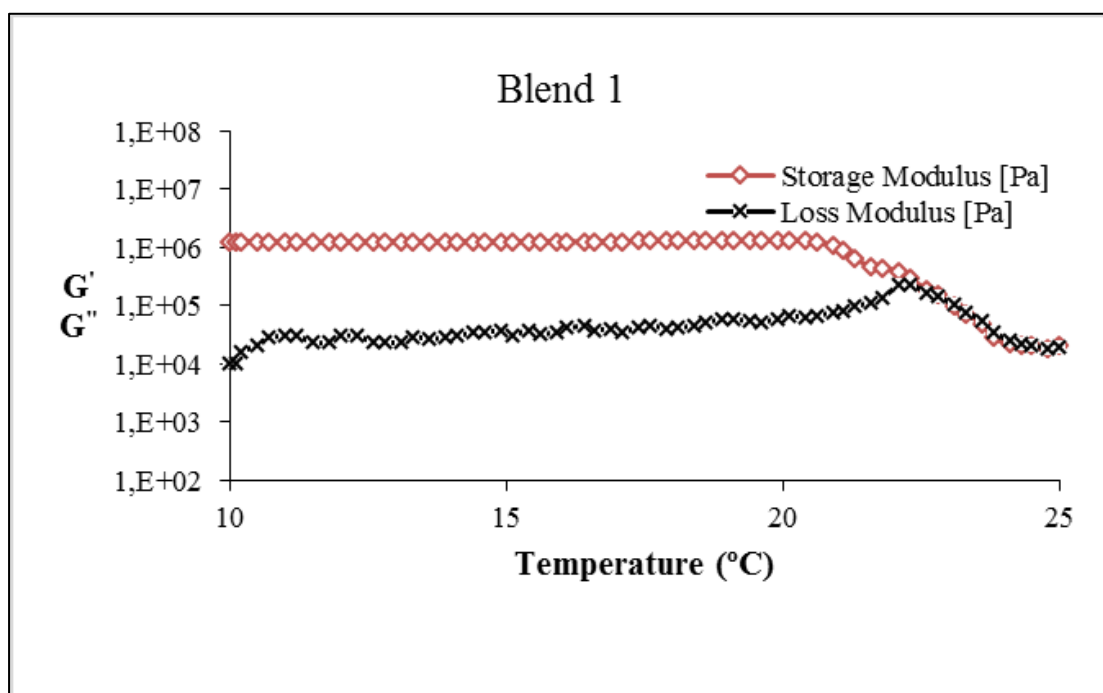


Figure 5. 14 Rheological properties in terms of storage modulus (G') and loss modulus (G'') of fat blend 1 as a function of temperature.

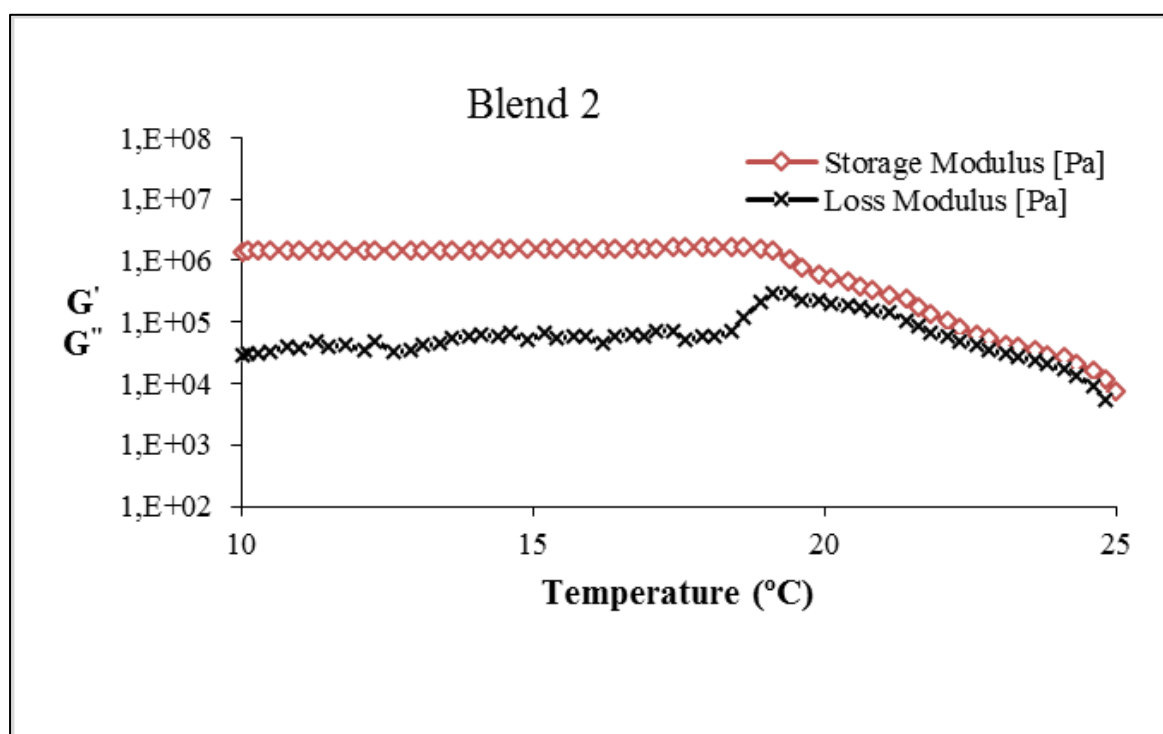


Figure 5. 15 Rheological properties in terms of storage modulus (G') and loss modulus (G'') of fat blend 2 as a function of temperature.

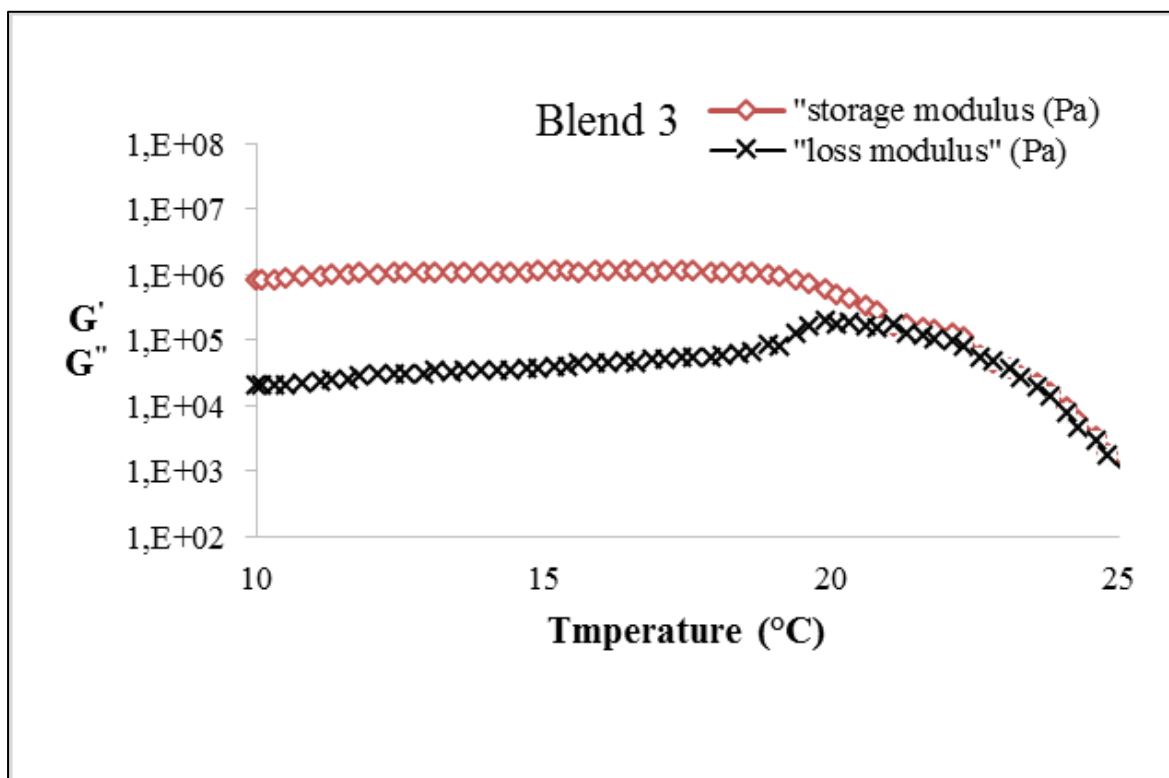


Figure 5. 16 Rheological properties in terms of storage modulus (G') and loss modulus (G'') of fat blend 3 as a function of temperature.

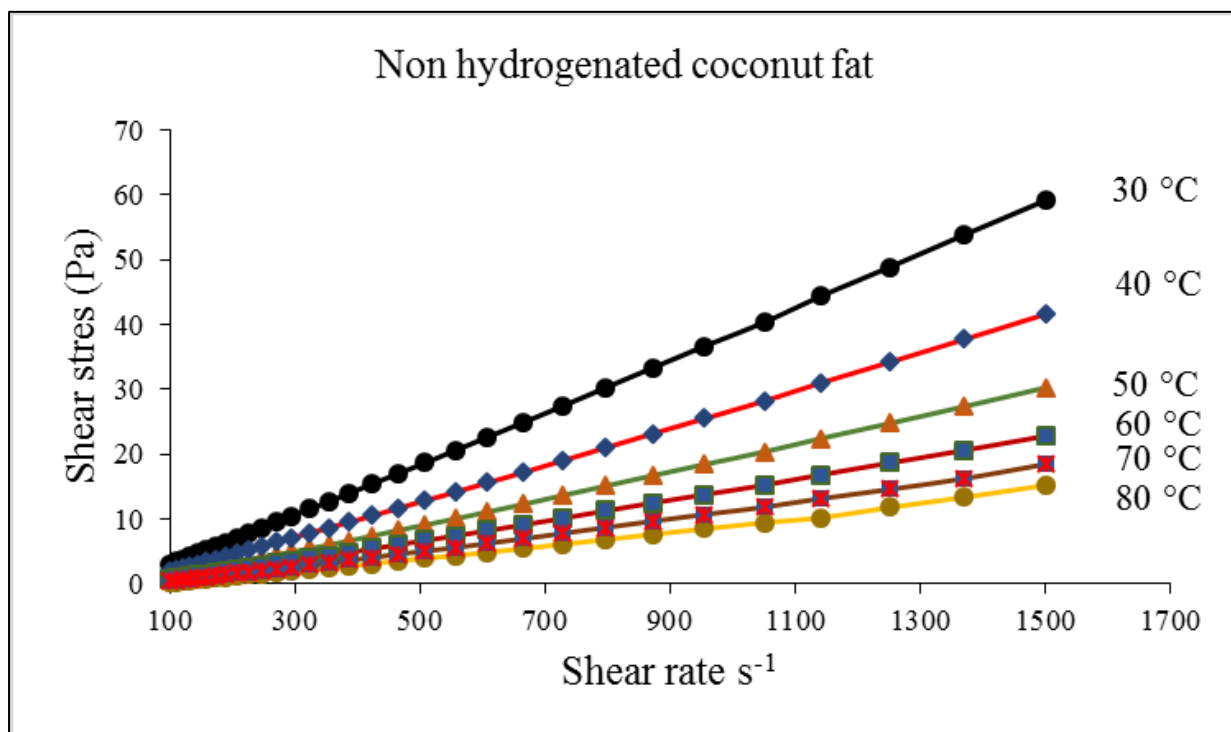


Figure 5. 17 Flow curve of non-hydrogenated coconut fat in a temperature range of 30 $^{\circ}\text{C}$ to 80 $^{\circ}\text{C}$.

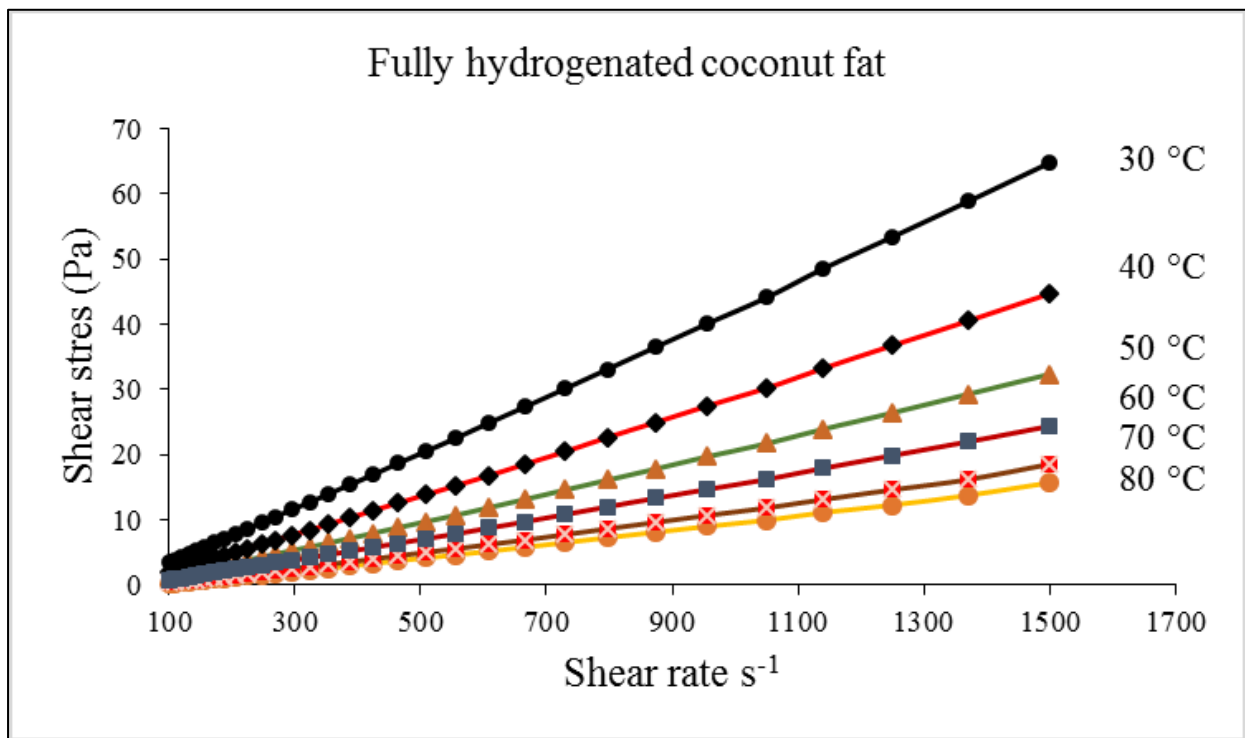


Figure 5. 18 Flow curve of fully hydrogenated coconut fat in a temperature range of 30°C to 80°C.

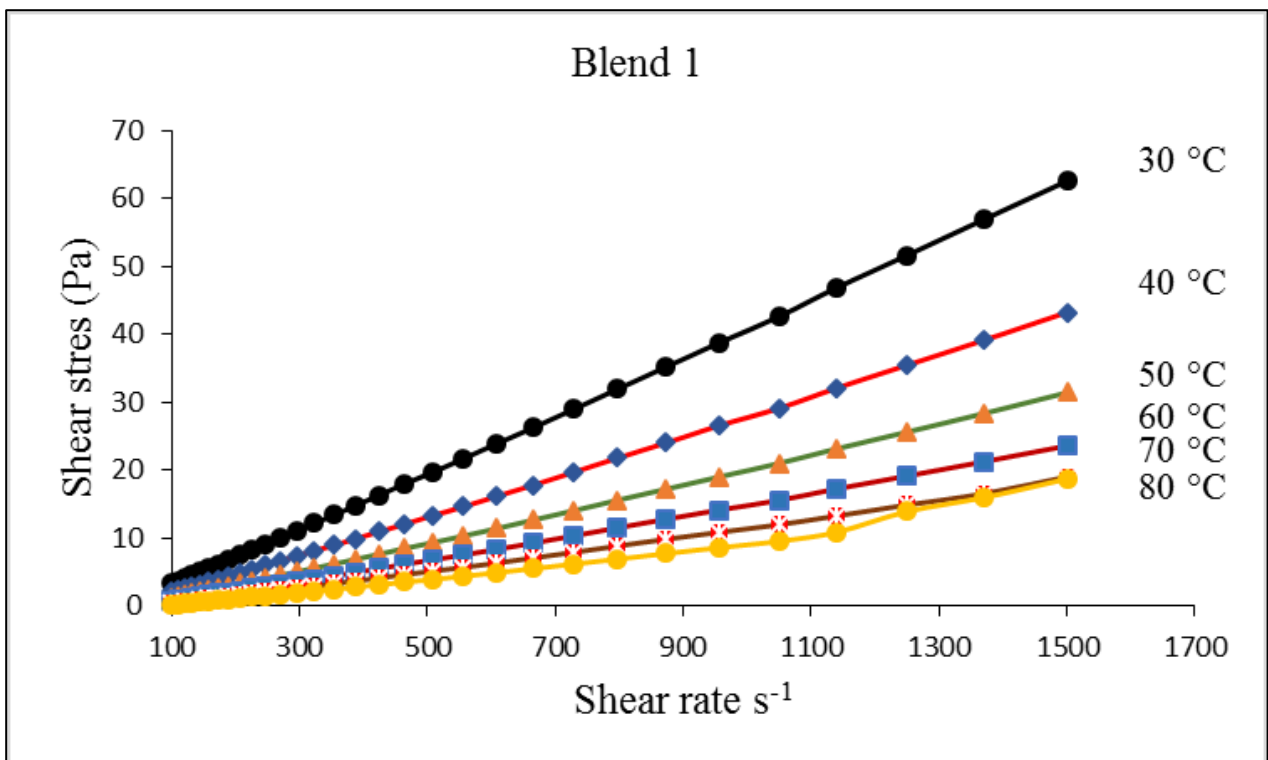


Figure 5. 19 Flow curve of fat blend 1 in a temperature range of 30°C to 80°C.

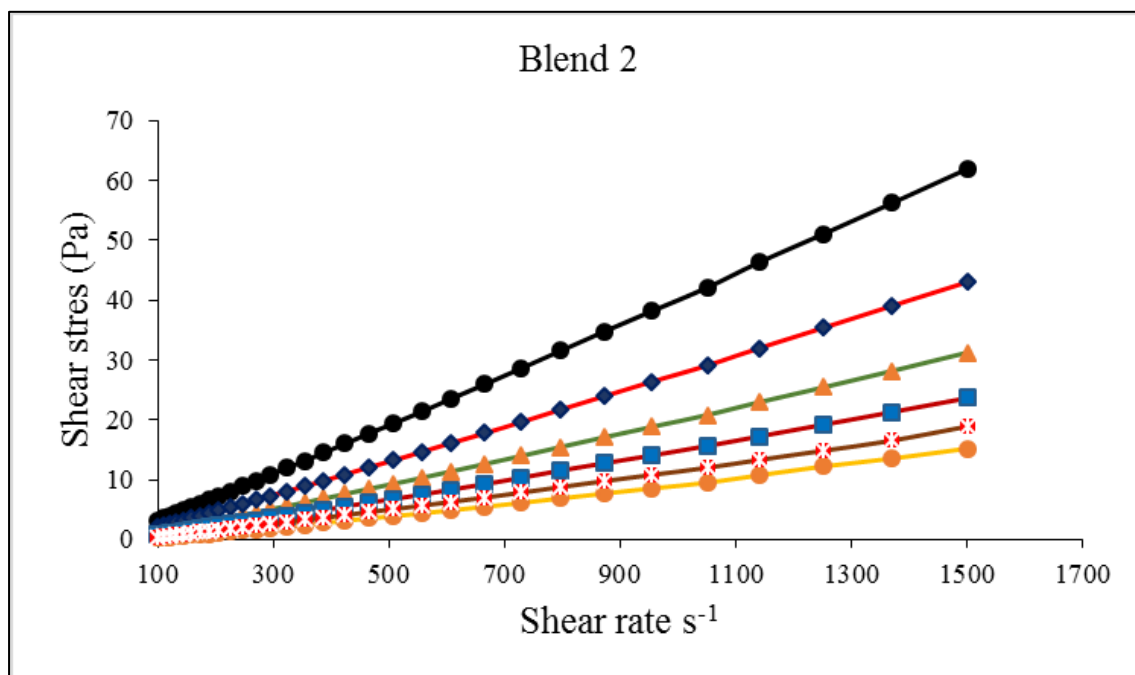


Figure 5. 20 Flow curve of fat blend 2 in a temperature range of 30°C to 80°C.

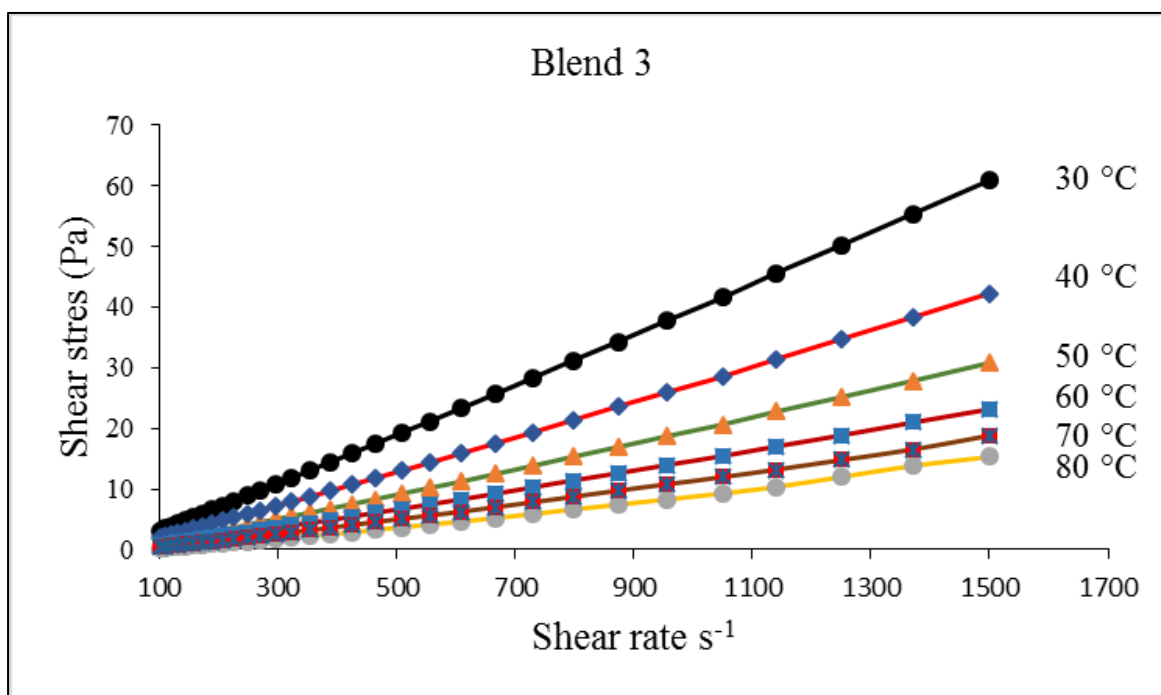


Figure 5. 21 Flow curve of fat blend 3 in a temperature range of 30°C to 80°C.

5.11 Microstructure of crystal

Fig 15.22 and Fig 15.23 show the microstructural of crystal network in two coconut oil samples and its three blends. The solid phase has a white or grey appearance while the liquid phase appears black. Some scientists proved experimentally that the cooling rate and crystallization temperature affect the rate of crystal formation.

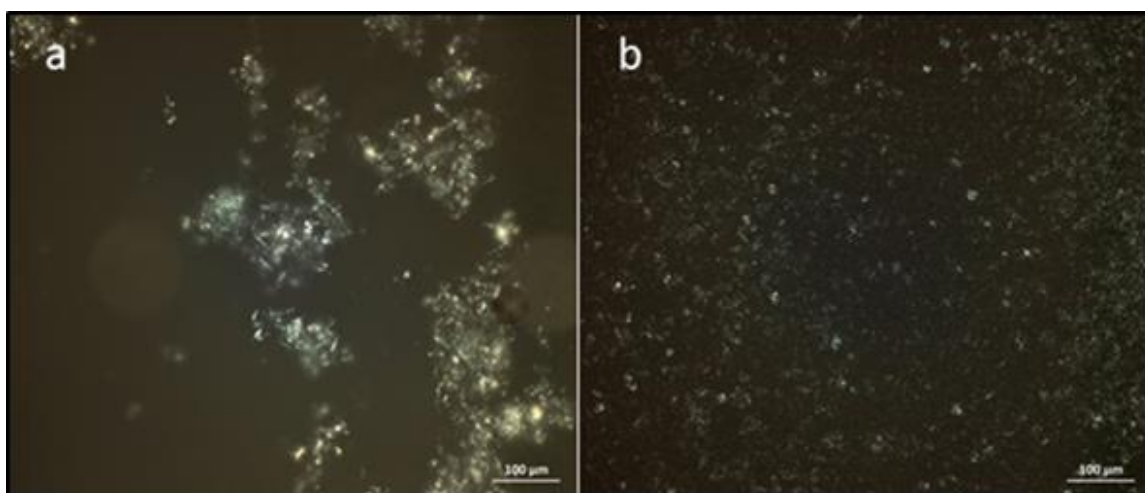


Figure 5. 22 Polarized-light microscopy images of coconut fats. (a). Non-hydrogenated coconut fat (b). Fully-hydrogenated coconut fat.

When a fat is cooled from a molten stage to a temperature below its melting point, the fat will become solid and form primary β crystals which aggregate to form clusters, resulting in the formation of a continuous three-dimensional network. Coconut oil crystals were spherulites consisting of fine needle-like crystals radiating and branching outward from densely-packed central cores. The fully hydrogenated coconut fat showed more granular crystals than the non-hydrogenated coconut oil because of its content of high-melting TAGs.

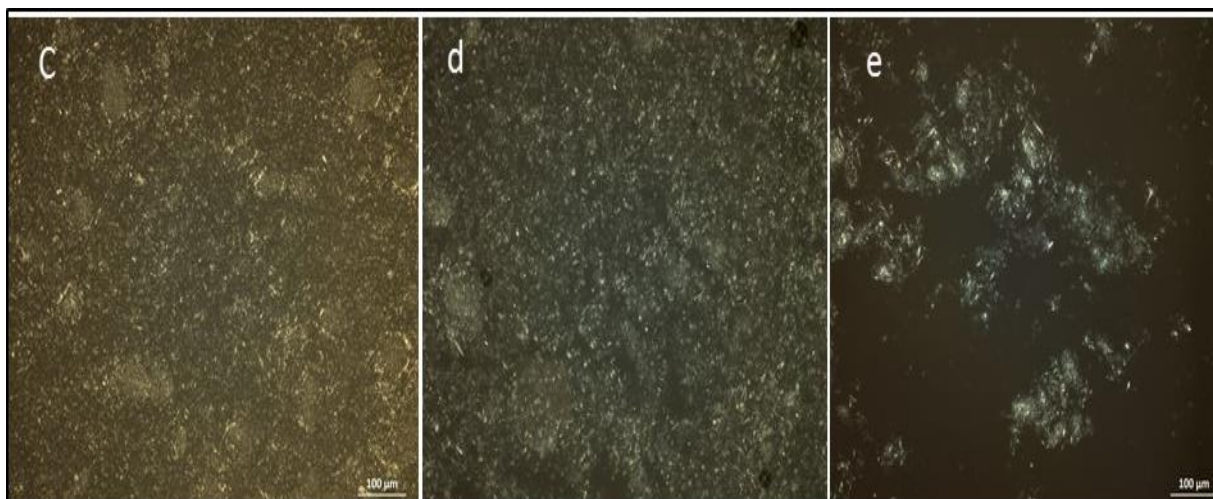


Figure 5. 23 Polarized-light microscopy images of coconut fat blends (c).25:75 (d).50:50 and (e).75:25 Non-hydrogenated coconut fat and Fully-hydrogenated coconut fat respectively.

Fig. 15.22 shows that as the percentage of non-hydrogenated coconut oil increased in the blend, there were significant changes in the crystal lattice. The crystal dispersion of fats with a large number of the small crystal can provide desirable properties such as good spreadability.

6. NEW SCIENTIFIC FINDINGS

My research experiment included mixing of non-hydrogenated and fully hydrogenated coconut fats which showed the following new scientific findings:

- The equilibrium SFC_{max} values were directly proportional to the blending ratio and temperature gradients.
- Based on the parameters of the AVRAMI model, the behaviour of solidification with instantaneous nucleation and one-dimensional focal growth was determined.
- Mixing the material did not modify the single peak on thermograph of the solid.
- The blending of fats did not change the cooling profile, whereas peak crystallization temperature increased with an increase in the proportion of fully hydrogenated coconut fat in non-hydrogenated coconut fat.
- These results proved that the addition of FHCO to NHCO at different concentrations leads to increased hardness, and therefore serves as a hardening agent.
- The rheological results proved that as the concentration of FHCO increased in NHCO, the linear viscoelastic region of rheological graphs slightly increased with an increase in relative temperature.
- The blend showed a large number of small crystals which modifies the spreadability of fats.

7. CONCLUSION

In conclusion, the blending of two different vegetable fats may be beneficial, as the modified physicochemical properties of blends can enhance their commercial food applications. The most important conclusions of our study are as follows:

- It has been demonstrated that the blends prepared in proportion of 25:75, 50:50 and 75:25 (w/w) NHCO to FHCO have positive interactions which results in the modification of melting, solidification and texture characteristics.
- The results prove that these two fats are completely miscible and the equilibrium SFC value of their blends are modified in accordance to the blending ratios and temperature gradient.
- Contrasting DSC measurements do not show any significant difference in crystallization curves of the samples. This statement is supported by the Avrami parameters too.
- DSC is dynamic and pNMR is static. A difference in the values of the solid fat indexes of samples was observed which may be due to fundamental differences between the two techniques.
- The oscillatory results show that there is a change in linear viscoelastic region, storage (G') and loss (G'') moduli with an increasing proportion of fully hydrogenated coconut fat in non-hydrogenated coconut fat.
- In rotational tests the blends show shear-thinning behaviour. The viscosity of oils and their blends are investigated at different temperatures. The Herschel-Bulkley model was fitted to flow curves (shear stress as a function of shear rate) of the samples.

- During heating, non-hydrogenated coconut oil approached Newtonian behaviour earlier than fully hydrogenated coconut oil, which indicated a more rapid viscosity change with temperature in the oils containing more double bonds due to their loosely packed structure. Thus, it indicated that the fatty acid composition affects the oils behaviour.
- The hardness, cohesiveness, chewiness and adhesiveness increase in proportion to fully hydrogenated coconut fat addition.
- The blending of fully hydrogenated coconut fat improved the elastic and textural characteristics of the non-hydrogenated coconut fat.
- Our results may be utilized in food technology, especially in the production of fat containing foods that need cooling such as the manufacturing of margarine, shortenings, and confectionary fats.

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