

Abstract

Coconut oil is one of the generally used edible fats in food industries. To modify its texture, coconut oil is frequently treated by full-hydrogenation. Since full-hydrogenation results in extremely hard fat; therefore, blending with more soft material is a good option to reach the required texture. The aim of the present study was to establish the solidification characters of the blends containing both fully hydrogenated and non-hydrogenated coconut oils. Investigations were carried out by means of pulsed nuclear magnetic resonance spectroscopy (pNMR) and differential scanning calorimetry (DSC). Solidification phenomenon was interpreted by the Avrami model. Based on the results, parameters of the Avrami model were calculated. The results proved that these two fats are completely miscible and the equilibrium SFC value of their blends modified in accordance to the blending ratios and temperature gradient. DSC measurements did not show any significant difference in crystallization curves of the samples. Our results may be utilized in food technology, especially when production of fat containing foods needs cooling, for example in the manufacturing of margarine, shortenings, and confectionary fats.

Keywords

Coconut Oil, pulsed Nuclear Magnetic Resonance, Differential Scanning Calorimeter, and Avrami Model

1 Introduction

Coconut oil is commonly used for food and industrial purposes. The oil is rich in medium chain fatty acids (MCFA) and exhibits good digestibility [11]. Coconut oil is frequently modified to produce products with high economic value [14].

Most natural oils and fats offer limited application in their unaltered state, due to their particular fatty acid and triacylglycerol composition [6]. According to Jang et al., oils and fats are modified chemically by hydrogenation to improve their plasticity and oxidation stability properties [8]. Partially hydrogenated edible fats may contain trans fatty acid isomers that are found to be nutritionally solicitous [1]. To avoid the presence of trans isomers, one of the possible solutions is to use fully hydrogenated oils because they are trans-free compounds [15]. Since full hydrogenation result in extremely hard texture, blending with more soft material is needed. Coconut oil, because of its long shelf life and melting point of 24.4 °C, is frequently used in the baking industry in western countries, being commonly treated by full-hydrogenation.

Melting and solidification of edible oils and fats are two of the most important properties for functionality in many prepared food products. In general, oils and fats exhibit complex thermal behaviour. Many of studies have investigated properties of oils and fats, the results being highly dependent on the detailed chemical composition and protocol in the experiments. The present research work was done to study the solidification of blends of fully hydrogenated coconut oil and non - hydrogenated coconut oil. This study involves the solidification curves, fitted Avrami lines, Avrami parameters and thermal behaviour.

2 Materials and methods

2.1 Materials

Fully hydrogenated coconut oil (FHCO) and non - hydrogenated coconut oil (NHCO) were provided by local industry from Budapest.

2.2 Blends preparation

The blends were prepared in the proportions of 25:75, 50:50, 75:25 (w/w%) non-hydrogenated coconut oil: fully

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hydrogenated coconut oil. 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.

2.3 Fatty acid content

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. The fatty acid content of the pure fats was given in relative percentage. Based on these results, the fatty acid content of the blends was calculated.

2.4 Solidification curves

Samples were melted (100 °C / 15 min) and kept in high precision dry bath at 80 °C for complete destruction of their crystal history [5]. The solid fat content increased in keeping with crystallization time, which was monitored by the Nuclear Magnetic Resonance spectrometer (NMR) Bruker pc 120 Minispec. Solid fat content (SFC) was measured as a function of time applying 70, 65 and 62 °C temperature gradients. Each sample tube was placed in the sample holder in the NMR equipment, with the reading compartment stabilized at 10, 15 or 18 °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 [13, 17].

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

In Eq. (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 [11]. 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.

2.5 Thermal analysis

Thermal analysis of the samples was performed by differential scanning calorimetry according to AOCS method Cj 1-94.

The equipment used was a Perkin Elmer DSC 7 thermal analyser coupled to a TAC 7/ DX Thermal Analysis Controller Cooler. The data processing software used was Pyris Series Thermal Analysis System. Samples of nearly 20 mg were loaded to the middle of the aluminium pans using small spatula and hermetically sealed with an empty pan serving as a reference. The analysis of blends and pure oil samples was performed between the 0 to 80 °C temperature interval by 1 °C/min cooling speed. The following parameters were used in evaluating the results: crystallization onset temperatures (Toc), crystallization peak temperatures (Tpc), crystallization enthalpies (ΔHc) and crystallization temperatures (Tfinal cryst) [4]. The thermal analysis was carried out in duplicate.

3 Results and discussion

3.1 Fatty acid composition

The fatty acid composition of non-hydrogenated coconut oil (NHCO), fully hydrogenated coconut oil (FHCO) and blends used for the experimental study are shown in Table 1. Dayrit reviewed that the primary fatty acid of coconut is lauric acid, which is present in the range of 45-53% [7]. For the NHCO the predominant fatty acids were lauric acid (45.8%), myristic acid (18.8%), palmitic acid (10.1%) and oleic acid (7.1%). The FHCO was high in lauric acid (53.3%), followed by myristic acid (21.3%). The percentage of unsaturated fatty acid in NHCO was around 9% but in FHCO it was smaller. A Previous research study found that coconut oil is rich in MCFA (59.7%) while deficient in PUFA (1.2%) and MUFA (6.1%) [3]. As expected, hydrogenation had reduced the level of unsaturation of the oils compared to the natural oils reported in literature.

Table 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	0.1	0.225	0.35	0.475	0.6
C8:0	1.9	3.175	4.45	5.725	7
C10:0	2.7	3.4	4.1	4.8	5.5
C12:0	53.3	51.425	49.55	47.675	45.8
C12:1	0.1	0.075	0.05	0.025	-
C14:0	21.3	20.675	20.05	19.425	18.8
C16:0	10	10.025	10.05	10.075	10.1
C18:0	10	8.25	6.5	4.75	3
C18:1 trans	0.03	0.0575	0.085	0.1125	0.14
C18:1 cis	0.3	2	3.7	5.4	7.1
C18:2 trans	-	0.02	0.05	0.08	0.11
C18:2 cis	0.1	0.5	0.9	1.3	1.7
C 20	0.1	0.1	0.1	0.1	0.1
Other	0.02	0.03	0.05	0.065	0.08

3.2 Solidification study

Solidification study of fats is highly important in order to obtain knowledge on the kinetics of phase transformation. This information helps in the optimization of their usage in industrial processing, especially when the technology requires cooling steps [18]. Crystallization kinetics deeply influences the final structure of fats and is intrinsically related to their rheological and plasticity properties.

Fig. 1, Fig. 2 and Fig. 3 show the solidification curves at 10, 15 and 18 °C respectively for non-hydrogenated coconut oil, fully hydrogenated coconut oil and for the three blends.

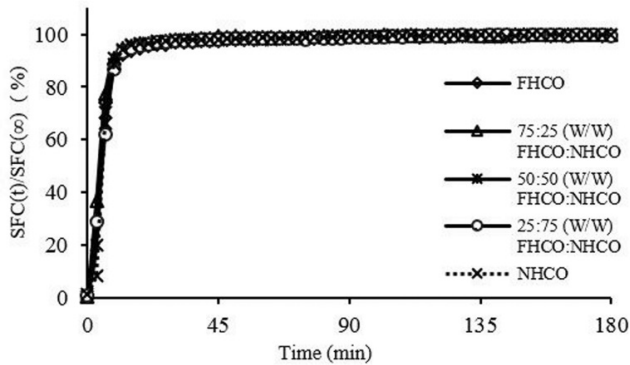


Fig. 1 Solidification curve at temperature 10 °C

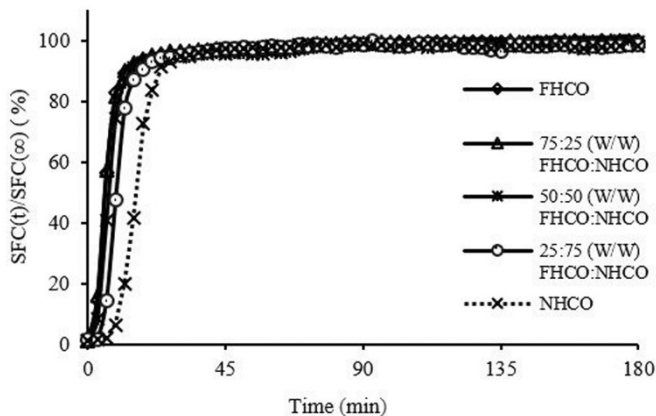


Fig. 2 Solidification curve at temperature 15 °C

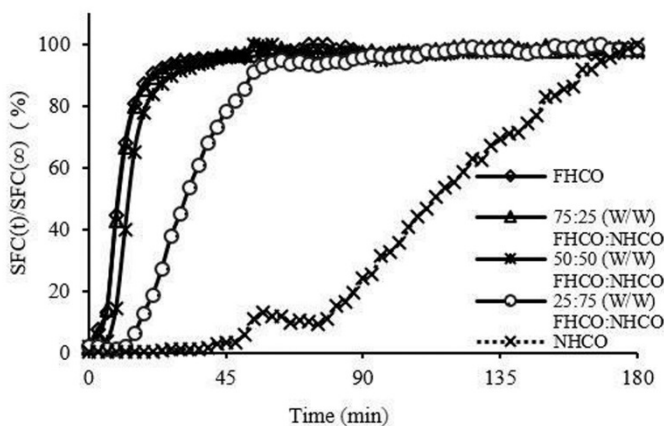


Fig. 3 Solidification curve at temperature 18 °C

Typical sigmoidal shaped curves were obtained, but as the concentration of fully hydrogenated fat increased the solidification process quickened and raised SFC_{max} . Ribeiro et al., also observed a similar effect on isotherms in the blending of fully hydrogenated soybean oil and soybean oil [14].

The analysis of the curves showed that the induction time of the crystallization decreased in parallel to increases in temperature gradients from 62 °C to 70 °C. The equilibrium SFC_{max} values 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. 1, Fig. 2 and Fig. 3 makes it apparent that at 18 °C all evaluated samples displayed longer times to attain complete crystallization equilibrium when compared to samples crystallized at 10 °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. 4, Fig. 5, Fig. 6). These straight lines were fitted to the values of $\ln[-\ln[1-SFC(t)/SFC(\infty)]]$ 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 2. 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 SFC_{max} value. Similar results were obtained additionally in the blending of fully hydrogenated cottonseed oil and canola oil [15].

In case of the high oleic sunflower oil study, fully hydrogenated soybean oil (FHSBO) induced the high SFC [10]. According to Rousseau et al, the increase of crystallization temperature promotes an effect related to formation of weaker fat crystal networks, which are reflected directly in the solid fat content [15].

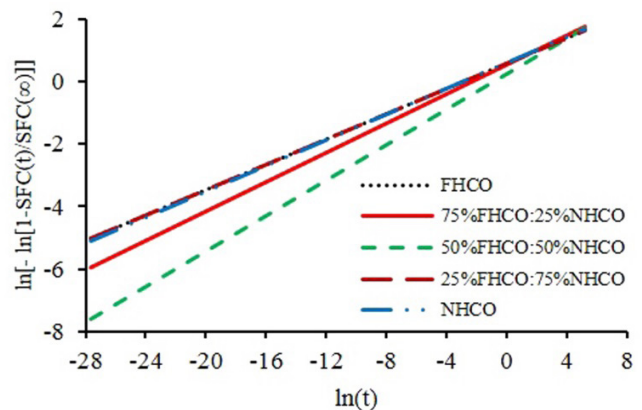


Fig. 4 Plots of $\ln[-\ln[1-SFC(t)/SFC(\infty)]]$ vs $\ln(t)$ at 10 °C

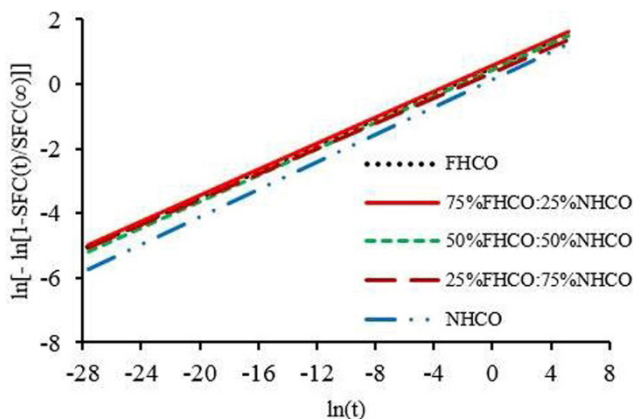


Fig. 5 Plots of $\ln[-\ln[1-SFC(t)/SFC(\infty)]]$ vs $\ln(t)$ at 15 °C

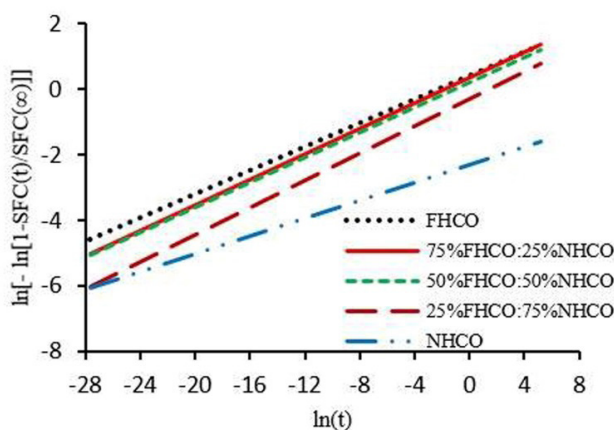


Fig. 6 Plots of $\ln[-\ln[1-SFC(t)/SFC(\infty)]]$ vs $\ln(t)$ at 18 °C

Table 2 Avrami constant (k), Avrami exponent (n), and R^2 for fat samples at different temperature

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

3.3 Thermal study

Differential scanning calorimetry (DSC) is a thermoanalytical technique for the study of oils and fats. Fat melting is an endothermic process in which the energy is absorbed, whereas crystallization is an exothermic process in which the energy is released [15]. In general, thermal behaviour of oils and fats depends on the chemical composition and on the protocol for the DSC experiment [20].

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.

Table 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	16.67
75% FHCO 25% NHCO	-76.28	14.32
50% NHCO 50% FHCO	-67.94	11.97
25% FHCO 75% NHCO	-66.82	11.55
NHCO	-62.10	11.11

Table 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 non-hydrogenated coconut fat. Same results were examined in the case of canola oil and fully hydrogenated canola oil [9]. 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, consequently the TAG structure must be more complex. This complexity results in a less-packed crystal structure and smaller equilibrium SFC, as well as less slow crystallization.

4 Conclusions

This study demonstrated the softening effect of the non-hydrogenated coconut oil. The equilibrium SFC values were modified in accordance to the blending ratio. It was also clear from this

study, that the effect of temperature gradient is greater than the effect of the mixing ratio. The DSC data showed that solidification of both fully-hydrogenated and non-hydrogenated coconut oil shows only one exothermic peak. This phenomenon indicates that the crystallization mechanism may be similar in each case. This statement is supported by the Avrami parameters too.

As a summary, we concluded that the presence of non-hydrogenated coconut oil does not modify the character of the solidification process and the type of the crystals remains the same regardless of the mixing ratio. As a conclusion, it can be stated that our results may help the optimization of unit operations in food technology.

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