Omega-3 fatty acids enriched chocolate spreads using soybean and coconut oils

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Abstract Chocolate spreads were developed by incorporating two different soybean oil margarines, fat phases prepared using 85 % soybean oil (M1) and 1:1 blend of soybean oil and coconut oil (M2) with commercial palm stearin. Eight formulations were tried by varying skim milk powder (SMP)/fluid skimmed milk (FSM), type of fats (M1, M2, a commercial margarine and a table spread), sugar and cocoa powder and their quality characteristics were compared with a commercial hazelnut cocoa spread. The moisture and fat content were 5–6.1 % and 31.4–32.8 % for formulations with SMP and 21.5–24.7 % and 15.6–21.4 % respectively for those with FSM. Rheological studies of FSM spreads showed higher G'' value (loss modulus) than G' (storage modulus) indicating better spreadability. Descriptive sensory analysis revealed that the products had acceptability score of 8.3 to 10.5 (maximum score: 15). Fat extracted from spreads prepared using M1 and M2 was found to contain 43.9 and 22.3 % linoleic acid and 2.1 and 4.4 % linolenic acid respectively, were free from trans fat while the commercial hazelnut spread had 9.8 % linoleic acid but did not contain linolenic acid. Hence, the developed chocolate spreads have the potential to overcome ω -3 deficiency, ω -6/ ω -3 imbalance and to enhance the health standard of people.

Keywords Chocolate spread · Soybean oil · Coconut oil · Omega-3 fatty acids

Introduction

Chocolate is a food product loved by many people because of its desirable qualities such as a shiny gloss on the surface, a snap when broken, a smooth texture and melt-in-mouth characteristics. These qualities are closely related to the uniqueness of cocoa butter, the fat component present in chocolates, which is hard and brittle at room temperature while melting completely at body temperature and is attributed to the presence of more than 80 % symmetrical 2-oleo-disaturated triglycerides (Talbot 1999). However, in addition to the higher cost of cocoa butter, chocolates suffer from fat bloom, a surface defect, as the fat crystals transform to unstable polymorphic form during storage and also lose the shape when stored in warm conditions. Attempts were made to increase the heat resistance of chocolates by incorporating stearic acid rich fractions into cocoa butter (Jeyarani and Yella Reddy 1999, 2001). In a recent review, Stortz and Marangoni (2011) concluded that though heat resistant chocolates could be prepared by using different methods, none of the techniques illustrated a simple, inexpensive and successful one and the quality of chocolates was lower than that of traditional chocolates.

The disadvantages in chocolates can be reduced to a certain extent by developing a spreadable chocolate which is a paste, eaten mostly as spread on breads, toasts or similar pastries such as muffins and pitas or can be consumed as such. Chocolate spreads can be formulated by utilizing soft margarines which are not very hard like cocoa butter at ambient conditions. Recently, El-Hadad et al. (2011) developed a functional chocolate spread by substituting butter fat with 20 to 100 % red palm olein and reported that the product with 20 % replacement was acceptable.

The world soybean oil (SBO) production is 38.01 MMT during 2009–10 and stands number two next to palm oil from 2003 to 2010 (Erickson 2011). The production has seen a dramatic growth as a result of its widespread availability,

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nutritional qualities, wide functionality and relatively low cost. The oil is rich in polyunsaturated fatty acids (PUFA), containing 49.8–57.1 % linoleic acid and 5.5–9.5 % linolenic acids (O'Brien 2009). These fatty acids, classified as essential fatty acids are not synthesised in the human body, hence need to be supplied through the diet.

In a clinical trial, to study the effects of ω -3 fatty acid on coronary artery diseases, 1,000 patients were examined by feeding a diet containing 1.8 ± 0.4 g of alpha linolenic acid (ALA) against a control group with 0.8 ± 0.2 g per day. After two years of follow up it was found that total cardiac events were significantly lower in the intervention group compared to the control group (Singh et al. 2002). The minimum intake levels to prevent deficiency symptoms are estimated to be 2.5 % energy contributed by linoleic acid plus 0.5 % energy by alpha linolenic acid (ICMR 2009). A joint WHO/FAO Organization committee advised the individuals to increase the dietary intake of ω -3 fatty acid in order to maintain a desirable ω -6 to ω -3 ratio (WHO/FAO 1995; ICMR 2009). Therefore, supplementation with foods rich in ω -3 fatty acids is highly beneficial.

Coconut oil (CNO) is principally composed of medium chain triglycerides (MCT) which have properties different from long chain triglycerides in their fatty acid composition, digestion, absorption and metabolic fate in the body. MCT are digested more easily and absorbed rapidly by the body than other fats (Bach and Babayan 1982; Dulloo et al. 1996). Palm stearin, a by-product of palm oil industries is highly saturated and provides natural hardness to fats. However, this texture does not provide a suitable plastic range to edible fats such as margarines and shortenings. Vegetable oils containing polyunsaturated fatty acids that are liquid at room temperature, when blended with palm stearin help to improve the fat plastic range (Jeyarani and Yella Reddy 2003) and can be an economical source for use in functional foods.

The objective of the present study was to develop a spreadable chocolate, utilizing the fat blends containing soybean oil, coconut oil and palm stearin, which can contribute to the dietary intake of ω -3 fatty acids.

Materials and methods

Soybean oil, coconut oil, table margarine, trans free table spread, a sample of hazelnut cocoa spread (HZCS) and other ingredients like sugar, skim milk powder (SMP), fluid skimmed milk (FSM), cocoa powder and vanilla essence (Bush Boake Allen Ltd., Chennai) were purchased from local market in Mysore, India. Palm stearin was obtained from a palm oil industry (KTV Health food Pvt Ltd., Chennai) and soya lecithin was from M/s Sakthi soya, Coimbatore, India. Standard fatty acid methyl esters were from M/s Sigma Chemical Co. (St. Louis, MO). Single

solution KF reagent (1 ml of the reagent = 6 mg. H_2O approximately), chloroform, methanol, toluene and other chemicals were of analytical grade from M/s Qualigens fine chemicals, Mumbai, India.

Preparation of blends The palm stearin was heated to 65 °C on a water bath and blended with soybean oil and in the ratio of 10 to 90 % levels (w/w basis) at 10 % intervals. The blended fats were again heated to 65 °C and used for further work.

Slip melting point Determination of slip melting point of blends was carried out using open capillary tubes according to standard procedure (AOCS 2003). The samples were melted and capillary tubes with thin wall and 1 mm i.d was dipped to fill fat for 10 mm height. The capillary was placed on a piece of ice to solidify the fat and then held at refrigerated temperature for about 10 h followed by holding for 1 h at 0 °C. Two capillaries were attached gently to a thermometer using a rubber band and fixed onto a Thiele tube. The side arm of the flask was heated slowly and the temperature at which the fat melts, slips and raises was noted. Quadruplicate measurements were made and average value is reported.

Response surface plots were generated for slip melting points as a function of SBO and HF. Both variables ranged between 0 and 100. An empirical relationship between response variable and input variables was constructed using a multiple regression equation by inbuilt in the statistical software—Statistics V 5.5 (StatSoft, Tulsa, OK, USA).

Preparation of margarines Based on the results of slip melting point, fat blends containing (a) 85 % SBO and (b) 85 % of SBO and CNO mixture (1:1) with 15 % palm stearin were prepared as described earlier. The two fat blends were melted separately and a fat phase containing 1 % lecithin and fat blend (80 %) was prepared. The molten mixture was gently homogenised using a mechanical stirrer and an aqueous phase containing water (16 %), salt (1 %) and SMP (2 %) was slowly added. After thorough mixing, the emulsions were transferred to a container and allowed to set overnight in a freezer. The set mixture was mixed using a spatula, coded as M1 and M2 respectively and then used in the formulation of chocolate spreads.

Preparation of chocolate spreads Two batches of chocolate spreads, A–D containing skim milk powder (Batch I-SMP) and E–H containing fluid skimmed milk (Batch II-FSM) were prepared according to the formulations provided in Table 1. The second batch using FSM was prepared according to the recipe from the literature (El-Hadad et al. 2011). Initially, the dry ingredients such as powdered sugar, milk powder and cocoa powder were sieved separately. Lecithin was added to the fat and mixed. For the preparation of Batch I-SMP, sugar and milk powder were added to the fat in a bowl and mixed. For Batch II-FSM, sugar was added

Table 1 Formulations for preparation of chocolate spreads using skim milk powder and fluid skimmed milk

Ingredients	Chocolate spread formulations (%)							
	Batch I With skim milk powder				Batch II With fluid skimmed milk			
	A	B	C	D	E	F	G	H
Soybean margarine (M1) Fat phase prepared using 85 % soybean oil	40	40	0	0	20	0	0	0
Soybean margarine (M2) Fat phase prepared using 85 % soybean oil and coconut oil (1:1) blend	0	0	40	40	0	20	0	0
Commercial margarine	0	0	0	0	0	0	20	0
Commercial table spread	0	0	0	0	0	0	0	20
Icing sugar	38	38	38	38	48	48	48	48
Skim milk powder	14	10	14	10	–	–	–	–
Fluid skimmed milk	–	–	–	–	24	24	24	24
Cocoa powder	6	10	6	10	6	6	6	6

Lecithin (1 %) and essence (1 %) were added in all formulations.

to milk, boiled, cooled in a bowl, then fat was added and mixed. Cocoa powder was added and the entire mixture was blended for 5 min using a hand blender at low speed. Vanilla essence was incorporated at the end and after thorough mixing, the products were transferred to air tight plastic containers.

Moisture Moisture content in the Batch I products was determined by Karl Fischer method using an automatic KF titrator (Make: Lasco, Chennai, India) and that of Batch II products was determined by toluene distillation method (AOAC 2005).

Fat Fat content of products was determined by Roese-Gottlieb method (AOAC 2005) by extraction using petroleum ether and diethyl ether.

Colour measurement Colour of the products was measured by a colour measuring system with a UV filter (Hunter Associates Laboratory Inc., Reston, Virginia, USA) in CIE scale at a view angle of 10°. Different parameters such as L^* , a^* , b^* and ΔE were measured. L^* indicates lightness, positive value for a^* indicates red and negative value indicates green colour, similarly positive value for b^* indicates yellow and negative value indicates blue colour. The ΔE indicates the total colour difference in a sample. All the measurements were performed in triplicate and the average value is reported.

Texture analysis Hardness of Batch I-SMP products was evaluated at 25 °C using a TA-HDi texture analyser (Stable Microsystems, Surrey, UK). A cone probe of 30° angle was used to penetrate the spread samples to a depth of 10 mm. The cross head speed was maintained at 100 mm/min and

peak force was recorded in Newtons (N). An average of four readings was taken and reported as hardness.

Dynamic rheological measurements Dynamic rheological measurements of Batch II-FSM products were done according to Mariotti et al. (2009). It was performed with a universal stress rheometer SR5 (Rheometric Scientific Inc, Piscataway, NJ, USA) at 25 °C using parallel plate system (2.5 cm dia) at a gap of 1 mm. The sample was loaded between the plates, and the dynamic shear data was obtained from frequency sweeps over the range of 0.1–20 Hz at a constant stress of 10 Pa. Rheological parameters G' (storage

Fig. 1 Response surface of slip melting point (SMP) as a function of soybean oil (SBO) and palm stearin (HF)

Table 2 Physico-chemical characteristics of the chocolate spreads

Formulations ^a	Moisture(%)	Fat (%)	CIE colour parameters			
			L*	a*	b*	ΔE
A	5.0±0.68 ^b	32.8±0.62 ^c	16.3±.035 ^d	7.8±0.21 ^b	7.3±0.18 ^b	75.2±0.75 ^c
B	6.1±0.54 ^b	32.7±0.25 ^c	12.8±0.42 ^b	5.8±0.32 ^a	5.2±0.14 ^a	78.3±0.42 ^d
C	5.3±0.47 ^b	31.4±0.74 ^c	19.3±0.36 ^c	8.3±0.24 ^b	8.5±0.20 ^b	72.3±0.32 ^b
D	5.0±0.42 ^b	31.7±0.43 ^c	14.7±0.44 ^c	7.8±0.45 ^b	6.9±0.15 ^b	76.7±0.56 ^c
E	21.5±1.26 ^c	15.6±0.23 ^b	12.0±0.33 ^b	12.3±0.36 ^c	13.3±0.54 ^f	79.3±0.71 ^d
F	23.0±1.45 ^c	15.6±0.31 ^b	12.4±0.52 ^b	9.3±0.52 ^c	9.1±0.31 ^c	78.8±0.62 ^d
G	24.7±1.64 ^c	15.8±0.22 ^b	16.7±0.58 ^d	12.1±0.46 ^c	15.3±0.48 ^e	76.3±0.74 ^c
H	23.6±0.78 ^c	13.7±0.45 ^a	11.3±0.24 ^a	11.8±0.44 ^d	12.3±0.44 ^d	79.9±0.85 ^d
HZCS	2.3±0.34 ^a	30.6±0.86 ^c	25.7±0.86 ^f	7.7±0.32 ^b	10.6±0.32 ^b	66.3±0.54 ^a

L*: lightness/darkness; ± a*: red/green; ± b*: yellow/green

Means in a column with different superscripts differ significantly at $p \leq 0.05$ by DMRT ($n=3$)

^a Refer Table 1 for formulations A–H; HZCS: Commercial hazelnut cocoa spread

modulus) and G'' (loss modulus) were determined for each sample. Triplicate measurements were made and the average values are reported.

Sensory analysis Sensory evaluation of the products was performed in a room especially equipped for sensory analysis by a pool of ten trained panellists. The samples were coded and presented to the assessors in a balanced random order, one sample at a time. The evaluation was performed in individual booths under fluorescent light. The samples were coded and served to the panellists along with breadsticks. Water was provided to cleanse their palate. The panellists were asked to rate on various sensory attributes of the spreads on a descriptive scale of 0 to 15 by marking 1 for low and 15 for high (Stone and Sidel 1998).

Fatty acid composition About 150–200 mg of the samples was taken in a test tube, 3 mL hexane was added and treated with methanolic KOH. The mixture was shaken vigorously in a cyclo mixer (M/s Remi Equipments Ltd, Mumbai, India) and allowed to settle (AOCS 2003). The upper hexane layer was dried using anhydrous sodium sulphate and analyzed using Fisons gas chromatograph (GC-8000 series), equipped with a flame ionization detector attached to CR-4A data processor, operating under the following conditions: fused silica capillary column: SP 2340; 30m×0.25 mm (Supelco, Bellefonte, PA) Detector; FID; column temperature: 180 °C; injector temperature: 220 °C; detector temperature: 240 °C; carrier gas: Nitrogen at a flow rate of 1 ml/min; Splitless injector. The peaks were identified by comparing the retention time with authentic standards and reported as relative percentage of individual fatty acids. Three injections were made and the average value is reported.

Statistical analysis Statistical analysis was done using Duncan's New Multiple Range Test (DMRT) with three replicates each (Duncan 1955). The significant level was established at $P \leq 0.05$.

Results and discussion

Slip melting point Fats with higher slip melting point leave a waxy mouth feel and are not suitable for use in foods while those with lower slip melting point are too soft. The slip

Fig. 2 Sensory profilograms of chocolate spreads with (a) skim milk powder and (b) fluid skimmed milk. Refer Table 1 for formulations A–H ($n=10$ panellists); HZCS: Commercial hazelnut cocoa spread

melting point is an essential parameter under legal requirements of India (FSSAI 2010). In order to find a suitable blend, a response surface was constructed as a function of slip melting point of the fat blends containing 10 to 90 % SBO with palm stearin (Fig. 1). Accordingly, the blend with 85 % SBO having slip melting point of 37.8 °C was selected. Because of the nutritional benefits of CNO, 50 % SBO was replaced with CNO and the slip melting point of the product, was found to be 33 °C. The lower melting point may be due to the softening effect caused by the formation of eutectics. The molecular size difference between lauric and other vegetable oils form the eutectic mixture (Timms 1985).

Physico-chemical characteristics The moisture and fat content of a commercial hazelnut cocoa spread (HZCS) was

found to be 2 and 30.6 % respectively (Table 2). Initial trials were conducted to obtain products containing about 30 % fat, thereby, four formulations (A–D) were prepared using skim milk powder. The moisture content of these spreads ranged from 5 to 6.1 % and the fat content from 31.4 to 32.8 % (Table 2). The spreads made using fluid skimmed milk (E–H) were found to have higher moisture content of 21.5–24.7 % which may be due to the higher moisture present in milk and also the lower fat content of 13.7 to 15.8 % of the products (Table 2). There was no mention about these parameters in the chocolate spreads formulated by replacing butter with red palm olein oil (El-Hadad et al. 2011).

Colour measurements It can be seen from Table 2 that in products made from skim milk powder, samples A and C had

Fig. 3 Rheograms of chocolate spreads prepared using fluid skimmed milk. Refer Table 1 for formulations E–H; HZCS: Commercial hazelnut cocoa spread

a lighter colour (L^* value of 16.3 and 19.4, respectively) than their counterparts B and D (L^* value of 12.8 and 14.7, respectively). This may be attributed to the presence of higher quantity of milk powder and lower quantity of cocoa powder compared to the latter. The total colour difference for HZCS sample was 66.3 while all the experimental spreads had ΔE value ranging between 72.37 and 79.35 similar to the ones prepared using commercial fats such as table margarine and table spread (76.35 and 79.94).

Texture analysis Texture measurements of spreads indicated that sample C (17.2N) had the highest hardness followed by sample D (10.9N). Both the spreads were prepared from M2 while the spreads with M1 were too soft as indicated by low values of hardness (0.8 and 1.2N). The resultant hardness in M2 can be attributed to the presence of CNO in the margarine used for the preparation of the spreads C and D.

Sensory evaluation The sensory evaluation of Batch I-SMP (Fig. 2a) samples revealed that the products were grainier, had lower spreadability and smoothness. The spreads prepared with fluid skimmed milk (Batch II-FSM) showed improved spreadability and smoothness with a maximum score of 8.4 and 9.5 respectively (Fig. 2b). The graininess was reduced and the overall acceptability was better (maximum score of 9.9) for the Batch II-FSM spreads than the ones with SMP (maximum score of 8.5). According to Kok et al. (1999), small but statistically significant differences existed in the sensory properties such as spreadability, graininess, and waxiness between the commercial and blended

margarines at 4.5 °C. Ribeiro et al. (2009) reported that the use of interesterified blends of SBO and fully hydrogenated SBO displayed characteristics suited for various applications such as liquid shortening, table margarine and all-purpose shortenings.

Rheological measurements While studying different approaches to increase the liquid continuous fat phase of butter, it was found that the dispersed phases consisting of fat crystals, water droplets and air bubbles played a role in rheology (Foley 1978). The rheological studies of the samples showed that the chocolate spreads E, F and H made using M1, M2 and commercial table spread have dominant elastic properties rather than the viscous ones. They showed a weak viscoelastic liquid property with the loss modulus (G'') higher than the storage modulus (G') like HZCS throughout the measured frequency range (Fig. 3), indicating better spreadability. This was similar to the results of melted fats in which rheology of three fat blends was studied (Bell et al. 2007). In the case of spread G, prepared using commercial table margarine, the storage modulus (G') was greater than the loss modulus (G''). Both moduli (G' , G'') showed the characteristic frequency dependency associated with essentially “liquid” behaviour (Ferry 1980).

Fatty acid composition The fatty acid profile of fat extracted from spreads of Batch II prepared using fluid skimmed milk (E–H) which had better sensory score compared to those prepared using skim milk powder was studied (Table 3). The experimental spreads E and F contained 43.9 and 22.3 % linoleic acid and 4.4 and 2.1 % linolenic acid respectively. In

Table 3 Fatty acid composition of fat extracted from chocolate spreads

Fatty acids (relative %)		Chocolate spread formulations ^a				
		E	F	G	H	HZCS
Caprylic acid	C8:0	0	1.6±0.11 ^b	1.5±0.07 ^b	0.3±0.02 ^a	0
Capric acid	C10:0	0	1.3±0.11 ^c	0.6±0.07 ^b	0.3±0.02 ^a	0
Lauric acid	C12:0	0	19.8±1.34 ^d	7.4±0.12 ^c	5.3±0.16 ^b	3.5±0.08 ^a
Myristic acid	C14:0	0.3±0 ^a	6.9±0 ^e	3.3±0.06 ^d	2.6±0.09 ^c	1.5±0.11 ^b
Palmitic acid	C16:0	19.8±1.22 ^a	19.8±0.83 ^a	45.5±1.26 ^d	40.6±1.28 ^c	31.0±1.05 ^b
Stearic acid	C18:0	4.8±0.46 ^b	4.1±0.37 ^a	5.2±0.14 ^{bc}	5.6±0.54 ^c	3.8±0.42 ^a
Elaidic acid	tr C18:1	0	0	4.5±0.06	0	0
Oleic acid	C18:1	26.8±1.20 ^b	22.0±1.75 ^a	27.8±0.15 ^d	36.2±1.23 ^c	50.4±1.77 ^d
Linoleic acid	C18:2	43.9±1.42 ^d	22.3±0.82 ^c	3.8±0.02 ^a	8.9±0.21 ^b	9.8±0.31 ^b
Linolenic acid (ω-3 fatty acid)	C18:3	4.4±0.23 ^b	2.1±0.19 ^a	0	0	0
Saturated fatty acids		24.9	53.5	63.5	54.7	39.8
Unsaturated fatty acids		75.1	46.4	36.1	45.1	60.2
Monounsaturated fatty acids (MUFA)		26.8	22.0	32.3	36.2	50.4
Polyunsaturated fatty acids (PUFA)		48.3	24.4	3.8	8.9	9.8

Means in a row with different superscripts differ significantly at $p \leq 0.05$ by DMRT ($n=3$)

^a Refer Table 1 for formulations E–H; HZCS: Commercial hazelnut cocoa spread

the chocolate spread F, there was 19.8 % lauric acid, a medium chain fatty acid, which is a source of disease fighting fatty acid derivative, the monolaurin having antiviral, antibacterial and antiprotozoal properties (Senanayake and Shahidi 2007). The major fatty acid in spread G prepared using commercial margarine was palmitic acid and contained 4.5 % trans fat which are known to produce adverse effects on coronary heart diseases (Mozaffarian et al. 2009). The sample H prepared using commercial trans free table spread contained higher amount of palmitic acid (40.6 %) and lower content of linoleic acid (8.9 %) compared to the experimental spreads. The commercial sample, HZCS was rich (50.4 %) in monounsaturated fatty acid, the oleic acid, which is the major fatty acid (78.8 %), reported for hazelnuts (Koyuncu et al. 2005). Thus, compared to the commercially available cocoa spread, and the spreads prepared using commercial fats, the developed spreads incorporating SBO margarines are rich in essential fatty acids, and can contribute to the dietary intake of ω -3 fatty acids to maintain the ω -6/ ω -3 fatty acids imbalance according to the recommendations of various health agencies.

Conclusion

Cocoa based spreads containing ω -3 fatty acids were prepared using SBO margarines (fat phase containing 85 % soybean oil and 50 % soybean oil replaced using coconut oil). Sensory evaluation showed that the spreads had acceptability of 8.3 to 10.5 on a scale of 15.0 among the consumers. The developed spreads are ready-to-eat and there is no involvement of heat treatment in the processing thus protecting the heat sensitive ω -3 fatty acids. Optimized chocolate spread formulations can provide consumers with an alternative flavored product and can help in maintaining ω -6/ ω -3 fatty acids imbalance.

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