Polymorphic Behavior of Some Fully Hydrogenated Oils and Their Mixtures with Liquid Oil

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Fully hydrogenated soybean oil, beef fat, rapeseed oil, a rapeseed, palm and soybean oil blend, cottonseed oil and palm oil were characterized by fatty acid composition, glyceride carbon number and partial glyceride content, as well as melting and crystallization properties. The latter were established by differential scanning calorimetry. Polymorphic behavior was analyzed by X-ray diffraction of the products in the flake or granulated form and when freshly crystallized from a melt. The hard fats were dissolved in canola oil at levels of 20, 50 and 80% and crystallized from the melt. Palm oil had the lowest crystallizaton temperature and the lowest melting temperature; rapeseed had the highest crystallization temperature and soybean the highest melting temperature. All of the hard fats crystallized initially in the α form. When diluted with canola oil, only palm oil was able to maintain β' stability.

Fully hydrogenated oils, also called hard fats or stearins, are used in shortenings, bakery-type margarines, frying oils and peanut butters. In the shortening industry the hard fats are also referred to as "plasticizers" and their main purpose is to extend the shortenings' plastic range (1). The addition of hard fats affects the SFI values of the shortening base oils more at high temperatures than at low temperatures (2) because of the high melting point of the hard fats. In all-purpose and emulsified shortening it is essential that the hard fat crystallizes in the β' form as the entire solids of the rest of the fat will also crystallize in the β' form (3). The small β' crystals contribute to the creaming ability. Hard fats in bakery margarines are incorporated for the same purpose. Pourable frying shortenings require a β' form hard fat (1). Beta crystals are desirable as their physical dimensions prevent the crystals from settling. In peanut butter, hard fats are incorporated to prevent the formation of an oily layer on the surface and to give the peanut butter a glossy appearance (2). A β' fat is also required in this case. Wiedermann (3) has grouped some common fats according to their crystal habits. In general, the more diverse the triglyceride structure of the highest melting portion of the fat, the lower the β forming tendency (4).

The purpose of this study was to examine six commonly used hard fats for their polymorphic behavior alone and in dilution with a liquid oil.

MATERIALS AND METHODS

The six fully hydorgenated oils were obtained from commercial suppliers, and included soybean oil, beef fat, rapeseed oil, a rapeseed oil blend with palm oil and soybean oil, cottonseed oil, and palm oil.

Fatty acid composition was determined by gas-liquid chromatography of the methyl esters (5), using a flame ionization detector and a packed column, 10% SP2330 on 100/200 mesh chromosorb AW (Supelco), 2 m length, operated at 170°C.

Analysis of trigycerides by carbon number was carried out by the gas-liquid chromatographic procedure of Shehata *et al.* (6).

Partial glycerides were determined by gas-liquid chromatography as described by Goh and Timms (7). The polymorphic forms of the fats were established by X-ray diffraction analysis as described by Yap *et al.* (8).

Dropping points were determined with the Mettler FP3 automatic dropping point apparatus (9). Melting and cooling curves were recorded by differential scanning calorimetry using a DuPont model 900 thermal analyzer. Cooling and heating rates were 5°C/min. The crystallization point was taken as the temperature at the start of the exothermic deflection. Sample size was 10 mg.

RESULTS AND DISCUSSION

The fatty acid composition of the fully hydrogenated oils is listed in Table 1. The triglyceride composition and the mono- and diglyceride content are displayed in Table 2. Because the fatty acid content of palm, cotton and soybean oils consisted mainly of 16 and 18 carbon fatty acids, it can be concluded that the triglycerides of 48 and 54 carbons (C_{48}, C_{54}) in Table 2 consisted mainly of tripalmitin and tristearin. In palm oil the triglyceride of 50 carbon atoms consisted mainly of PSP with small amounts of PPS and SPP. In Palm oil the 2-position of the glycerides contains approximately 13.5% of palmitic acid (10). Palm oil contains a high percentage of POP (11) which becomes PSP upon hydrogenation. In cottonseed oil PPS prevails upon hydrogenation (12). The 16:0 fatty acid in soybean oil is exclusively located in the 1- and 3-positions (13) and therefore PSP prevails. In beef fat 12% of the total of 28% of palmitic acid is in the 2-position. After hydrogenation, PPS and PSP are present in equal

TABLE 1

Fatty Acid Composition of Fully Hydrogenated Oils (%)

Fatty acid	Hard fats					
	Soybean	Beef fat	Rapeseed	Rapeseed blend	Cottonseed	Palm
12:0		0.2	0.3			0.4
14:0	trace	3.4	0.2	0.3	0.7	1.1
14:1[1]		1.1				
16:0	10.6	27.3	6.3	14.5	22.3	42.6
16:0[1]		3.0				
18:0	88.6	63.1	48.1	53.1	76.2	54.3
18:1	trace	1.2	4.4		trace	0.8
20:0	0.6	0.7	6.7	5.2	0.4	0.5
22:0	0.3	0.1	34.0	26.7	0.1	

[1]Including odd numbered and branched fatty acids.

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TABLE 2

Triglyceride Composition (%) and Mono- and Diglyceride Content of Fully Hydrogenated Oils (%)

Carbon number	Hard fats					
	Soybean	Beef fat[1]	Rapeseed	Rapeseed blend	Cottonseed	Palm
44		0.2				
46		1.4		0.1		0.5
48	0.2	7.5		3.4	0.9	6.4
50	3.3	21.0	1.6	8.8	13.6	40.0
52	27.6	44.9	11.6	15.2	43.5	41.9
54	66.7	24.5	28.3	25.9	40.5	10.7
56	1.7	0.4	6.7	6.2	1.3	0.4
58	0.5		6.8	7.2		
60			12.3	9.0		
62			31.9	23.6		
64			0.8	0.8		
Mono	0.4	0.1	0.5	0.5	0.3	0.9
Di	3.6	2.0	3.7	4.4	5.8	8.2

[1]Glycerides contain odd numbered and branched fatty acids.

TABLE 3

X-ray Diffraction Short Spacings of Fully Hydrogenated Oils in the Flake or Grain Form

Product	Short Spacing Å						
Soybean[1]	5.31W	5.18W	4.53VS			3.97W	3.81VS
Beef fat					4.13–4.11VS[2]		3.80VW
Rapeseed			4.56S		4.28–4.12VS[2]		3.78S
Rapeseed blend					4.10S		3.78S
Cottonseed			4.57VW		4.25–4.13VS[2]		3.81S
Palm				4.32M	4.16S		3.80M

[1]Also 5.02VW, 4.81VW, 354VW and 3.41VW, 3.65VS.

[2]Extended shadow which indicates mixtures of α and β'.

α major short spacing = 4.1

β' major short spacings = 4.2 and 3.8

β major short spacing = 4.6

Indication of band intensities:

S = strong, M = medium, W = weak, V = very

amounts (14). In palm oil, cotton, soya and beef fat the triglycerides of 52 carbons consist mainly of SSP or PSS (11–14). It is more difficult to estimate the triglyceride content of the rapeseed oils because more than two fatty acids are involved. The erucic acid is mainly located in the external positions of the triglyceride molecule (12). Palm oil contained the highest level of mono and diglyceride (Table 2).

The polymorphic forms and the short spacings of the fully hydrogenated oils as received from the manufacturer are displayed in Table 3. Only soy stearin was exclusively in the β form. All of the others were mixtures of α, β', and β polymorphic forms. Therefore, only soy stearin is applicable, when ground up and homogenized, in pourable frying shortening. The major short spacing of the α form is 4.1 Å, that of the β' is 4.2 and 3.8 Å of almost equal intensity. It is difficult to distinquish between 4.1 and 4.2 Å. Very often there is a shadow that extends—e.g. from 4.23 to 4.13 Å—as is the case in cottonseed in Table 3. If β' crystals are present, it will show up in the short spacing of approximately 3.8 Å. Crystals of the β polymorphic form are identified by the spacing of 4.6 Å. Unfortunately β crystals also display short spacings at 3.8 Å. Timms reviewed short spacings of the different polymorphic forms (11). The intensity at 3.8 Å of the β form is usually much less than that at 4.6 Å. The exception is that of the short spacings of soybean flakes in Table 3 which exhibited numerous diffraction lines except for the short spacing at 4.2 Å which is typical for β'. When the hard fats were melted at 90°C and then quickly cooled at 0°C in 1 cm diameter tubes to assure quick heat transfer, all hard fats except rapeseed crystallized in the α form with short spacings at 4.1 Å only. Rapeseed showed additional short spacings at 3.8 Å of medium and 4.56 Å of weak intensity indicating the presence of all forms. After six weeks of storage at 23°C, only the beef fat showed an additional short spacing at 3.8 Å. All other hard fats remained unchanged. The DSC melting thermograms exhibited three endothermic peaks and one exothermic peak for soy, two endothermic and two exothermic peaks for beef fat, cotton and palm while rapeseed and rapeseed blend exhibited only two

TABLE 4

DSC Melting Characteristics of Hard Fats and Hard Fats Mixed with 20% Canola Oil, Crystallized at 0°C and Stored at 23°C

Product	Peak temperature (C)				
	Hard fats				Hard fats and Canola oil
	Exothermic	Endothermic			Endothermic
Soybean	60	56	66	71	71.5
Beef fat	55	52		66	63.5
Rapeseed			60	65	63.5
Rapeseed blend			59	64	64
Cottonseed	55	53		66	66
Palm	54	52		62	61

TABLE 5

Crystallization and Melting Temperature by DSC and Mettler Dropping Point of Fully Hydrogenated Oils

Product	Dropping point °C	DSC-melting of flakes °C	Crystallization temp. °C
Soybean	70.1	73.5	53.5
Beef fat	63.6	65.5	49.5
Rapeseed	65.6	65.4	57.0
Rapeseed blend	63.8	64.8	55.5
Cottonseed	65.3	66.5	51.5
Palm	61.9	62.0	49.0

endothermic peaks. The peak temperatures are displayed in Table 4. An exothermic peak signifies a polymorphic transition and shows up above the baseline. A polymorphic transition can also occur without an exothermic peak. In this case the endothermic peak will be split. Not sufficient heat is evolved during the polymorphic transition for the peak to appear above the baseline. It should be kept in mind that separate endothermic peaks do not necessarily mean a polymorphic transition. A fat may consist of high and low melting components. The last endothermic peak can be compared with the melting point. Table 5 shows the temperatures of the melting peak of the commercial flakes which are comparable to those of the last melting peaks of the quickly cooled fats in Table 4. The Mettler dropping points are also very close to the temperatures of the DSC melting peaks (Table 5). Fully hydrogenated oils contain 100% solids at 23°C. Once crystallized there is little room for movement of the crystals because no liquid oil is present. For this reason the hard fats were mixed with canola oil. Canola oil was chosen as it stays liquid at 0 °C. Mixtures were prepared at the following levels: 80, 50 and 20% of hard fats in canola oil. The mixtures were heated at 85°C and then quickly cooled in 1 cm diameter tubes to 0°C. The 80 and 50% mixtures were transferred after 1.5 hr at 0°C to a 23°C incubator and the 20% mixtures were left at refrigerator temperature. The 80 and 50% mixtures (Table 6) were mainly in the β form (short spacing 4.6 Å). Rapeseed and palm oil were the only ones that showed β' crystallinity (4.2 Å) with palm oil showing more β' than rapeseed. More short spacings appeared in the 50% mixtures. The significance of the additional spacings cannot at present be explained. Yap (15) examined the polymorphic behavior of mixtures of palm oil and hydrogenated canola oil during temperature cycling and observed that the short spacings became more numerous with cycling time. In this study they become more numerous with dilution.

Of of the 20% mixtures that were stored at refrigerator temperature only palm hard fat showed 100% β' crystallinity and cottonseed showed a mixture of β' and β (Table 5).The cottonseed short spacings were 4.2 Å(S) and 4.57 Å(M) representing the β' and β form respectively.

Palm hard fat was the most stable β' fat. This may be explained by its unique composition, its balanced C48–C54 content with an equally balanced C50–C52 content (Table 1, 2). Palm oil also contains the highest amount of palmitic acid which is distributed mainly between the 1, 3-positions of the triglyceride molecule. The greater diversity of fatty acids in the rapessed hard fats did not enhance their β' polymorphic stability. Another reason for the β' stability of palm oil may be in its mono- and diglyceride content which was the highest of all of the hard fats. Hernqvist (16) reported that diglycerides stabilize the β' crystals in margarines and fats. Palm hard fat also had the lowest melting temperature and the lowest crystallization temperature (Table 5).

In the shortening industry palm hard fat is incorporated at levels of 10 to 12% to give a solids content at room temperature of 16% (3). In spite of the fact that these shortenings are tempered at about 30°C they maintain β'

TABLE 6

X-ray Diffraction Short Spacings of Blends of Fully Hydrogenated Oils in Canola Oil crystallized at 0°C and stored at 23°C or 4°C

Product	Short spacings (Å)									
Hard fats with 20% canola oil (23°C)										
Soybean	5.31W	5.20W	4.55VS				3.97W	3.83M		3.67M
Beef fat	5.34VW		4.56VS					3.83W		3.70M
Rapeseed	5.33W		4.56VS			4.15W		3.88M		3.67M
Rapeseed blend	5.31W		4.60S					3.88M		3.69M
Cottonseed	5.35W		4.56S				3.97W	3.85S		3.69S
Palm			4.55M		4.30W	4.17S			3.78S	
Hard fats with 50% canola oil (23°C)										
Soybeans	5.36M	5.26W	4.57VS	4.47W			3.98M	3.85S		3.70S
Beef fat	5.36M	5.26W	4.57VS	4.47W			3.98M	3.85S		3.70S
Rapeseed	5.34M	5.21W	4.57S			4.13M		3.86M		3.70M
Rapeseed blend	5.34M	5.21W	4.57S					3.86M		3.70M
Cottonseed	5.35M	5.24W	4.56S	4.46W			3.99W	3.84S		3.69S
Palm			4.57M		4.33M	4.18S	4.02W		3.79S	
Hard fats with 80% canola oil (4°C)										
Soybean	5.36VW		4.55VS				3.98VW	3.84M		3.67M
Beef fat	5.36VW		4.57VS					3.84M		3.69M
Rapeseed	5.30VW		4.55VS					3.86VW		3.70VW
Rapeseed blend			4.56VS					3.85M		3.66M
Cottonseed			4.57M		4.35W	4.20S			3.78S	
Palm					4.29W	4.18S	4.03W		3.75S	

β' major short spacings = 4.2 and 3.8

β major short spacing = 4.6

Indication of band intensities: S = strong, M = medium, W = weak, V = very

crystallinity. It would be important to analyze the solids in these shortenings to compare their polymorphic behavior with the hard fats analyzed in this study. The possibility that the liquid phase has an effect on the polymorphism of the solid phase needs further investigation.

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