EFFECT OF PALM STEARIN AND HYDROGENATED PALM OIL ON THE

PODYMORPHIC

STABILITY

OF HYDROGENATED CANOLA OIL

Keywords:

Palm stearin; Polymorphic stability; Hydrogenated palm oil; Hydrogenated canola oil; Crystallization

C.F. SHEN, L. DEMAN* and J.M. DEMAN
Department of Food Science University of Guelph
Guelph, Ont. Canada NIG 2W1

Permanent address: * Fujian Research Institute of Light Industry, Fuzhou, People's Republic of China

ddition of palm stearin (fractionated) at a level of 10%, or, hydrogenated palm oil of dropping point 42°C at a level of 15%, to hydrogenated canola oil in a stick margarine formulation was effective in delaying the polymorphic transition from the β' to B crystallinity of the solids. Addition of 15% hydrogenated palm oil of dropping point 42°C was slightly more effective. The delaying effect is thought to be due to the tripalmitin and the solid 50-carbon triglyceride content of the palm products, which counteract the homogeneity of the 54-carbon triglycerides of the solids in hydrogenated canola oil. Crystallization characteristics were determined by differential scanning calorimetry (DSC). A soyabean stick margarine was included for comparison. Compositions of suggested formulations are presented.

INTRODUCTION

ydrogenated canola oil is widely used in various food products such as margarines and shortenings. The canola cultivar which was developed from rapeseed is low in erucic acid and glucosinolates. It is well documented that hydrogenated canola oil has a tendency to recrystallize from the β' to β polymorphic form owing to its triglyceride homogeneity (it has about 95% of 18-carbon fatty acids) (Hernqvist et al., 1981; Weinberg, 1972; Lee and deMan, 1984; Naguib Mostafa and deMan, 1985; deMan et al., 1985; Moziar et al., 1989). The beta crys-

⁺deMan Food Technology Services Inc. Guelph NIH 6B5.

tals can grow into large needle-like agglomerates which make the products gritty and crumbly. One way in which the beta crystal formation can be delayed is by the addition of palm oil (Yap et al., 1989b). Palm oil has a high content of 16-carbon fatty acids (44% palmitic acid) and is a beta prime tending fat (Yap et al., 1989a). When palm oil is mixed with canola oil the homogeneity of the fatty acid chain length is reduced, which promotes β' crystalline stability. Beta prime crystals are small crystals which contribute to the smoothness of the margarines. In shortening, the small crytals aid in the aeration of cakes.

Yap et al. (1989b) studied the polymorphic behaviour of hydrogenated canola oil with different levels of added palm oil. They also studied the effect of different levels of palm oil added to canola oil before hydrogenation. (The palm oil was then also partially hydrogenated). They found that for a formulation with similar SFC curves to those of stick (packet) margarines the level of palm oil addition should be at least 15%; when palm oil is added before hydrogenation the level should be at least 10% for improved polymorphic stability.

In the study reported here the effect of fractionated palm stearin on the polymorphic stability of hydrogenated canola oil was investigated. In the study of Yap et al. (1989b) the palm oil was hydrogenated along with the canola oil; however, the extent of the hydrogenation of palm oil was not known. For this reason the effect of addition of palm oil, hydrogenated to different levels, on the polymorphic behaviour of hydrogenated canola oil was investigated.

MATERIALS AND METHODS

artially hydrogenated canola oil (HCO) was obtained from commercial margarine. This brand-named margarine was found to be of consistently poor quality: it was grainy, crumbly and with large crystals as seen under the polarizing microscope. The margarine was melted; the water layer was removed and the fat was dried and filtered. Fractionated palm stearin (PS) and palm oil (PO)

were supplied by PORIM, Bandar Baru Bangi, 43000 Kajang, Selangor, Malaysia. Partially hydrogenated palm oil (HPO#1 and HPO#2) were supplied by Lam Soon (M) Bhd. (P.O. Box 8, 46050 Petaling Jaya, Selangor, Malaysia). Palmoil was also hydrogenated in this laboratory at 175°C and 103 KPa hydrogen pressure with 0.2% nickel catalyst (HPO #3). The above mentioned palm products were added at a level of 10% to the margarine canola oil. Slightly hydrogenated canola oil of dropping point 23.2°C was supplied by Canada Packers Inc. Toronto, M6N 1K4. Partially hydrogenated soyabean oil (HSBO) was obtain from a soyabean margarine which had been shown to contain beta prime crystals of very small size. Fatty acid composition, diglyceride content, trans-isomer content, dropping point and X-ray diffraction patterns were determined as described by Yap et al. (1989b).

The solid fat content (SFC) of the samples was determined by pNMR with a Bruker PC/20 series NMR analyzer (Minispec). Samples were heated at 60°C, cooled in ice and water for 15 min, then tempered at 25°C for 30 min, cooled in ice and water again for 15 min and left at the appropriate temperatures for 30 min before measurement.

The differential scanning calorimetry (DSC) analyses were carried out with a model 900 DuPont Analyzer. Melting diagrams were run from 10°C to 70°C at 5°C/min. Cooling diagrams were run from 70°C to 30°C at 5°C/min and left at 30°C for 2 min and then cooled from 30°C to 15°C at 3°C/min.

The following procedure was followed in the study of polymorphic transition in the fats. Fat samples were transferred into small tubes (6 cm long, 1 cm diameter) in order to assure quick heat transfer during cooling. The fat samples were heated in the tubes at 70°C in order to destroy crystal memory. The samples were crystallized in ice and water and left in a 5°C refrigerator for one day; Cycle 1 consisted of tempering the samples at 23°C for one day and storage at 5°C for one day. Cycle 2 was a continuation of cycle 1 with additional tempering at 23°C for two days and storage at 5°C for one day. Cycle

3 was a continuation of cycle 2 with additional tempering at 23°C for 3 days and storage at 5°C for one day. Cycle 4 was a continuation of cycle 3 with additional tempering at 23°C for two days and storage at 5°C for one day.

Texture measurement was carried out as follows. Polypropylene stoppers (Bacti-Capall, Fisher Scientific), which are small cups 18 mm in diameter and 20 mm in height, were filled

with fat that had been melted at 70°C. The samples were crystallized in a freezer for two hours and stored in a 5°C refrigerator overnight. Measurement of the texture took place the next day at 10°C after samples had been conditioned at 10°C for three hours. Fat-filled sample cups were also tempered at 23°C for 48 hours after freezing and initial storage at 5°C and the texture was then measured at 10°C after conditio-

TABLE 1. FATTY ACID COMPOSITION OF PALM OIL AND PALM OIL PRODUCTS (%)

Fatty acid			Sample		
	PO	PS	HPO#1	HPO #2	HPO #3
14:0	1.0	1.3	1.1	1.5	1.0
16:0	44.7	58.1	43.4	42.9	44.8
18:0	4.0	4.8	5.2	19.3	29.9
18:1	40.1	28.6	48.3	33.6	23.7
18:2	9.5	6.3	0.7	0.3	0.1
18:3/20:0	0.2	0.5	0.4	0.4	0.4
20:1	0.2	0.1	0.2	0.1	_

PO = palm oil

PS = palm stearin (fractionated)

HPO = hydrogenated palm oil

TABLE 2. TRIGLYCERIDE COMPOSITION, TRANS, AND MONO-AND DIGLYCERIDE CONTENT (%) AND DROPPING POINTS (°C) OF PALM OIL PRODUCTS

Triglyceride		Sample		
carbon number	PS	HPO #1	HPO #2	HPO #3
46	1.7	0.4	0.7	0.5
48	26.2	7.1	7.9	7.5
50	42.6	41.1	40.5	41.0
52	24.1	41.0	40.3	40.6
54	5.1	9.8	9.8	9.8
56	0.3	0.5	0.4	0.5
TI	0	8.5	19.4	13.4
MG	0.2	0.5	0.6	0.2
DG	8.3	8.2	12.8	6.8
DP	53.8	42.1	52.6	56.3

TI = trans isomers

MG = monoglyceride

DG = diglyceride

DP = dropping point

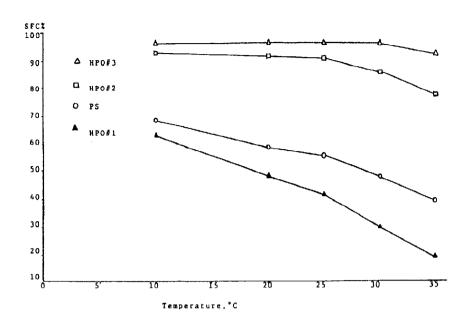


Figure 1. Solid fat content (%) of palm stearin (PS), hydrogenated palm oil # 1 (HPO #1), hydrogenated palm oil #2 (HPO #2) and hydrogenated palm oil #3 (HPO #3).

ning at 10°C for 3 hours. Hardness of the fat samples was measured by means of penetration of a probe with a diameter of 4 mm and a 45°C angle at the trip, using the Intron Universal Testing Machine which was hooked up by means of an A-D convertor to an Apple IIe computer. ESRI software was used to compute the various textural attributes (Buckley *et al.*, 1984). The tests were performed in quadruplicate and peak forces at 1.5 cm penetration were recorded.

RESULTS AND DISCUSSION

ables 1 and 2 show the chemical composition and physical properties of the following palm oil products: palm oil (PO), fractionated palm stearin (PS) partially hydrogenated palm oils (HPO #1, HPO #2 and HPO #3).

Palm stearin was dry-fractionated from palm oil and contained a higher percentage of palmitic acid than palm oil (Table 1). The hydrogenated palm oils had increased stearic acid (18:0) content with increasing degree of hydrogenation. Their dropping points (Table 2) were likewise affected. Trans-isomers increased and then decreased (Table 2) because of the decline in 18:1 fatty acid content (Table 1). Diglyceride content

varied because the hydrogenated palm oils came from different batches. The triglyceride compositions (carbon number) of the hydrogenated palm oils were identical (*Table 2*). The triglyceride composition of palm stearin was quite different from that of palm oil. The 48-carbon triglyceride content was much higher in palm stearin than in the palm oils.

According to Timms (1984, 1985) palm oil consists of three main types of triglycerides: trisaturates (mainly PPP), disaturates (mainly POP but with significant amount of PLinP and PPO) and monosaturates (mainly POO but some OPO and PLinO). In the fractionation process the PPP, PPO and some POP are concentrated in the solid fraction called palm stearin, while POO and OPO end up in the liquid part called palm olein. Deffense (1985) stated that PPO crystallizes more in the stearin fraction while POP occurs more in the olein. Rossell et al. (1985) found that the 2position of the triglyceride molecules in palm oil contains 16% palmitic acid, which is enriched in the palm stearin fraction from 20% to 59% depending on the fractionation process. This enrichment is mainly due to PPP (tripalmitin) and can be seen by the increased C48 content as compared with those control the hydrogenated palm oils in Table 2.

TABLE 3. FATTY ACID COMPOSITION OF SIX FAT SAMPLES(%)

			Samp	le		
Fatty Acid	нсо	HSBO	10%PS	10%HPO#1	10%HPO#2	10%HPO#3
14:0	0.1	0.1	0.2	0.2	0.2	0.2
16:0	4.5	10.2	9.9	8.5	8.5	8.5
16:1	0.3	0.1	0.3	0.3	0.3	0.3
18:0	8.8	7.7	8.4	8.5	9.9	10.7
18:1	80.9	59.4	75.6	77.6	76.1	75.1
18:2	2.4	19.7	2.7	2.2	2.2	2.1
18:3/20:0	1.0	2.2	0.9	0.9	0.9	1.0
20:1	1.4	0.3	1.3	· 1.2	1.3	1.6
22.0	0.4	0.3	0.3	0.3	0.3	0.3
22:1	0.5		0.4	0.4	0.4	0.3
HCO -	Hydroge	enated Canola Oil	10	% HPO#1	- HCO plu	us 10% HPO#1
HSBO -		enated Soybean Oil		% HPO#2	_	us 10% HPO#2
10%PS -		lus 10% Palm Stearin		% HPO#3		us 10% HPO#3

Figure 1 shows the SFC curves of the palm products. The fractionated palm stearin had a higher level of solids than HPO#1while HPO#2 and HPO#3 contained much larger amounts of solids than PS and HPO#1. The palm oil products were added to the partially hydrogenated canola oil obtained from the margarine at levels of 10%. Their fatty acid compositions are displayed in Table 3. Partially hydrogenated soyabean oil obtained from a USA soyabean stick margarine is also included for comparison. Palmitic acid content was increased in all of the canola-palm product mixtures. Yet the palmitic acid content of the soyabean sample (HSBO) was still slightly higher. The triglyceride composition, trans, mono- and diglyceride contents and melting points are displayed in Table 4. Addition of palm stearin increased the C48 and C50 triglycerides in the canola sample. In the case of HPO additions, the C50 triglycerides and to a small extent the C52 triglycerides were increased. Diglyceride content was only slightly increased by the addition of palm oil products (Table 4). Diglycerides, according to Hernqvist and Anjou (1983), can also delay the polymorphic transition from β' to β . The dropping point increased slightly with the addition of 10% palm stearin (Table 4), it did not change with the addition of 10% HPO#1, but it increased considerably with addition of 10% HPO#2 and HPO#3. Postmus et al. (1989) examined 24 North American stick margarines and found dropping points of the fats to vary from 31.5°C to 35°C. Dropping points of 38.1°C and 40.5°C would therefore seem too high for household stick margarines but not for baking margarines. The SFC curves of the mixtures are displayed in Figure 2. Addition of any of the palm oil products resulted in increased solid fat content. DeMan et al. (1990) examining the same margarines as Postmus et al., (1989) found that the SFC of the stick margarines varied from 23 to 35% at 10°C. Therefore the mixtures containing 10% palm stearin and 10% of HPO#1 would qualify in the formulation of household stick margarines.

Short spacings obtained by X-ray diffraction analysis at the start of the temperature cycling study and the consequent temperature cycles are displayed in *Table 5*. The characteristic short spacings of the β' polymorphic form are at 4.2 and 3.8Å and that of the β form is at 4.55Å. Additional short spacings of the β' form

TABLE 4. TRIGLYCERIDE COMPOSITION, TRANS, AND MONO- AND DIGLYCERIDE CONTENT (%) AND DROPPING POINTS (°C) OF THE SIX FAT SAMPLES.

			S	ample		
Triglyceride Carbon Number	НСО	HSBO	10%PS	10%HPO#1	10%HPO#2	10%HPO#3
48	_	-	2.5	0.6	0.7	0.7
50	0.9	2.6	4.6	4.3	4.2	4.5
52	13.0	27.1	14.3	15.2	15.4	15.9
54	78.9	68.1	71.4	72.5	72.8	72.1
56	4.7	1.5	4.6	4.3	4.3	4.6
58	1.3	0.5	1.3	1.3	1.3	1.2
TI	32.6	27.2	29.3	30.2	31.3	30.3
MG	0.3	0.4	0.3	0.2	0.5	0.3
DG	3.2	2.9	4.2	3.4	3.6	4.0
DP	33.6	33.9	35.4	33.4	38.1	40.5

^{*} for key to abbreviations, see Table 3.

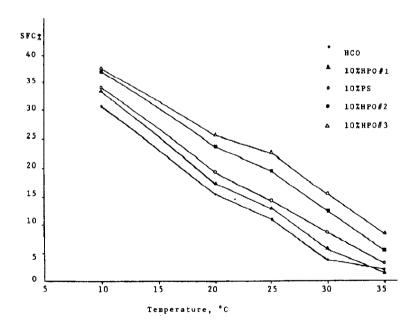


Figure 2. Solid fat content (%) of hydrogenated canola oil (HCO), hydrogenated canola oil + 10% hydrogenated palm oil #1,hdrogenated canola oil + 10% hydrogenated palm oil #2,hydrogenated canola oil + 10% hdrogenated palm oil #3 and hydrogenated canola oil + 10% palm stearin

TABLE 5. X- RAY DIFFRACTION OF HYDROGENATED CANOLA OIL, HYDROGENATED SOYBEAN OIL AND HYDROGENATED CANOLA OIL MIXED WITH 10% OF VARIOUS PALM OIL PRODUCTS UPON TEMPERATURE CYCLING BETWEEN 5°C AND 23°C

Polymorphic form	β, β>>>β,	<u>జ</u> .జ	β. β.>>>β β.>>β	β' β'>>>β β'>>β β' = β β>β'	9. 8, 8, 8, 8,	β' β' β'>>>β
	3.62 W			3.62 W 3.63 W		
	3.74 M			3.74 W 3.74 W		
				3.81 S 3.81 W		
Short spacing (Å)*	3.82 S 3.86 S	3.82 S 3.81S	3.85 S 3.81 S 3.81 S 3.81 S	3.83 S 3.83 S 3.86 M 3.86 S 3.85 S	3.85 S 3.81 S 3.80 S 3.81 S	3.84 S 3.82 S 3.80 S
	4.25 S 4.22 W	4.25 S 4.25 S	4.21 S 4.20 S 4.20 S 4.19 S	4.20 S 4.21 S 4.21 S 4.19 S 4.20 M	4.21 S 4.21 S 4.20 S 4.20 S	4.19 S 4.21 S 4.19 S
	4.53 S		4.54 VW 4.54 M	4.56 VW 4.56 W 4.54 S 4.55 S	4.51 VW 4.59 W	4.52 VW
Sample	HCO	HSBO "	10%PS	10%HPO#1	10%HPO#2 "	10%HPO#3 "
Cycle#	0 1	0 4	0 7 m 4	0 1 7 8 4	0 7 K 4	0 to 4

 $\boldsymbol{\ast}$ Additional weak short spacings for all samples were observed at 4.3 and 4.0 Å.

are also present in the region of 4.3 and 4.0Å which are of weak intensity. In the case of crystals in the \beta form, additional spacings other than the one at 4.55Å appear below the 3.8Å region. As can be seen from Table 5, the canola sample containing no palm oil (HCO) changed to the \beta form at the first cycle with a strong diffraction line showing at 4.53Å and a weak line at 4.22Å. meaning that little of the β' crystallinity was left. The soybean sample (HSBO) remained in the β ' form after four cycling periods. The canola sample containing 10% palm stearin (10%PS) exhibited a weak spacing at 4.55Å after the third cycle, which increased to medium intensity after the fourth cycle. The canola sample containing 10% HPO#1 showed a very weak appearance of β crystallinity at cycle 1, which increased to a strong appearance at cycle four, although some β' crystallinity was still present as indicated by a spacing of medium intensity at 4.2Å. The 10% HPO#2 - canola mixture showed a very weak spacing of the β form in the third cycle which increased slightly in the fourth cycle (4.59Å W), while in the 10% HPO#3-canola mixture a very small amount of β crystals appeared only in the fourth cycling period.

The results show that lightly hydrogenated palm oil (HPO#1) considerably delayed polymorphic transition from β to β as compared to no palm oil addition. The delay was increased with the addition of palm stearin. The best results were obtained with palm oil hydrogenated to higher melting points.

The DSC-melting diagrams are displayed in Figure 3. The change in melting characteristics was most pronounced from cycle 0 to 1. In cycle 0 the crystals were mixed. Tempering at 23°C caused partial melting of mixed crystals and upon cooling recrystallization into a slightly higher melting form (Figure 3, cycle 1). Further temperature cycling resulted in little change in the shape of the melting diagrams except that in the mixtures which contained B crystallinity the temperature of the melting peak was slightly in creased. On average the temperature of the melting peaks was 5°C higher than that of the dropping points. This difference can be explained by the different heating rates of these determinations. (1°C/min in the dropping point determination and 5°C/min in the DSC-melting).

The DSC-crystallization diagrams are displayed in Figure 4. Additions of any palm pro-

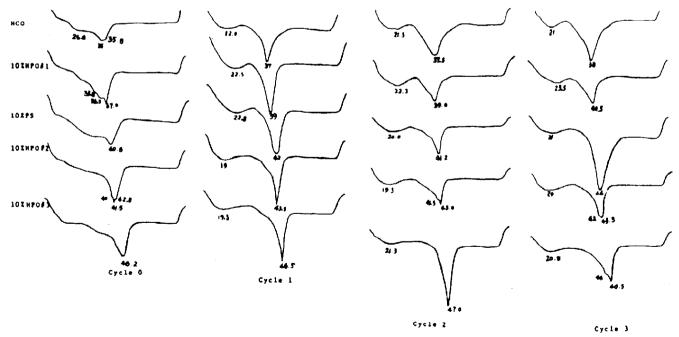


Figure 3. DSC-melting curves of hydrogenated canola oil (HCO) with addition of 10% HPO #1, 10% HPO #2, 10% HPO #3 and 10% PS at cycle 0 (no tempering treatment) and cycle 1, cycle 2 and cycle 3 (after first, second and third tempering treatment).

Sample	Peak fo	orce (N)
	Before tempering	After tempering ·
HCO	3.85	1.30
HSBO-	4.09	1.59
10% PS	6.22	1.55
10% HPO#1	6.95	1.97
10% HPO#2	8.82	3.89
10% HPO#3	11.20	4.90
5% HPO#3	7.16	2.43

TABLE 6. HARDNESS AS MEASURED BY PEAK FORCE (N) AT 1.5 cm PENETRATION OF FAT SAMPLES BEFORE AND AFTER TEMPERING.

ducts increased crystallization temperature – from 17.5°C in canola to 27.1°C in the case of the mixture containing 10% of HPO#3. In the study of Postmus *et al.*, (1989) the crystallization temperatures of stick margarines ranged from 14.1°C to 21.5°C. Isothermal crystallization was delayed more in the case of palm stearin addition. Little isothermal crystallization took place in mixtures containing HPO#2 and HPO#3.

Results of textural evaluation of the crystalized and the tempered crystallized fats are displayed in *Table 6*. It can be seen that tempering greatly decreases hardness measured by the peak forces of penetration. Addition of palm oil increased the hardness. The soyabean sample was harder than the canola sample. Judging from the textural evaluations, the canola mixtures containing 10% HPO#1 and 10% PS would qualify in formulations for stick margarine manufacture, which confirms the previous statement regarding the SFC curves of these mixtures.

Since some of the above-mentioned mixtures were unsuitable for margarine stick manufacture a number of other mixtures were also tested. In these a portion of the canola margarine fat (HCO) was substituted by a canola oil that was hydrogenated to a lesser degree with a dropping point of 23.2°C. Two mixtures were found to be very promising. Mixture 1 consisted of 70% of hydrogenated canola margarine fat (HCO), 15% of HPO#1 and 15% of soft canola with dropping point 23.2°C (Soft CO). Mixture 2 consisted of 60% of hydrogenated canola

margarine fat, 30% of soft canola (Soft CO) and 10% of palm stearin. The dropping point of mixtures 1 and 2 were 33.2°C and 34.6°C respectively. Table 7 displays the fatty acid compositions of the two mixtures which are very similar. The SFC curves of the mixtures (Figure 5) compared favourably with that of the soybean sample and so did the DSC crystallization temperatures (Figure 4). X-ray diffraction patterns after temperature cycling are displayed in Table 8. Mixture 1 containing 15% HPO#1 was the most effective in delaying polymorphic transition (Table 8). Mixture 2 containing 10% PS and the soft canola fat in addition to hydrogenated canola margarine fat was slightly better in polymorphic stability than the 10% PS containing no soft canola fat (Table 5).

From this study it can be concluded that in household stick margarine formulations a lightly hydrogenated palm oil of dropping point 42.1°C at a level of 15% is very effective in delaying polymorphic transition from the β ' to the β form. Fractionated palm stearin of dropping point 53.8°C is also effective in delaying polymorphic transition.

To better understand the principle of the delay of polymorphic transition of palm oil products in hydrogenated canola oil, two of the palm products were fractionated by means of isobutanol (deMan et al., 1989). Palm stearin was left to crystallize at 23°C. Isobutanol at 23°C was used to separate the crystals from the liquid portion of the palm stearin by mixing the palm

TABLE 7. FATTY ACID COMPOSITION OF MIXTURES 1 AND 2 (%)

Fatty Acid	Mixture 1	Mixture 2	
. 14:0	0.2	0.2	
16:0	10.4	10.1	
16:1	0.4	0.4	
18:0	7.6	7.0	
18:1	76.6	76.9	
18:2	1.8	2.3	
18:3/20:0	0.8	0.8	
20:1	1.3	1.4	•
22:0	0.3	0.3	
22:1	0.4	0.4	
Trans	28.2	27.8	

Mixture 1: 70% of HCO + 15% HPO#1 + 15% Soft CO Mixture 2: 60% of HCO + 10% PS + 30% Soft CO

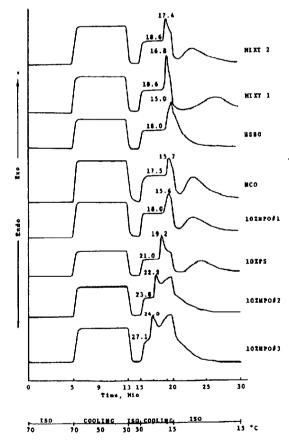


Figure 4. DSC-crystallization curves of hydrogenated canola oil (HCO), hydrogenated canola oil + 10% hydrogenated palm oil #1, hydrogenated canola oil + 10% hydrogenated palm oil #2 hydrogenated canola oil + 10% hydrogenated palm oil #3, hydrogenated canola oil + 10% palm mixture 1 of hydrogenated canola oil ((70%) soft canola (15%) and hydrogenated palm oil #1, (15%) - (Mixt. 1), mixture 2 consisting of hydrogenated canola oil (60%), soft canola (30%) and palm stearin (10%)- (Mixt. 2).

TARLE 8 X-RAY DIFFRACTION	CATTECLIA	~~ ***********	44100
		- C 3 - RAIX -	ANIJZ

Cycle	Sample		Short Spacing (A)•	Polymorphic form
2 3 4	mixt 1 mixt 1 mixt 1	4.52W	4.20S 4.22S 4.19\$	3.82S 3.83S 3.80S	β' β' β'>>>β
2 3 4	mixt 2 mixt 2 mixt 2	4.53W 4.55M	4.19S 4.20S 4.21S	3.80S 3.81S 3.85S 3	β' β'>>>β .79M β'>> β

^a Additional weak short spacing were observed for both samples at 4.3 and 4.0 Å.

Mixture 1:70% of HCO + 15% HPO#1 + 15% soft CO Mixture 2:60% of HCO + 10% PS + 30% soft CO

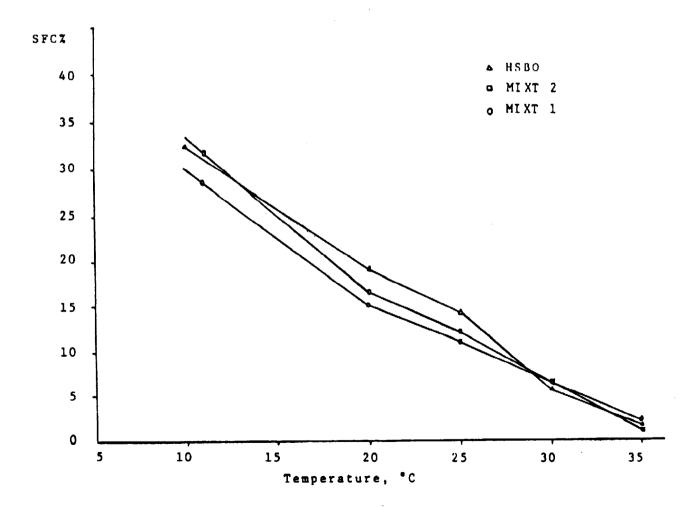


Figure 5. Solid fat content (%) of soybean oil stick margarine (HSBO) and canola-palm mixtures 1 and 2 (Mixt.1, Mixt. 2).

TABLE 9. FATTY ACID COMPOSITION, TRIGLYCERIDE COMPOSITION, AND MONO-AND DIGLYCERIDE CONTENT (%) OF TRIPALMITIN AND FRACTIONS OF PALM STEARIN AND HYDROGENATED PALM OIL.

	TPM	Palm S	Stearin	Hydrogenated	Palm Oil #3
Fatty acid		PSS	PSLS	HPO#3S	HPO#3L
14:0	0.3	1.6	1.0	0.7	1.1
16:0	97.8	83.6	58.1	50.8	43.8
18:0	1.1	5.6	5.4	39.5	27.8
18:1	0.4	7.4	30.5	8.7	26.5
18:2	0.1	1.2	4.4		0.1
20:0		0.3	0.4	0.4	0.5
arbon Number					
46	1.0	3.5	0.6	0.3	0.7
48	96.6	62.6	3.7	9.7	8.2
50	2.4	29.7	74.5	49.3	39.5
52		3.6	18.7	34.5	39.1
54		0.4	2.2	5.8	1.6
56		0.1	0.2	0.3	0.7
1G%	ND	ND	ND	ND	0.3
G%	ND	ND	6.1	0.4	7.8

ND = Not Detected

stearin with isobutanol in an all-glass tissue homogenizer and filtering the solids, called fraction PSS. The isobutanol—containing liquid fraction was then cooled to 5°C and the solids were filtered again and called fraction PSLS. HPO#3 was like wise fractionated but at a temperature 40°C. This resulted in a solid fraction called HPO#3S and a supernatant fraction HPO#3L. Tripalmitin (TPM) was supplied by J.T. Baker Chemicals Company (Phillipsburg, NY 08865).

The fatty acid composition, triglyceride composition (carbon number), and the mono- and diglyceride content of the compounds are listed in *Table 9*. This table shows that the solid fraction of palm stearin (PSS) consisted mainly of palmitic acid in the form of tripalmitin, with a considerable amount of 50-carbon triglycerides which would

contain PSP and PPS, both β'-tending compounds (Timms, 1984), and POP and PPO. The solids of the liquid fraction of palm stearin (PSLS) contained small amounts of tripalmitin (C48) with large amounts of 50-and 52-carbon triglycerides. Fraction PSLS also contained a high percentage of diglycerides (6.1%). Fraction HPO#3S contained a high percentage of stearic acid with a larger percentage of 52-carbon triglycerides than the palm stearin fractions. The 52-carbon triglycerides of fraction HPO#3S consisted mainly of PSS with small amount of SPS. The tripalmitin content was small. Fraction HPO#3L contained a fairly high percentage of stearic acid and 26.5% of 18:1. Part of the 18:1 was in the trans form. The 50- and 52carbon contents were the same (Table 9). HPO#3L contained the diglycerides while the more satu-

TABLE 10. X-RAY DIFFRACTION PATTERNS AFTER CYCLE 2 OF CANOLA MARGARINE FAT MIXED WITH FRACTIONS OF PALM STEARIN AND HPO#3 AT A LEVEL OF 5%

Fraction or compound		Short spacing Å				Poly	Polymorphic form
TPM	558	4.20S	3.86W	3.75VW	3.63VW		$\beta = \beta'$
Palm stearin PSS	4.53W	4.20S	3.84M	3.79 S			β<>>β
Palm Stearin PSLS	4.548	4.20M	3.865	3.75W	3.64 W		β > β'
HPO#3S	4.56W	4.218	3.818				β'>>>β
HPO#3L	4.54M	4.20S	3.85S	3.808	3.72VW	3.63VW	β'>β

Each sample showed additional short spacing of weak intensity at $4.3\,$ and $4.0\,$ Å.

rated fraction HPO#3S had a very low diglyceride content.

The tripalmitin and isolated fractions listed in *Table 9* were added to the canola margarine fat at a level of 5%. This level was chosen as the fractionated solids represented only part of the original material which was added at a level of 10%.

The mixtures were heated, cooled and temperature cycled as previously described. After cycle 2 the samples underwent X-ray analysis. Short spacings are reported in Table 10. All the fractions including tripalmitin delayed the polymorphic transition of the canola margarine fat. Fraction PSS was more effective than tripalmitin (TPM), because fraction PSS was more diverse in fatty acid and triglyceride composition. The more unsaturated fractions PSLS and HPO#3L were less effective in delaying the polymorphic transition from β ' to β than the more saturated fractions PSS and HPO #3S, although the more unsaturated fractions contained the diglycerides. Diglyceride content is also higher in the palm oleins than in the palm stearins (Deffense, 1985) and is associated with the solids to a leser extent. As mentioned before, fraction PSS contained large amounts of tripalmitin and 50-carbon triglycerides while fraction HPO# 3S contained a large amount of 50-and 52carbon triglycerides (Table 9). The only reason for retardation of polymorphic transition in canola oil by palm oil products seems to be that palm oil products contribute to the diversity of the triglyceride chain length. The 48-, 50- and 52-carbon triglycerides of the palm oil products, especially the more saturated ones, counteract the beta tending properties of the solid 54-carbon triglycerides in canola oil. The diglycerides of palm oil are not involved in the retardation of polymorphic transition.

A future experiment will examine the composition of the solids of mixtures of canola and palm oil in order to test this hypothesis.

REFERENCES

BUCKLEY, D J; TIMBERS, G E; KLOEK, M and

LALONDE, M J L (1984). Texture profile analysis with curve smoothing using a personal computer. *J.Texture Studies* 15, 247.

DEFENSE, E J (1985). Fractionation of palm oil. J. Am. Oil Chem. Soc. 62, 376.

DEMAN, J M; NAGUIB MOSTAFA, A and SMITH, A K (1985). Thermal analysis microscopy for the study of phase changes in fats. *Food Microstructure*, 4, 233.

DEMAN, J M; CHAWLA, P and DEMAN, L. (1989). Particle size analysis of fat crystals. J. Am. Oil Chem. Soc., 66, 443.

DEMAN, L; POSTMUS, E. and DEMAN, J M (1990). Textural and physical properties of North-American stick margarines. J. Am. Oil Chem. Soc., 67,323.

HERNQVIST, L; ERSLOF, B; LARSSON, K and POODLAKA, O (1981). Polymorphism of rapeseed oil with a low content of erucic acid and possibilities to stabilize the beta prime crystal form in fats. J. Sci. Food Agric., 32, 1197.

HERNQVIST, L and ANJOU, K (1983). Diglycerides as a stabilizer of beta-prime crystal form in margarines and fats. Fette Seifen, Anstrichmittel, 85,64.

LEE, S and DEMAN, J M (1984). Effect of surfactants on the polymorphic behaviour of hydrogenated canola oil. Fette Seifen Anstrichmittel 86, 460.

MOZIAR, C; DEMAN, J M and DEMAN, L (1989). Effect of tempering on the physical properties of shortening. Can. Inst. Food Sci. Technol. J., 22, 238.

NAGUIB MOSTAGA, A and DEMAN, J M (1985). Application of infrared spectroscopy in the study of polymorphism of hydrogenated canola oil. J. Am. Oil Chem. Soc, 62, 181.

POSTMUS, E; DEMAN, L and DEMAN, J M (1989). Composition and physical properties of North American stick margarines. Can. Inst. Food

Sci. Technol, J., 22,481.

ROSSELL, J B; KING B and DOWNES, M J (1985). Compostion of Oil. J. Am. Oil Chem. Soc., 62,221.

TIMMS, R E (1984). Phase behaviour of fats and their mixtures. In: *Progress in Lipid Research*. R.T. Holman, Ed. Pergamon Press, Oxford and New York pp. 1-38.

TIMMS, R E (1985). Physical properties of oils and mixtures of oil. J. Am. Oil Chem. Soc., 62, 241.

WEINBERG, B (1972). Processing of low-erucic acid rapeseed and canbra oil Can. Inst Food Sci

Technol J., 5, A57.

YAP, PH; DEMAN, JM and DEMAN,L(1989). Polymorphism of palm oil and palm oil products *J. Am. Oil Chem. Soc.*, 66,693.

YAP,P H;DEMAN, J M and DEMAN, L(1989 b). Polymorphic stability of hydrogenated canola as affected by addition of palm oil. J. Am. Oil Chem. Soc., 66,1784.

YAP, PH; DEMAN, J M and DEMAN, L (1989c). Crystallization characteristics of hydrogenated canola oil as affected by addition of palm oil. J. Am. Oil Chem. Soc., 66.,1792.

Editor's Note

Studies on the Utilization of Palm Oil Wastes as the substrates for Butanol Fermentation Elaeis 1 (2) December 1989.

In the above paper, it was mentioned that the Palm Oil Industry contributed 83% of the industrial organic pollution load. This is very much outdated and the references quoted were works done in 1974. It is acknowledged that considerable works had been done by the Malaysian Department of Environment (DOE) and the Malaysian palm oil industry to improve and reduce industrial pollution from palm oil industries since 1981.

Several treatment technoogies for palm oil mill effluents (POME) have been successfully developed by the palm oil industries. All palm oil mills have built their treatment systems which are capable of producing good quality discharge meeting the DOE's requirement for watercourse discharge. Through concerted R&D efforts by both the public and private sectors a new management concept on POME has emerged. POME has been found to contain high plant nutrients and is increasingly used by the industry as fertilizer / soil conditioner. Beneficial effects both on crop yield and soil properties have been reported. POME is now being considered as a resource rather than a waste-product.