Preparation of Plastic Fats with Zero *trans* FA from Palm Oil

T. Jeyarani and S. Yella Reddy*

Lipid Science & Traditional Foods, Central Food Technological Research Institute, Mysore-570013, India

ABSTRACT: A series of plastic fats containing no *trans* FA and having varying melting or plastic ranges, suitable for use in bakery, margarines, and for cooking purposes as vanaspati, were prepared from palm oil. The process of fractionating palm oil under different conditions by dry and solvent fractionation processes produced stearins of different yields. Melting characteristics of stearin fractions varied depending on the yield and the process. The lower-yield stearins were harder and had a wider plastic range than those of higher yields. The fractions with yields of about 35% had melting profiles similar to those of commercial vanaspati. The plastic range of palm stearins was further improved by blending them with corresponding oleins and with other vegetable oils. The plasticity or solid fat content varied depending on the proportion of stearin. Blends with higher proportions of stearins were harder than those with lower proportions. The melting profiles of some blends, especially those containing 40–60% stearin of about 25% yield and 40–60% corresponding oleins or mahua or rice bran oils, were similar to those of commercial vanaspati and bakery shortenings. These formulations did not contain any *trans* FA, unlike those of commercial hydrogenated fats. Thus, by fractionation and blending, plastic fats with no *trans* acids could be prepared for different purposes to replace hydrogenated fats, and palm oil could be utilized to the maximum extent.

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KEY WORDS: Bakery shortenings, differential scanning calorimetry, mahua oil, palm oil, plastic fat, rice bran oil, *trans* fatty acids, vanaspati.

Plastic fats having varying melting or plastic ranges are used as bakery shortenings, as margarines, and for cooking purposes as vanaspati, especially in the Indian subcontinent. Several processes are used to modify the phase change properties of vegetable oils and to improve plasticity and therefore the versatility for use by food industry. The processes used most often are hydrogenation and interesterfication (1). Chemical or enzymatic interesterification process technologies, used mainly in European countries, have particular drawbacks that are associated mainly with yield efficiency and cost of the processes (2). Currently, these plastic fats are prepared by hydrogenation of vegetable oils and are characterized by high contents of *trans* FA (20–50%) depending on the degree of hydrogenation and the nature of the oils. *Trans* FA reportedly contribute to several health problems including thrombogenesis that leads to coronary heart disease (3). Consumer concerns associated with the atherogenic effects of *trans* FA limit the future of this process as a way to modify the solid-to-liquid ratio in vegetable oils/fats. Interest has therefore grown in producing fats that will simulate hydrogenated fat but will not contain *trans* FA. An additional alternative involves fractionation and direct blending of high-melting fractions with vegetable oil. This process has the additional advantage that no chemical process is involved and is consistent with the consumer trend toward natural products.

Trans-free margarines were prepared from saturated soybean oil by interesterification (4). *Trans*-free vanaspatis were made by using ternary blends containing commercial palm oil fractions, palm oil, and palm kernel oleins, and physicochemical properties were studied (5). Also, the comparative nutritional quality of commercial palm stearins (PSt) blended with liquid oils was reported (6). Physicochemical and baking performance of shortenings based on blends of hydrogenated commercial stearins of palm and of their blends with liquid oils and interesterified palm fractions has been studied (7).

The purpose of the current paper was to prepare plastic fats, having varied melting ranges suitable for different end uses, from palm oil by fractionation and blending. An additional goal was to utilize every fraction of the palm oil because PSt is a by-product generated during preparation of palm olein, the cooking medium.

MATERIALS AND METHODS

Materials. Crude palm oil was procured from M/S Palmtech India Ltd. (Mysore, India). Mahua oil was procured from M/S Sarvodaya (Mumbai, India). Refined rice bran oil (RBO), commercial vanaspati samples of different brands, and bakery shortenings were procured from the local market. FAME standards and 14% BF_3/methanol were from Sigma Chemical Co. (St. Louis, MO). Other chemicals used were of Analar grade.

Fractionation. (i) Dry fractionation. Palm oil was melted by heating it to about 50°C and cooled gradually to the predetermined temperature and held at that temperature in a circulating water bath for a specific period. The partially crystallized mass was filtered under vacuum to separate solid (stearin) and liquid (olein) fractions, and the yields were calculated (Table 1).

(ii) Solvent fractionation. Palm oil was dissolved in an equal volume of acetone by warming to about 40°C, gradually cooled to the predetermined temperature, and then held for a specified period in the water bath (Table 1). The mass was filtered under vacuum to separate the solid and liquid fractions. The solvent from both fractions was removed under vacuum, and the yields were calculated (Table 1).

TABLE 1
Fractionation of Palm Oil to Obtain Different Fractions

Conditions		Yield (%) of stearin[a]
Temp. (°C)	Time (h)	
Dry fractionation		
36	5	14
32	2	16
33	4	20
30	5	24
28	7	28
20	3	38
Solvent fractionation		
20	7	14
15	6	16
10	5	20
9	5	26
8–9	6	35

[a]Stearin: solid fraction of palm oil at indicated temperature.

DSC. A Mettler (Zurich, Switzerland) differential scanning calorimeter (DSC-30) was used to determine melting characteristics of the samples. The heat flow of the instrument was calibrated using indium. The PT-100 sensor was calibrated using indium, zinc, and lead. To ensure homogeneity and to destroy all crystal nuclei, samples were heated to 60°C. About 15 mg of molten sample was accurately weighed into a standard aluminum crucible and the cover was crimped in place. An empty aluminum crucible with a pierced lid was used as a reference. For melting characteristics, the samples were stabilized according to the IUPAC method (8), which includes keeping the samples at 0°C for 90 min, 26°C for 40 h, then 0°C for 90 min prior to introduction into the DSC cell. Thermograms were recorded by heating at a rate of 2°C/min from −5 to 60°C. The peak temperatures, heats of fusion (ΔH), and percent liquid at various temperatures were recorded directly using a TC-10A data processor and STARe program. The solid fat contents (SFC) were calculated from percent liquid, and the melting profiles were drawn by plotting SFC against temperature.

FA composition. FA compositions of the samples were determined by analyzing FAME, prepared by using 14% BF_3/methanol, with a Fisons GC 8000 series gas–liquid chromatograph equipped with an FID operating under the following conditions: fused-silica capillary column, 30 m × 0.25 mm (SP2340; Supelco, Bellefonte, PA); column temperature, 180°C, injector temperature 220°C; carrier gas, nitrogen, 0.5 mL/min; splitless injector. The peaks were identified by comparing retention times with those of authentic standards and reported as relative percentages of individual FA.

FTIR. FTIR is a rapid analytical technique that measures vibrations of bonds within functional groups. The *trans* absorption region is 995–937 cm^{-1}, and a peak was found at 966 cm^{-1} (9,10). The presence of *trans* FA in the samples was determined by using an FTIR spectrometer (PerkinElmer Spectrum 2000; Norwalk, CT). The samples were spread onto KBr windows, and the spectra were recorded from 400 to 4000 cm^{-1}.

RESULTS AND DISCUSSION

Palm oil fractions. Unfractionated palm oil is a semisolid containing about 25% solids, which separate at ambient (25°C) temperature and consist of a high proportion of low-melting glycerides, as shown by the DSC endotherm (Fig. 1). This is reflected in a low SFC at all temperatures (Table 2) showing its poor plasticity. To improve the plasticity, palm oil was fractionated by dry and solvent processes to obtain a series of stearins; adjustment of temperature and time allowed removal of a certain quantity of low-melting glycerides (Table 1). The proportion of low-melting fraction gradually decreased as the yield of stearin decreased; correspondingly, the high-melting fraction increased or showed an additional peak at higher temperatures depending on the yield of the fraction (Fig. 1; Table 2). This fractionation resulted in increased SFC at all temperatures (Table 2) and increased plasticity or melting range. Stearins obtained by dry fractionation were softer than those obtained by solvent fractionation, although the yields were the same (Tables 1,2), as expected, owing to entrapment of the liquid fraction in the solid phase during dry fractionation; also lower-viscosity, purer fractions could be separated by using solvent. The results showed that the stearin fractions with 14–25% yield had very high SFC at and above 37.5°C, which may affect the edibility of the end products. On the other hand, the stearin fractions with about
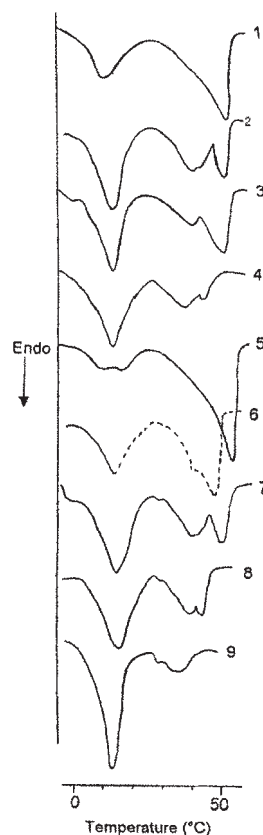

FIG. 1. DSC endotherms of stabilized samples of palm stearins of different yields. 1–4: stearins of yields 14, 20, 24, and 38%, respectively, obtained by dry fractionation; 5–8: stearins of yields 14, 20, 26, and 35%, respectively, obtained by solvent fractionation; 9: palm oil.

TABLE 2
Solid Fat Content (%) of Palm Oil Fractions Obtained by Solvent and Dry Fractionation Processes at Selected Temperatures[a]

Sample	Temperature (°C)											Peak 1/ΔH[b]	Peak 2/ΔH[b]
	20	25	30	32.5	35	37.5	40	42.5	45	47.5	50		
Palm oil	19	18	13	10	5	0.5	0					11/33	35/12
Dry fractionation													
14% St	70	69	68	66	64	59	54	47	39	16	2	11/31	51/60
16% St	60	57	53	50	45	40	35	28	20	9	0	11/36	51/60
20% St	50	47	45	43	39	34	27	20	15	11	4	13/4	41,50/46
24% St	51	49	48	46	43	38	32	27	21	13	3	12/44	49/46
28% St	41	38	35	32	28	23	17	12	8	3	1	12/48	38,44/32
38% St	41	36	32	29	24	17	12	8	3	0.5	0	12/56	37,45/29
Solvent fractionation													
14% St	82	81	80	80	77	74	69	62	54	44	29	17/22	53/79
16% St	82	77	76	75	72	66	57	46	34	25	22		45,52/19
20% St	59	54	51	48	45	40	32	24	13	1	0	12/37	47/54
26% St	51	46	44	41	38	32	25	19	16	10	3	13/47	49/44
35% St	45	37	34	32	27	21	13	6	0	0		15/57	43/29
Commercial shortenings	55–60	50–55	40–50	35–40	25–35	10–25	1–12	0–1					
Commercial vanaspati	50–65	40–60	35–50	30–45	25–40	15–30	3–8	0–6	0				

[a]St, stearin.
[b]Values in this column are given as "temperature/ΔH," where the temperature is in °C and ΔH in J/g.

35% yield had SFC and plasticity values that were similar to those of commercial hydrogenated shortenings or vanaspati samples (the SFC for commercial samples are given as a range, because different brands showed different values).

Blends of palm stearin with oleins. The plasticities or melting characteristics of PSt fractions were further improved by blending them with the corresponding oleins. In Table 3 one can see that the consistency of stearin at ambient temperature improved (SFC fell to lower values) after blending with oleins. SFC at all temperatures declined as the percentage of olein increased in the formulation. This is in accordance with the literature indicating that the melting peak shifted toward the right (melting temperature increased) as PSt increased in the blends with palm olein (5). The blends containing stearins of lower yields showed an additional peak at higher temperatures, which gradually disappeared in blends containing higher yields of stearins (Fig. 2). Thus, the formulations containing lower yields of stearin and their oleins were harder than those containing stearins of higher yields (Table 3). The formulations containing 40–50% stearins, especially of higher yields (20–25%), and 50–60% oleins showed SFC and plasticities similar to those of commercial vanaspati samples.

Blending of palm fraction with other vegetable oils. The consistency and plasticity of the PSt fraction also were improved by blending it with other vegetable oils. The oils chosen for the experiment were mahua or rice bran, and the PSt (20–25%), obtained by dry fractionation. The temperature and enthalpy of the higher-melting peaks gradually increased as PSt increased, but those of the lower melting peak remained similar (Figs. 3,4; Table 4), owing to the solubility of higher-melting glycerides of PSt in lower-melting glycerides of mahua. SFC at all temperatures and plasticities gradually increased as the proportion of PSt increased in the blend
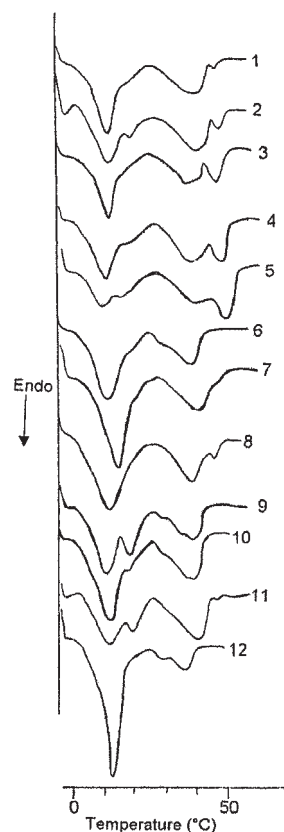

FIG. 2. DSC endotherms of blends of palm stearin with corresponding oleins. 1–3: blend of 13.5% stearin obtained by dry fractionation with its olein in the ratios of 40:60, 50:50, and 60:40, respectively; 4, 5: 14% stearin obtained by solvent fractionation and its olein at 50:50 and 60:40, respectively; 6–8: blend of 24% stearin by dry fractionation and its olein at 40:60, 50:50, and 60:40, respectively; 9–11: blends of 26% stearin by solvent fractionation and its olein at 40:60, 50:50, and 60:40; 12: palm oil.

TABLE 3
Solid Fat Content (%) of Blends of Palm Stearin Fractions with Their Respective Oleins

|	Temperature (°C)										
Sample	20	25	30	32.5	35	37.5	40	42.5	45	47.5	50
Stearins obtained by dry fractionation											
14% St + olein (40:60)	42	38	34	30	24	16.7	9	3	1.4	0.3	0.2
14% St + olein (50:50)	51	48	43	39	33	24	17	8.2	5	0.6	0
14% St + olein (60:40)	49	47	43	40	34	27	20	14	10	3	0
24% St + olein (40:60)	39	36	30	25	19	10.6	4	1.5	0.8	0.6	0.4
24% St + olein (50:50)	35	32	28	24.3	19	13	6.2	2.6	0.6	0.1	0
24% St + olein (60:40)	42	39	36	32.5	27	19.4	11	5.5	2.2	0	
24% St + olein (70:30)	48	44	42	39	34	27	21	15	8.5	2	0.2
Stearins obtained by solvent fractionation											
14% St + olein (40:60)	47	44	40	3.5	31	24	17	10.7	7	1.5	0
14% St + olein (50:50)	57	54	50	47	41	33.5	26	20	15	6.7	0.5
14% St + olein (60:40)	62	59	55.5	52	47	39.5	32	26	21	12	2.5
26% St + olein (4:60)	31	27	22	18	12	5	0				
26% St + olein (50:50)	39	35	30	26	20	12	4.7	1	0.5	0.3	0.2
26% St + olein (60:40)	49	45	40	35	28	19	10	3	1	0.2	0.1
26% St + olein (70:30)	40	36	34	31.6	27	20.5	13	4.4	0.8	0.3	0.1
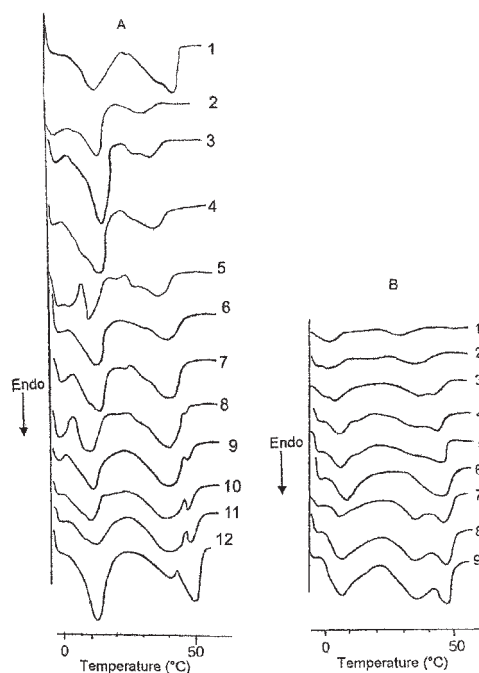
FIG. 3. DSC endotherms of stabilized samples of palm stearin blends with mahua and rice bran oils. (A) 1: Commercial hydrogenated shortening; 2: mahua oil; 3–11: blends containing 10, 20, 30, 40, 50, 60, 70, 80, and 90%, respectively, of palm stearin with mahua; 12: palm stearin. (B) 1–9: blends containing 10, 20, 30, 40, 50, 60, 70, 80, and 90% of palm stearin with rice bran oil.

TABLE 4
Solid Fat Content (%) of Formulations Containing Palm Stearin (PSt), Mahua Oil, and Rice Bran Oil (RBO)[a]

Sample	Temperature (°C)										
	20	25	30	32.5	35	37.5	40	42.5	45	47.5	50
PSt (24%)	51	49	48	46	43	38	32	27	21	13	3
PSt + RBO											
(10:90)	41	34	18	10	3	1	0.2	0			
(20:80)	55	49	37	30	21	13	5.7	2.7	2	1.5	1
(30:70)	56	52	42	36	28	20	12	4	1.5	1.2	1
(40:60)	60	57	48	42	34	26	18	8	0		
(50:50)	55	54	47	42	35.5	28.5	21	12	2.5	0	
(60:40)	55	54	49	44	38	31.5	24	16.6	7.4	0.1	0
(70:30)	64	61	54	48	40	33.7	27	20.6	11	2	0
(80:20)	62	59	53	47	40	32	26	20.5	14	5	0.6
(90:10)	66	63	57	52	45	36	29	23	16	7.6	0.4
RBO	No melting endotherm										
Mahua fat	13	11	8.5	6.3	3	2	1.3	1	0.6	0.3	
PSt + mahua											
(10:90)	22	20	13	9	5	9	4.7	2.5	2	1.6	1.2
(20:80)	25	24	17	13	7	2	0.6	0.4	0.2	0.1	
(30:70)	39	37	29	23.6	16	8	2	1	0.8	0.6	0.3
(40:60)	38	35	29	25	18	11	3	0.2	0		
(50:50)	49	46	39	34	27	18	9	2	0.5	0.3	0
(60:40)	56	53	47	41	33	23	13	4	0.6		0
(70:30)	58	56	50	45	37	28	18	9.4	4.6	1	0
(80:20)	61	59	53	48	41	32	22	14	8.6	2.7	0
(90:10)	63	61	56	50.6	43	34	25	16	11	4.4	0

(Table 4). After blending PSt with mahua oil, the SFC of the resultant product was improved at ambient temperatures (20–25°C) with respect to the desired consistency for use in bakery and other culinary purposes. As the PSt content increased, SFC at 37.5°C and above also increased, which may affect the mouthfeel of the product. Blends, especially those containing 40–70% PSt and 30–60% mahua, could be used in

FIG. 4. Melting enthalpy of higher-melting peaks of blends containing palm stearin with mahua and rice bran oils (RBO).

some processes because they show plasticities and SFC similar to those of commercial shortenings and vanaspati (Table 4, Fig. 3). Where soft consistency at ambient temperature is required (as for creams and salad dressings), blends containing a higher percentage of liquid oil could be used. Because RBO is a liquid, the higher-melting peak of PSt gradually decreased and became flat as the percentage of RBO increased (Fig. 3). For blends containing 50–60% PSt, the peak temperature gradually increased as the percentage of PSt increased in the blend, as reflected in the melting characteristics, i.e., increased plasticity extending to higher temperatures. This shift is greater than that observed with mahua blends although the enthalpy is the same. This may reflect preferential crystallization of PSt in RBO. These results indicated that a series of plastic fats suitable for various purposes could be prepared by blending PSt with mahua or RBO in selected proportions.

FTIR spectra showed an absorption peak at 966 cm^{-1} for commercial hydrogenated fats, indicating the presence of *trans* FA, whereas there was no corresponding peak for samples prepared from palm oil (Fig. 5). The presence of *trans* FA was confirmed by GLC. Commercial hydrogenated fats contained 18–29% *trans* FA, whereas samples prepared from palm had none (Table 5).

Plastic fats prepared by using PSt have higher concentrations of palmitic acid (Table 5), which imparts a desirable smooth consistency required for purposes such as shortenings and margarines. Shortenings with higher palmitic acid content are reportedly more stable in β′-crystal form than those with less palmitic acid (11).
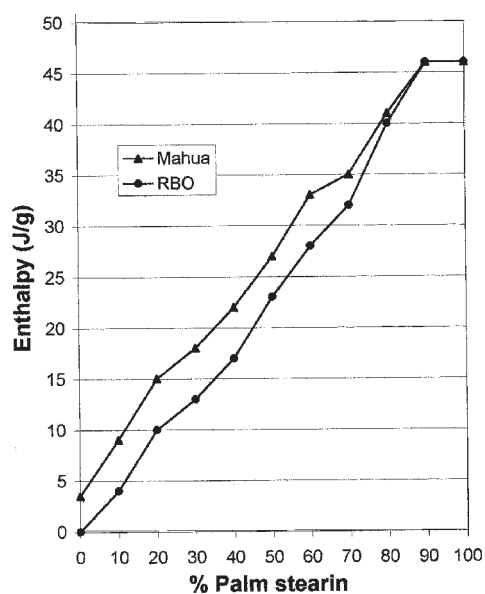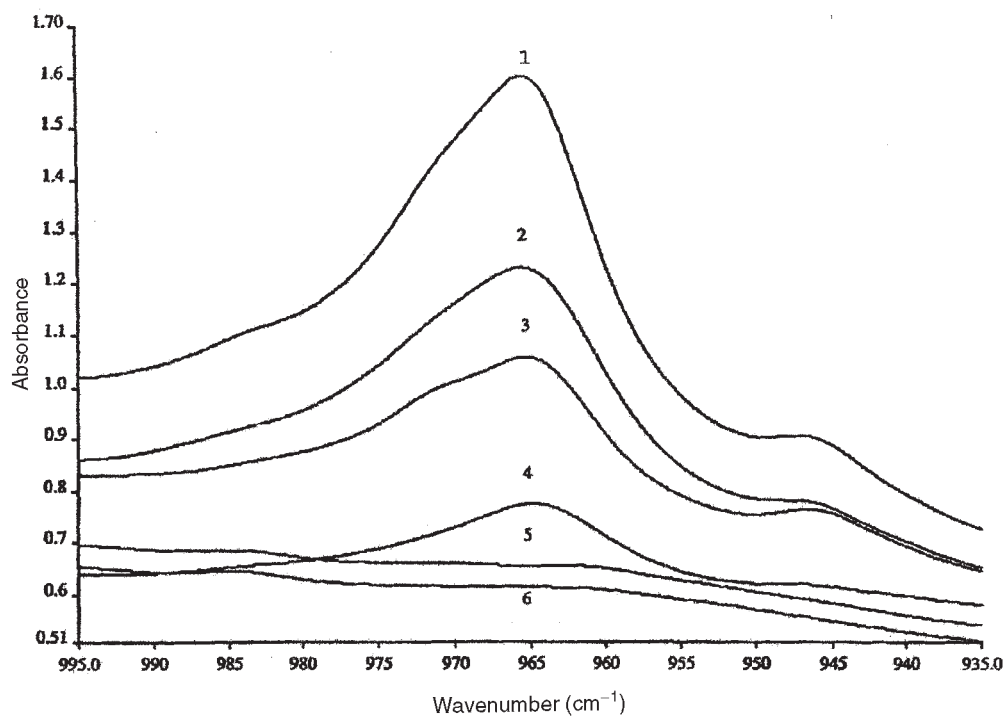
FIG. 5. FTIR spectra of plastic fats prepared from palm oil and commercial hydrogenated fats. 1–4: commercial hydrogenated fats; 5 and 6: plastic fats from palm oil.

TABLE 5
FA Composition of Plastic Fats Prepared from Palm Oil[a]

Sample	14:0	16:0	18:0	18:1	18:1 trans	18:2
			% of total FA			
Palm oil	—	45.6	1.6	41.4	Nil	10.4
PSt 24%	1.5	56.8	2.4	34.2	Nil	4.5
Mahua oil	0.7	29.8	20.3	37.6	Nil	10.7
RBO	1.7	24.3	1.1	38.6	Nil	33.1
PSt + mahua						
60:40	0.8	41.7	12.7	34.5	Nil	6.9
50:50	0.8	45.5	12.5	33.2	Nil	6.8
PSt + RBO						
30:70	2.0	38.2	0.7	36.3	Nil	21.5
40:60	1.0	42.8	2.1	36.8	Nil	14.4
PSt 24% + olein 60:40	3.1	36.3	0.7	38.9	Nil	10
PSt 14% + olein 40:60	1.4	59.3	0.7	32.2	Nil	5.8
PSt 14% + olein 50:50	1.0	48.6	0.6	40.1	Nil	9.8
Commercial shortening						
Puff (Lily brand)	1.3	37.6	9.7	17.9	28.9	3.0
Commercial shortening						
Cake (margarine)	2.4	46.3	6.9	20.4	18.5	1.6
Commercial shortening						
Biscuit (Marvo brand)	1.1	39.4	10.7	27.0	17.5	2.9

[a]For abbreviations see Table 4.

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