

# Comparison of Lipase-Transesterified Blend with Some Commercial Solid Frying Shortenings in Malaysia

B.S. Chu<sup>a</sup>, H.M. Ghazali<sup>a</sup>, O.M. Lai<sup>a,\*</sup>, Y.B. Che Man<sup>a</sup>,  
S. Yusof<sup>a</sup>, S.B. Tee<sup>a</sup>, and M.S.A. Yusoff<sup>b</sup>

<sup>a</sup>Faculty of Food Science and Biotechnology, Universiti Putra Malaysia, 43400 UPM Serdang, Selangor D.E., Malaysia, and

<sup>b</sup>Malaysian Palm Oil Board, Persiaran Institusi, Bandar Baru Bangi, 43000 Kajang, Selangor D.E., Malaysia

**ABSTRACT:** A transesterified experimental solid frying shortening was prepared from a palm stearin/palm kernel olein blend at 1:1 ratio (by weight) by using *Rhizomucor miehei* lipase at 60°C for 6 h. The fatty acid (FA) and triacylglycerol compositions, polymorphic forms, melting and cooling characteristics, slip melting point (SMP), and solid fat content (SFC) of the transesterified blend were then compared with five commercial solid frying shortenings (three domestic and two imported) found in Malaysia. All the domestic shortenings contained nonhydrogenated palm oil or palm olein and palm stearin as the hard stock, whereas the imported frying shortenings were formulated from soybean oil and cottonseed oil and contained high levels of  $\beta'$  crystals. *Trans* FA were also found in these samples. The lipase-transesterified blend was found to be more  $\beta'$ -tending than the domestic samples. The SMP of the transesterified blend (47.0°C) fell within the range of the domestic samples (37.8–49.7°C) but was higher than the imported ones (42.3–43.0°C). All samples exhibited similar differential scanning calorimetry cooling profiles, with a narrow peak at the higher temperatures and a broad peak at the lower temperatures, even though their heating thermograms were quite different. Imported samples had flatter SFC curves than both the experimental and domestic samples. The domestic samples were found to have better workability or plasticity at higher temperatures than the imported ones, probably because they were formulated for a tropical climate.

Paper no. J9842 in *JAACS* 78, 1213–1219 (December 2001).

**KEY WORDS:** Enzymatic transesterification, high-melting glycerides, melting characteristics, polymorphism, shortenings, solid fat content.

Frying shortenings function as a heat transfer medium during deep-fat frying and also react with components in foods to develop unique, savory flavors and odors. They may be clear or opaque, liquid or fluid (semisolid), or solid at room temperature. Solid frying shortenings are normally produced through simple blending of a hard stock with one or more types of liquid oils (1–3). The hard stock can be obtained from the hydrogenation of liquid oil such as canola, soybean, and sunflower oil. Hydrogenated fats consist in part of *trans* fatty acids (FA), which may be related to several health problems including thrombogenesis, which leads to coronary heart dis-

ease (4,5). Thus, there has been great interest in producing healthier fat products that will simulate hydrogenated fat products but contain zero *trans* FA.

Palm stearin (PS), the solid fraction of palm oil, is a fully natural hard component. PS consists of a high level of palmitic acid (47–74%) and stearic acid (16–37%) (6). Although PS basically lacks the ability to impart plasticity and body to the end products, it is a good source of hard stock to produce zero-*trans* fat products. By simply blending the desired PS and liquid oil, one can produce products with desirable organoleptic attributes. However, physical blending tends to cause the formation of coarse  $\beta$  crystals (7).

One of the most appropriate fat modification methods is transesterification, which involves the FA rearrangement of fat and oil mixtures and leads to changes in both chemical and physical properties of the blends. However, chemical transesterification is the preferred method in industry. Unfortunately, this process is usually carried out at high temperature (>100°C) which may lead to deterioration of the finished products (8,9). Hence, a nitrogen blanket may be needed to prevent oxidation of the fat. On the other hand, in enzymatic transesterification, the lipases perform catalysis under mild conditions and may also be more specific in their reactions (10,11). For example, *Rhizomucor miehei* lipase reacts well at 60°C and causes desirable chemical and physical changes in the fat mixtures (10–14). No nitrogen blanket is needed, no deleterious side reactions occur, and no *trans* FA are formed during the reaction (15,16). Furthermore, enzymatically transesterified fat products are reported to have better nutritional quality than chemical ones with respect to serum cholesterol level (17).

In this study, three domestic and two imported solid frying shortenings available in Malaysia were evaluated for their physical and chemical properties. Among the major fat and oil manufacturers, only a limited number produce solid frying shortenings, which are used mainly for local fast-food outlets and the export market. Cooking oil, not solid frying shortening, is the more common frying medium used in the household. Thus, domestic solid frying shortenings were not available in any of our local retail outlets during our market survey. Solid baking shortenings are more easily available in the local market. Only two imported solid frying shortenings are available in major supermarket outlets in Malaysia. Therefore, the five samples used in this work may represent

\*To whom correspondence should be addressed.  
E-mail: lom@fsb.upm.edu.my

the solid frying shortening market available in Malaysia. PS and a palm kernel olein (PKO) blend were enzymatically transesterified using a commercial 1,3-specific lipase (Lipozyme IM60; NovoNordisk, Bagsvaerd, Denmark) to produce an experimental shortening that had properties similar to commercial ones. The physical and chemical properties of these commercial and experimental solid frying shortenings were then compared.

## MATERIALS AND METHODS

**Materials.** Three domestic solid frying shortenings, Samples A, B and C, were obtained directly from local manufacturers, whereas the two imported frying shortenings, Samples D and E, were purchased from a local supermarket in Kuala Lumpur, Malaysia. Samples D and E originated from Canada and United States, respectively. Refined, bleached, and deodorized (RBD) PKO [slip melting point (SMP) 23.4°C] and RBD PS (SMP 54.4°C) were donated by Cargill Specialty Oils and Fats Pte. Ltd., Port Klang, Malaysia, and purchased from Ngo Chew Hong Oils and Fats Pte. Ltd., Semenyih, Malaysia, respectively. A commercial immobilized *R. miehei* lipase (Lipozyme IM60), obtained from Novo Nordisk Industries, was used as the biocatalyst in the transesterification reaction. The moisture content of the enzyme was *ca.* 2.5% w/w. All chemicals used were of either analytical or high-performance liquid chromatography (HPLC) grade.

**Transesterification.** PS was melted at 60°C in an oven prior to use. A mixture of PKO and PS (20 g) at a ratio of 1:1 w/w was prepared in a 500-mL Erlenmeyer flask. The mixture was reacted with 1.0% w/w of Lipozyme IM60 lipase and shaken at 200 rpm in a 60°C incubator. The reaction was stopped after 6 h by filtering out the enzyme, by means of a Whatman filter paper #4 (10–13). Similar procedures were done for the control, with the enzyme omitted.

**Removal of free fatty acid (FFA).** FFA were removed from the transesterified blend according to the method of Long *et al.* (18). The melted transesterified blend was placed in a 250-mL Erlenmeyer flask, and 20 mL of acetone/ethanol (1:1 vol/vol) was added. The mixture was shaken slowly to dissolve the sample and titrated with 0.1 N NaOH to a phenolphthalein end point. The titrated sample was diluted with 5 mL hot water (about 80°C) and transferred into a 100-mL separating funnel. After shaking and standing for several minutes, the bottom layer (aqueous phase) containing the FFA was discarded. The oil-containing top layer was transferred into a McCartney bottle and dried overnight at 80°C in a vacuum oven. The absence of FFA was confirmed by thin-layer chromatography with a solvent system of petroleum ether, diethyl ether, and formic acid (210:90:0.4 by vol) and viewed in iodine vapor.

**Extraction of high-melting glycerides (HMG).** HMG were prepared according to the method of D'Souza *et al.* (19). Each sample (commercial shortenings and experimental blend) was melted in an oven at 60°C and dissolved in acetone (1:20 wt/vol). The solution was left overnight to crystallize at

10 ± 1°C in a refrigerator. The fat crystals were filtered on a sintered glass filter through a 0.45-µm nylon filter. Subsequently, the solvent residue was removed from the crystals by drying at 30°C in a vacuum oven. Duplicate runs were carried out for the HMG extraction.

**FA composition.** The shortenings and their HMG fractions were melted completely at 60°C in an oven and filtered using a Whatman filter paper #4. A total of 50 mg of each sample was then weighed in a 2-mL screw-capped vial, and 1 mL of hexane and 0.05 mL of 30% sodium methoxide methanolic solution were added. The mixture was vortexed and left to stand for 5 min at room temperature (20). From the clear upper ester-containing layer, 0.3 µL was injected into a gas chromatograph (model GC-17A; Shimadzu Corporation, Kyoto, Japan) equipped with a flame-ionization detector. The column used was a polar capillary column model BPX70 (0.32 mm internal diameter, 30 m length, 0.25 µm film thickness; SGE Australia Pty. Ltd., Ringwood, Australia). The detector and injector temperatures were 240°C. The oven temperature, initially at 115°C, was increased to 180°C at a rate of 8°C/min. The carrier gas (helium) flow rate was 50 mL/min.

**Triglyceride (TG) composition.** The TG compositions of the shortenings and their HMG fractions were determined using HPLC as described by Ghazali *et al.* (11). The sample was dissolved in chloroform (5% wt/vol), and 10 µL of the sample was autoinjected (Shimadzu SIL-10 AD) into the HPLC system (Shimadzu LC-10 AD liquid chromatograph and RID-6A Shimadzu refractive index detector). The average particle size of the column was 5 µm, and a mixture of acetone and acetonitrile (63.5:36.5 vol/vol) was used for the mobile phase. The flow rate was 1 mL/min, and the oven temperature was set at 30°C.

**Polymorphic form.** X-ray diffraction analysis was used to determine the polymorphic forms of the fat crystals in the shortenings, as described in AOCS method Cj 2-95 (21). The camera was an Enraf Nonius Model FR592 (Delft, The Netherlands). The samples were analyzed using a compartment cell with a temperature-controlled holder. Kodak scientific imaging film (Eastman Kodak Co., Rochester, NY) was used, and the spacing on the X-ray was measured with an Enraf Nonius Guinier viewer. The instrument was fitted with a fine-focus copper X-ray tube. The sample holders were flat stainless-steel plates with a rectangular hole.

**Melting and cooling characteristics and SMP.** A differential scanning calorimeter (DSC), model PerkinElmer DSC-7 (Norwalk, CT), was used to measure the melting and crystallization temperatures of the samples. The samples were first melted in the DSC pans at 80°C and held for 15 min before cooling to -40°C at a rate of 10°C/min. The samples were then held for another 15 min before heating from -40°C to 80°C at a heating rate of 5°C/min. Endothermic and exothermic peak temperatures were then designated as the melting and crystallization temperatures, respectively. SMP of the samples were determined as described in AOCS method Cc 3-25 (21).

**Solid fat content (SFC).** The solid content of the shortenings at temperatures ranging from 5 to 50°C, at 5°C intervals, were recorded by using a Bruker Minispec pNMR Analyzer Model no.120 (Rheinstetten, Germany). This was done according to PORIM method p4.9 (22).

## RESULTS AND DISCUSSION

**FA and TG compositions.** The FA compositions of the solid frying shortenings and the experimental PS/PKO blend, as well as their respective HMG, are shown in Table 1. Both of the imported frying shortenings (Samples D and E) contained more unsaturated FA (about 67%) than Samples A, B, and C (about 45%). Judging from the 18:1*t* content, Samples D and E contained some hydrogenated fats. *Trans* FA were not found in Samples A, B, and C. In both Samples D and E, the majority of *trans* FA were monoene (18:1). The liquid oil of Samples A, B, and C, was most likely to be palm oil or palm olein, based on their high 16:0 (palmitic acid content). The level of 16:0 in palm oil is 38.0% (23), while other oils have lower levels of 16:0. Since Samples A, B, and C did not contain any hydrogenated fat, the hard stock of the shortenings was most likely PS. By assuming that (i) PS contains 60.5% of 16:0 (24), (ii) palm olein contains 38.0% of 16:0 (23), and that no other oil is added to the formulations, back calculation shows that Samples A, B, and C contained about 53% PS; hence, the experimental shortening was produced by incorporating PKO with 50% (by weight) PS.

On the other hand, Samples D and E were made from soybean oil as stated on the labels. The presence of *trans* 18:1 indicated the use of hydrogenated soybean oil as hard stock. Cottonseed oil was another constituent. Its addition greatly increased the content of 16:0 FA in the two shortenings because cottonseed oil contains higher levels (21.6%) of 16:0 FA than soybean oil (10.6%) (23). Cottonseed oil is added to increase the diversity of FA chain lengths and thereby

delay/prevent the formation of  $\beta$  crystals (25). Sample E contained more *trans* FA, and less 18:2 and 18:3 (linoleic and linolenic acids, respectively) FA than Sample D, indicating that its degree of hydrogenation was higher. Unlike the domestic samples, 12:0 (lauric acid) was the main FA in the experimental shortening and this was contributed by PKO.

For all the commercial samples, the 16:0 FA levels in HMG were higher than in their respective original fats (samples before extraction). The main FA remaining in Samples A, B, and C was 16:0 (>80%). The 18:0 levels in HMG of the domestic samples decreased somewhat compared to the original samples. This was probably due to the removal of oleic acid-containing TG with lower melting points, such as POL and POO (P, palmitic; O, oleic; L, linoleic), during the extraction. HMG of Samples D and E contained mainly 16:0, 18:0, 18:1, and 18:1*t*. The ratio of 18:1*t* to 18:1*c* in the HMG of Samples D and E was higher than in their original samples because of the higher melting points of *trans* FA than their *cis* counterparts (26). Levels of 18:0 FA in HMG of Samples D and E increased compared to the original samples.

For both the transesterified PS/PKO blend and its control (untransesterified), the level of 12:0 decreased, whereas 16:0 increased in the HMG fraction. This is mainly due to the removal of TG containing 12:0 FA, which is mostly present in the TG with lower melting points during the extractions. Transesterification did not much alter the composition of 12:0 and 16:0 in the blend, but it increased the level of 12:0 and reduced the 16:0 level in the HMG compared to the control.

Table 2 shows the TG composition of the frying shortenings by carbon number, as well as that of their HMG fractions. High levels of C<sub>50</sub> TG and low levels of C<sub>54</sub> TG in the original samples confirmed that Samples A, B, and C contained palm oil or palm olein (27). The level of C<sub>48</sub> TG, mainly consisting of tripalmitin (PPP), increased greatly in the HMG fractions of these samples. The reverse was true for C<sub>52</sub> TG. Since Samples D and E consisted mainly of C<sub>16</sub> and

**TABLE 1**  
Fatty Acid Composition<sup>a</sup> (% peak area) of the Experimental and Commercial Solid Frying Shortenings and Their High-Melting Glyceride (HMG) Fraction

Fatty acid	8:0	10:0	12:0	14:0	16:0	18:0	18:1 <i>c,i</i>	18:1 <i>t</i>	18:2 <i>c,c</i>	18:2 <i>ct,tc</i>	18:2 <i>t,t</i>	18:3
Sample												
A	—	—	0.59	1.95	49.28	3.78	37.57	—	6.82	—	—	—
B	—	—	0.42	1.92	49.55	4.49	37.60	—	6.01	—	—	—
C	—	—	2.51	2.55	46.49	3.33	38.53	—	6.58	—	—	—
D	—	—	—	0.47	22.34	10.36	29.65	9.57	23.75	0.69	1.03	2.12
E	—	—	—	Trace	24.13	8.95	31.46	12.25	17.19	4.17	1.84	Trace
Transesterified blend	3.71	3.75	41.40	10.10	27.93	2.11	8.65	—	2.35	—	—	—
Control	4.04	4.09	43.23	10.59	27.87	1.07	7.63	—	1.48	—	—	—
HMG												
A	—	—	0.19	2.10	80.16	3.49	11.79	—	2.25	—	—	—
B	—	—	Trace	2.46	84.69	3.02	8.21	—	1.46	—	—	—
C	—	—	1.20	3.42	82.55	2.90	8.31	—	1.51	—	—	—
D	—	—	—	1.04	40.05	29.88	9.32	13.62	5.85	Trace	Trace	0.32
E	—	—	—	1.65	42.10	33.60	8.03	12.81	2.47	—	—	Trace
Transesterified blend	Trace	0.98	14.58	8.01	72.48	2.04	2.42	—	Trace	—	—	—
Control	Trace	Trace	9.51	6.05	79.73	2.07	2.66	—	Trace	—	—	—

<sup>a</sup>*c* = *cis*; *t* = *trans*; and *i* = positional and geometrical isomers not identified.

**TABLE 2**  
**Triglyceride Composition (% peak area) in Carbon Number of the Experimental and Commercial Solid Frying Shortenings and Their High-Melting Glycerides (HMG) Fraction**

Triglyceride	C <sub>28</sub>	C <sub>30</sub>	C <sub>32</sub>	C <sub>34</sub>	C <sub>36</sub>	C <sub>38</sub>	C <sub>40</sub>	C <sub>42</sub>	C <sub>44</sub>	C <sub>46</sub>	C <sub>48</sub>	C <sub>50</sub>	C <sub>52</sub>	C <sub>54</sub>
Sample														
A	—	—	—	—	—	—	Trace	0.52	1.85	0.81	10.08	38.77	39.03	8.94
B	—	—	—	—	Trace	Trace	Trace	0.47	1.24	1.04	15.43	40.34	34.94	6.54
C	—	—	—	—	—	—	Trace	0.68	1.91	4.30	9.30	37.91	35.79	10.11
D	—	—	—	—	—	—	—	—	—	Trace	2.04	8.83	32.30	56.83
E	—	—	—	—	—	—	—	—	—	Trace	1.81	3.27	30.45	64.47
Transesterified blend	0.24	1.29	2.78	4.48	8.94	4.63	9.59	2.33	8.36	5.53	16.52	17.20	11.56	6.55
Control	0.18	0.88	3.96	6.27	9.48	6.80	6.89	1.45	6.24	2.85	19.48	19.37	11.36	4.79
HMG														
A	—	—	—	—	—	—	—	—	0.43	—	27.27	51.57	14.90	5.83
B	—	—	—	—	—	—	—	—	0.48	—	30.63	48.82	13.72	5.35
C	—	—	—	—	—	—	—	Trace	0.59	0.34	43.41	38.12	10.73	6.81
D	—	—	—	—	—	—	—	—	—	—	6.38	10.06	34.72	48.84
E	—	—	—	—	—	—	—	—	—	—	4.13	9.96	36.49	49.42
Transesterified blend	0.01	0.12	0.29	0.50	0.88	0.72	1.79	1.60	3.24	0.89	57.88	20.62	3.14	8.32
Control	0.05	0.06	0.41	0.56	1.05	0.74	1.03	0.71	0.47	0.36	66.66	21.28	1.44	5.18

C<sub>18</sub> FA, it can be concluded that the C<sub>48</sub> TG in the HMG consisted mainly of PPP, which was derived from cottonseed oil. Levels of C<sub>54</sub> TG in both samples were slightly higher in the original fats than their HMG.

The blending of PS and PKO in the transesterified blend gave a fat mixture that is composed of almost all TG species that can be found in palm oil fruit. The TG types ranged from C<sub>28</sub> to C<sub>54</sub>. A high diversity of TG and FA is important in fat products, particularly in the production of margarines and shortenings. The concentrations of TG with carbon numbers ranging between C<sub>40</sub> and C<sub>46</sub> in the transesterified blend increased, and TG with higher (C<sub>48</sub>, C<sub>50</sub>) and lower (C<sub>32</sub> to C<sub>38</sub>) carbon numbers decreased compared to the control. Thus, the net change of TG was due to the rearrangement of the FA from the lower- and higher-melting TG to form more TG that had melting points in between. Some TG were also hydrolyzed to form mono- and diglycerides and FFA. Most of the TG with carbon numbers below C<sub>46</sub> in both blends were removed during the extraction of the HMG fraction. The two main TG that remained were C<sub>48</sub> and C<sub>50</sub>, which consisted mainly of PPP and POP, respectively. The levels of these TG (C<sub>48</sub> and C<sub>50</sub> TG) were lower in the HMG fraction of the transesterified blend than the control, as some have been hydrolyzed or transformed into low-carbon-number TG.

**Polymorphic forms.** The short spacings of the  $\beta'$  form are at 4.2 and 3.8 Å, and that of the  $\beta$  form is at 4.6 Å (28). Levels of  $\beta$  and  $\beta'$  crystals in mixtures are estimated by the relative intensity of the short spacings at 4.2 and 4.6 Å. The polymorphic forms of the samples are shown in Table 3. Sample B was found to contain only  $\beta$  crystals. Samples A and C contained mixtures of  $\beta'$  and  $\beta$  crystals, with the  $\beta$  form predominating; Samples D and E also contained mixtures of  $\beta$  and  $\beta'$  crystals, but with the  $\beta'$  crystals predominating. This explained why, by visual inspection, the imported samples had a smoother surface than the domestic ones.

The levels of C<sub>48</sub> and C<sub>54</sub> TG in the HMG of domestic shortenings ranged between 27.3 and 43.4 % and between 4.2 and 4.9%, respectively, whereas the levels of C<sub>50</sub> TG, which mainly contained POP, were high, ranging between 38.1 and 51.6%. POP is a  $\beta$ -tending TG (29). The relatively high level of C<sub>48</sub> and C<sub>50</sub> TG in the domestic shortenings explained their tendency for  $\beta$  crystallinity. In the HMG of Samples D and E, the C<sub>54</sub> TG consisted mainly of 18:0 and 18:1t FA. The 18:1t FA in the TG molecule were polymorphically similar to 18:0 FA. TG containing 18:0 and 18:1t are very  $\beta$ -tending. Therefore, Samples D and E had both  $\beta'$  and  $\beta$  forms.

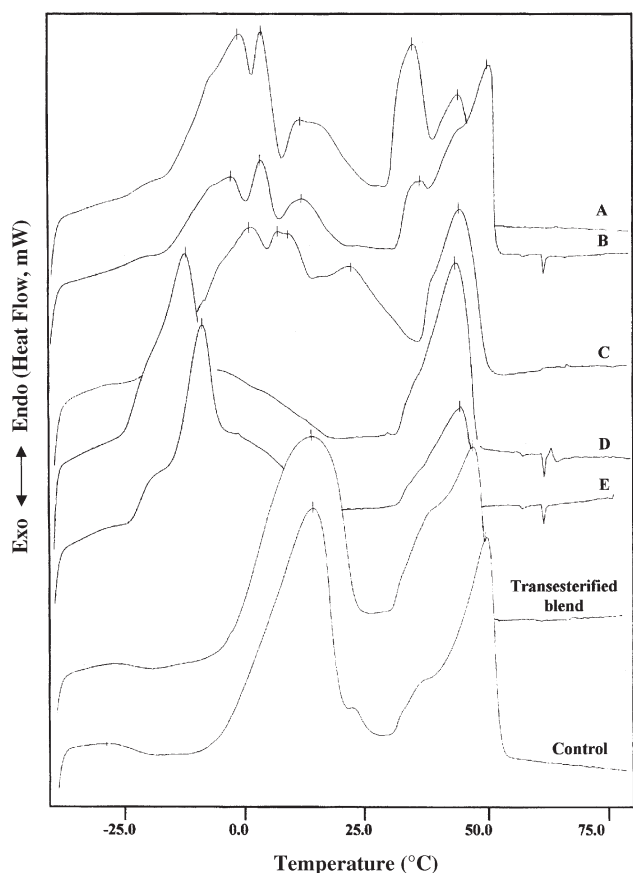
For the transesterified and control blends, incorporation of PKO into PS increased the diversity of TG and FA pools in the mixture and thus altered the crystal forms of PS, which were primarily of  $\beta$  crystals with a small percentage of  $\beta'$ , to a much more  $\beta'$ -tending fat. HMG of the transesterified fat exhibited more  $\beta'$  crystals than the control. High levels of C<sub>48</sub> and C<sub>50</sub> TG in HMG of the control blend were responsible for the formation of more  $\beta$  crystals. D'Souza *et al.* (25) reported that HMG of margarines that consisted of high levels (>50%) of C<sub>48</sub> or C<sub>54</sub> TG were normally in the  $\beta$  form. This is because the C<sub>48</sub> TG (3 × 16-carbon number FA) and C<sub>54</sub> TG (3 × 18-carbon number FA) result in a more ordered packing near the methyl end regions, leading to more chances of a tightly knit crystal lattice. Therefore, the more C<sub>48</sub> and C<sub>54</sub> TG are in the fats, the more ordered the structure and the higher the tendency for  $\beta$  crystals to be formed. Transesterification reduced the C<sub>48</sub> and C<sub>50</sub> TG in the HMG, and hence contained more  $\beta'$  crystals. Unlike HMG of the control blend, HMG of the transesterified blend also consisted of relatively higher levels of C<sub>40</sub> to C<sub>46</sub> TG, which contributed to a greater diversity in the FA pool in HMG, thus promoting  $\beta'$  crystal formation. Compared to the domestic shortenings, the experimental sample should have better polymorphic stability over wider storage temperature ranges (1).



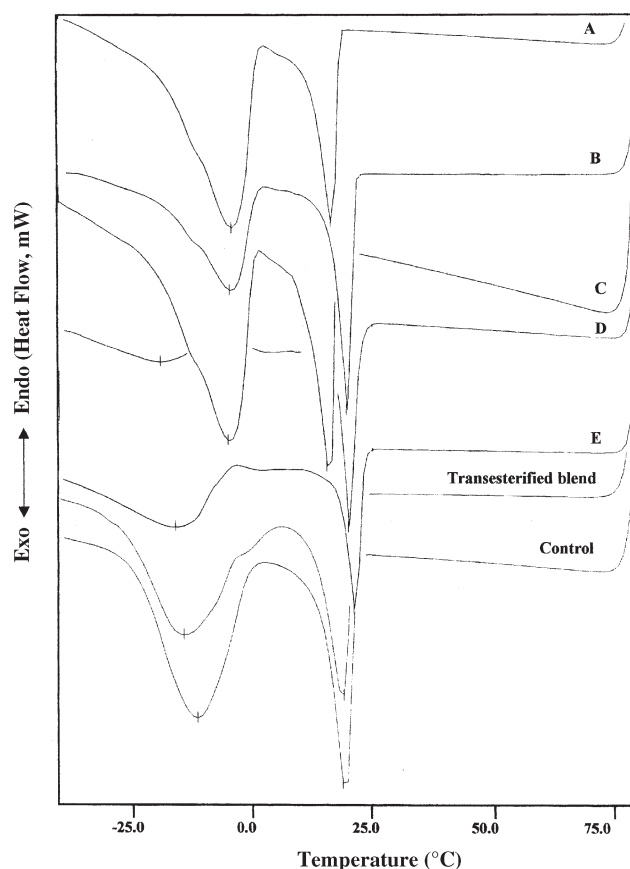
**TABLE 3**  
Polymorphic Forms and Slip Melting Point (SMP) of the Experimental and Commercial Solid Frying Shortenings

Sample	Polymorphic form	SMP (°C)
A	$\beta \gg \beta'$	44.0
B	$\beta$	49.7
C	$\beta \gg \beta'$	37.8
D	$\beta' \gg \beta$	42.3
E	$\beta' \gg \beta$	43.0
Transesterified blend	$\beta' \gg \beta$	47.0
Control	$\beta' > \beta$	49.3

**Melting and cooling characteristics and SMP.** The DSC melting thermograms of the commercial and experimental frying shortenings are displayed in Figure 1. All the shortenings exhibited more than one endothermic peak, indicating that the samples contained different-melting components. With reference to previous studies (30–32), the endothermic peaks at high melting region (35–55°C) in Samples A, B, and C mostly contained mixtures of  $\beta$  and  $\beta'$  crystals, as the peaks' temperature ranges were rather wide (35–50°C), with  $\beta$  crystals predominating. On the other hand, the melting profiles of soybean oil-based Samples D and E were found to be similar to each other but different from palm oil-based shortenings (Samples A, B, and C) in that the former exhibited



**FIG. 1.** Differential scanning calorimetry heating thermograms of the experimental and commercial solid frying shortenings run at  $-40$  to  $80^\circ\text{C}$ . The heating rate was  $5^\circ\text{C}/\text{min}$ .

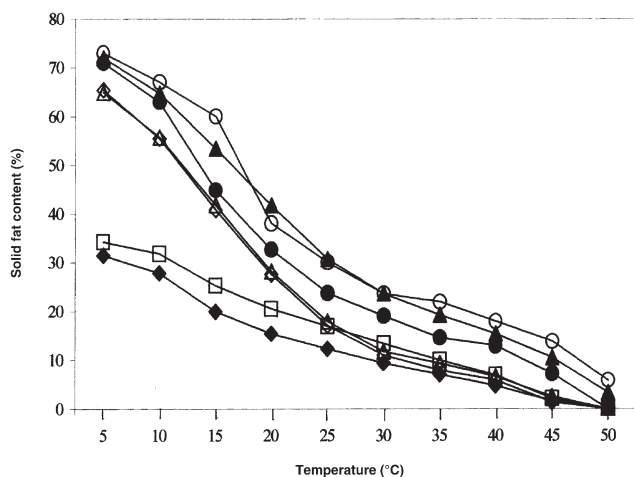


**FIG. 2.** Differential scanning calorimetry cooling thermograms of the experimental and commercial solid frying shortenings run at  $80$  to  $-40^\circ\text{C}$ . The cooling rate was  $-10^\circ\text{C}/\text{min}$ .

only one melting peak at the lower temperature range. This was similar to the findings of deMan *et al.* (33) in their work on shortenings that contained mixtures of  $\beta$  and  $\beta'$  crystals, with  $\beta'$  predominating.

Meanwhile, both the transesterified and control PS/PKO blends exhibited two endothermic peaks. After transesterification, the size of the endothermic peak at high temperature region was reduced. Since the peak represents the higher-melting TG of the blend, reduction in peak size resulted in a lower SMP in the transesterified blend ( $47.0^\circ\text{C}$ ) (Table 3) than the control ( $49.3^\circ\text{C}$ ). Formation of more lower- and middle-melting TG caused the peak at low temperature region ( $-10$  to  $25^\circ\text{C}$ ) of the transesterified blend to broaden compared to the control.

Figure 2 shows the cooling curves of the frying shortenings. The thermograms of the cooling process were simpler than those from the heating process. All samples had a sharp exothermic peak at the high temperature region ( $15$ – $25^\circ\text{C}$ ) and a broad exothermic peak at the lower temperature region ( $-25$ – $0^\circ\text{C}$ ). These were duly named high-T and low-T peaks, respectively. For palm oil products, high-T and low-T peaks represent stearin and olein fractions, respectively (32). The high-T peak for palm oil-based commercial samples had a higher crystallization temperature than the imported ones.



**FIG. 3.** Changes in solid fat content of the experimental and commercial solid frying shortenings as a function of temperature ( $^{\circ}\text{C}$ ). ( $\Delta$ , Sample A;  $\blacktriangle$ , Sample B;  $\diamond$ , Sample C;  $\square$ , Sample D;  $\blacklozenge$ , Sample E;  $\bullet$ , transesterified blend; and  $\circ$ , control).

The crystallization temperatures of low-T peaks of both the transesterified and control blends were more comparable to the imported samples than the domestic ones. Transesterification introduced more low-melting TG, and this broadened the low-T peak and reduced the crystallization temperature.

The SMP of the samples are shown in Table 3. SMP of frying shortenings must not be too high even though it eases bulk handling, because the shortenings will take a longer time to melt during frying and leave a waxy aftertaste in the mouth (26). In this study, Sample C had an SMP ( $37.8^{\circ}\text{C}$ ) close to body temperature. This is much desired compared to the rest, which had SMP above  $40^{\circ}\text{C}$ . The flavors of the fried food trapped by Sample C may be released when the shortenings melt in the mouth. This will provide better eating characteristics (23) than other samples. The SMP of Samples A, B, D, E, and the experimental sample could be reduced by reducing the levels of the high-melting components in the shortenings. The SMP of the transesterified blend ( $47.0^{\circ}\text{C}$ ) fell within the range ( $37.8$ – $49.7^{\circ}\text{C}$ ) of the domestic samples but was higher than the imported ones ( $42.3$ – $43.0^{\circ}\text{C}$ ).

**SFC.** Hard fats are added to shortenings to extend the plastic range, which improves the tolerance to high temperatures, and for crystal type and stability. Shortenings become brittle above their plastic range and soft below the range (34). Figure 3 shows the changes in SFC of the frying shortenings with temperature. By taking the plastic range of the samples at SFC of 15–25% (34), Samples A, B, and C fell within a higher plastic temperature range than the imported samples (Samples D and E). The domestic shortenings are manufactured to have a better workability at higher temperatures because they are used in a tropical climate (35). Sample B had the steepest SFC profile. All samples melted completely at  $50^{\circ}\text{C}$  except Sample B. Even though Samples A, B, and C had similar FA compositions, the SFC of Sample B were higher than those of Samples A and C throughout the temperature

ranges. This might be due either to Sample B containing palm oil instead of palm olein or consisting of slightly more PS. The more PS the fat contains, the higher the SFC is at a given temperature.

The SFC values of Samples D and E were low (30–35%) even at  $5^{\circ}\text{C}$ . It is a trend in Western countries to incorporate liquid oil into shortenings and margarine as much as possible (35). On the other hand, the domestic shortenings contain relatively high levels of SFC at low temperatures. Generally, imported samples fell within a wider plasticity range than the domestic samples. Sample D, for instance, had a wider plastic range of  $12^{\circ}\text{C}$  ( $15$ – $27^{\circ}\text{C}$ ) than Sample C, which had a plastic range of  $6^{\circ}\text{C}$  ( $21$ – $27^{\circ}\text{C}$ ).

The transesterified blend had a lower SFC than the control for all temperatures, with both profiles mimicking each other. The SFC profile of the transesterified blend was similar to those of Samples A, B, and C. The SFC of the control shifted from  $15$ – $20^{\circ}\text{C}$  to  $10$ – $15^{\circ}\text{C}$  in the transesterified blend. This drop is due to the production of more low-melting TG, which melted at this temperature range, and is similar to the results of Lai *et al.* (12). The plastic range ( $10^{\circ}\text{C}$ ) of the transesterified blend was between  $25$  and  $35^{\circ}\text{C}$ , which fell within the commercial samples ( $5$ ,  $13$ ,  $6$ ,  $12$ , and  $8^{\circ}\text{C}$  for Samples A, B, C, D, and E, respectively).

Characterization of the commercial plastic frying shortenings provides a better understanding of the relationship between the functionality of the frying shortenings and their physical properties, such as polymorphic forms, SMP, melting and cooling profiles and SFC. These physical properties are dictated by the TG and FA compositions of the shortenings, especially their HMG fractions. The experimental shortening (transesterified PS/PKO, at 1:1 w/w ratio) had physical properties especially similar to the domestic samples. However, the blend still needs to be optimized to meet its function as a frying shortening.

## ACKNOWLEDGMENTS

The authors acknowledge the financial support received from the Intensification of Research in Priority Areas (IRPA) program awarded to Prof. H.M. Ghazali, and would like to thank Dr. Chong Chiew Let of the Malaysian Palm Oil Board (MPOB) and his assistants for assisting in the SFC and X-ray diffraction analyses.

## REFERENCES

- Scavone, T.A., Beta-Prime Stable Low-Saturated, Low *Trans*, All Purpose Shortening, U.S. Patent 5,470,598 (1995).
- Crosby, T.G., Pourable Shortening Containing Lauric Fat and Method for Preparing the Same, U.S. Patent 5,268,191 (1993).
- Price, J.E., Pourable Shortening and Process for Its Preparation, U.S. Patent 4,889,740 (1989).
- Almendingen, K., O. Jordal, P. Kierulf, B. Sandstad, and J.I. Pederden, Effects of Partially Hydrogenated Fish Oil, Partially Hydrogenated Soybean Oil, and Butter on Serum Lipoproteins and Lp(a) in Men, *J. Lipid Res.* 36:1370–1384 (1995).
- Kris-Etherton, P.M., *Trans* Fatty Acid and Coronary Heart Disease Risk: Report of the Expert Panel on *Trans* Fatty Acids and Coronary Disease, *Am. J. Clin. Nutr.* 62:655–667 (1995).

6. Pantzaris, T.P., *Pocketbook of Palm Oil Uses*, Palm Oil Research Institute of Malaysia, Ministry of Primary Industries, Kuala Lumpur, 1987, pp. 23–47.
7. Teah, Y.K., T. Suzukim, M. Shaarin, and H.H. Chuan, Increased Usage of Palm Oil by Interesterification in Japanese Margarine, *PORIM Report*:1–7 (1993).
8. Bhattacharyya, S., and D.K. Bhattacharyya, Utilization of Mowrah Oil in Edible Fat Products by Fractionation, Enzymatic Acidolysis and Their Combination, *J. Oil Tech. Assoc. India* 2:39–41 (1996).
9. Graille, M., D. Montet, and J.M. Muderhwa, Making Value-Added Products from Palm Oil by 1,3-Regioselectivity Enzymatic Interesterification, *Elaeis* 4:1–10 (1992).
10. Ghazali, H.M., A. Maisarah, S. Yusof, and M.S.A.M. Yusoff, Triglyceride Profiles and Melting Properties of Lipase-Catalyzed Transesterified Palm Stearin and Coconut Oil, *Asia Pac. J. Mol. Biol. Biotechnol.* 3:280–289 (1995).
11. Ghazali, H.M., S. Hamidah, and Y.B. Che Man, Enzymatic Transesterification of Palm Olein with Nonspecific and 1,3-Specific Lipases, *J. Am. Oil Chem. Soc.* 72:633–639 (1995).
12. Lai, O.M., H.M. Ghazali, and C.L. Chong, Physical Properties of *Pseudomonas* and *Rhizomucor miehei* Lipase-Catalyzed Transesterified Blends of Palm Stearin: Palm Kernel Olein, *Ibid.* 75:953–959 (1998).
13. Lai, O.M., H.M. Ghazali, and C.L. Chong, Effect of Enzymatic Transesterification on the Melting Points of Palm Stearin–Sunflower Oil Mixtures, *Ibid.* 75:881–886 (1998).
14. Zeitoun, M.A.M., W.E. Neff, G.R. List, and T.L. Mounts, Physical Properties of Interesterified Fat Blends, *Ibid.* 70:467–471 (1993).
15. Cho, F., J.M. deMan, and O.B. Allen, Physical Properties and Composition of Low *Trans* Canola/Palm Blends Modified by Continuous Enzymatic Interesterification, *Elaeis* 6:39–49 (1992).
16. Graille, J., M. Pina, and D. Montet, Biotechnology of Lipids: Some Possible Applications, *Oleagineux* 43:188–190 (1998).
17. Ray, S., and D.K. Bhattacharyya, Comparative Nutritional Study of Enzymatically and Chemically Interesterified Palm Oil Products, *J. Am. Oil Chem. Soc.* 72:327–330 (1995).
18. Long, K., H.M. Ghazali, A. Ariff, and C. Brucke, Acidolysis of Several Vegetable Oils by Mycelium-Bound Lipase of *Aspergillus flavus* Link, *Ibid.* 74:1121–1128 (1997).
19. D'Souza, V., J.M. deMan, and L. deMan, Chemical and Physical Properties of the Solid Fats in Commercial Soft Margarines, *Ibid.* 69:1198–1205 (1992).
20. Timms, R.E., Artifact Peaks in the Preparation and Gas–Liquid Chromatography Determination of Methyl Esters, *Aus. J. Dairy Technol.* 33:4–6 (1978).
21. AOCS, *Official and Tentative Methods of the American Oil Chemists' Society*, 4th edn., American Oil Chemists' Society, Champaign, 1990.
22. PORIM, *PORIM Test Methods*, Malaysian Palm Oil Board, Ministry of Primary Industries, Kuala Lumpur, Malaysia, 1995, pp. 134–142.
23. O'Brien, R.D., *Fats and Oils: Formulating and Processing for Applications*, Technomic, Lancaster, PA, 1998, pp. 10–18, 336–338.
24. Chong, C.L., Chemical and Physical Properties of Palm Oil and Palm Kernel Oil, in *Selected Readings on Palm Oil and Its Uses*, edited by the Technical Committee of 1994 Palm Oil Familiarization Program, Kuala Lumpur, MPOB, Ministry of Primary Industry, Malaysia, 1994, pp. 60–70.
25. D'Souza, V., L. deMan, and J.M. deMan, Chemical and Physical Properties of the High-Melting Glyceride Fractions of Commercial Margarines, *J. Am. Oil Chem. Soc.* 68:153–162 (1991).
26. Idris, N.A., L. deMan, T.S. Tang, and C.L. Chong, Chemical Composition and Physical Properties of Soft (tub) Margarines Sold in Malaysia, *Ibid.* 73:995–1001 (1996).
27. Siew, W.L., T.S. Tang, F.C.H. Oh, C.L. Chong, and Y.A. Tan, Identity Characteristics of Malaysian Palm Oil Products: Fatty Acid and Triglyceride Composition and Solid Fat Content, *Elaeis* 5:38–46 (1993).
28. D'Souza, V., J.M. deMan, and L. deMan, Short Spacings and Polymorphic Forms of Natural and Commercial Solid Fats: A Review, *J. Am. Oil Chem. Soc.* 67:835–843 (1990).
29. deMan, J.M., and L. deMan, Palm Oil as a Component for High Quality Margarine and Shortening Formulations, *Malaysian Oil Sci. Technol.* 4:56–60 (1995).
30. Kawamura, K., The DSC Thermal Analysis of Crystallization Behavior in Palm Oil II, *J. Am. Oil Chem. Soc.* 57:48–52 (1980).
31. Busfield, W.K., and P.N. Proschogo, Thermal Analysis of Palm Stearine by DSC, *Ibid.* 67:171–175 (1990).
32. Che Man, Y.B., and P.Z. Swe, Thermal Analysis of Failed-Batch Palm Oil by Differential Scanning Calorimetry, *Ibid.* 72:1529–1532 (1995).
33. deMan, L., J.M. deMan, and B. Blackman, Physical and Textural Characteristics of Some North American Shortenings, *Ibid.* 68:63–69 (1991).
34. Metzroth, D.J., Shortening: Science and Technology, in *Bailey's Industrial Oil & Fat Products*, 5th edn., edited by Y.H. Hui, John Wiley & Sons, New York, 1996, Vol. 3, pp. 115–160.
35. deMan, J.M., Functionality of Fats in Food Products, in *Teach-in Program* organized by Malaysian Oil Scientists and Technologists Association (MOSTA), on 21 March, 1999, at Crystals Crown Hotel, Petaling Jaya, Kuala Lumpur, Malaysia.

[Received December 14, 2000; accepted September 13, 2001]