Production of Zero-trans Margarines from Blends of Virgin Coconut Oil, Palm Stearin and Palm Oil

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This research investigated the possibility of producing zero-trans packet margarines from virgin coconut oil (VCO). VCO was mixed with palm stearin (PS) and/or palm oil (PO) in six weight proportions in order to prepare feedstocks for the production of experimental margarines. The fat blends included two binary blends of PS/VCO (40:60 and 30:70) and four ternary blends of PS/VCO/PO (30:40:30, 20:40:40, 30:50:20 and 20:50:30). The six fat blends and the experimental margarines produced from the blends were characterized and compared with commercial trans- (CTM) and zero-trans (CZTM) margarines in terms of microstructure, polymorphism, solid fat content, melting and crystallization behavior, textural and sensory properties. It was found that the binary fat blend which contained 30% PS and 70% VCO was the most suitable blend to be used as feedstock for the production of zero-trans packet margarine. The blend exhibited a tendency to crystallize into β’ structure with a good cooling effect and a low SFC value at body temperature, indicating that it would not cause waxy mouthfeel when consumed. In addition, the margarine produced from the blend demonstrated good consistency with a hardness characteristic close to that of a commercial trans-packet margarine and also received the highest score for overall acceptability.

Keywords: margarine, virgin coconut oil, palm stearin, palm oil, zero-trans

Introduction

Margarine is a water-in-oil emulsion food product and by U.S. FDA standards of identity must contain at least 80% fat (Fomuso and Akoh, 2011). Margarine was originally developed in 1869 as an alternative to butter which, during that period, was in short supply and expensive (Chrysan, 1996). The aqueous phase of margarine is composed of water, salt, and preservatives. The fat phase consists of a blend of liquid and solid triglycerides, antioxidants and emulsifiers (Fomuso and Akoh, 2011). Lecithin, distilled monoglyceride, and distilled diglyceride are common emulsifiers added to the fat phase together with flavoring agents and coloring agents (Miskandar et al., 2002). Characteristics which determine margarine quality, such as spreadability and consistency, are important. These characteristics are influenced by many process conditions, such as crystallization temperature, emulsion temperature, agitation rate, cooling rate, etc. The structural stability of margarine is influenced by the actual amount of solid fat present and by the characteristics of the crystal lattice (Chrysan, 1996). The β’ form is the most desirable in margarines because it gives smooth texture to the products (D’Souza et al., 1990).

The product range of margarine consists of table margarines, bakery margarines, and specialized puff pastry margarines. Table margarines can be divided into two main types: packet margarines, which are designed to be spreadable at ambient temperature, and tub margarines, which are spreadable on removal from the refrigerator at a temperature of 5 – 10°C (Laia et al., 2000). Packet margarines usually exhibit much higher solid fat content (SFC) than those of tub margarines in the SFC curves. When packet margarines are intended for use in a tropical climate, with ambient temperatures around 30°C, higher solid contents are required (Rasid et al., 1996).

Most margarine fats are prepared from partial hydrogenation where trans fatty acid (TFA) formation is inevitable (Adhikari et al., 2010a). The partial hydrogenation process

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is used to impart desirable physical and textural properties to margarines (Kim et al., 2008). Recently, it has become known that potential adverse health effects, such as increased risk for coronary heart disease, have been associated with the consumption of semi-solid fats containing trans fatty acids from partially hydrogenated oils (Enig, 1996). Therefore, semi-solid fat with low or no trans fatty acids needs to be developed in the food industry (Adhikari et al., 2010b).

Coconut oil is edible oil obtained from matured coconuts. Commercial coconut oil is produced from the dried kernel meat of coconut or copra, which is exposed to very high temperatures until most of the moisture is removed, and goes through refining, bleaching and deodorizing processes (Marina et al., 2009). On the contrary, virgin coconut oil (VCO) is obtained from fresh, mature kernel of the coconut by mechanical or natural means, with or without the use of heat and without undergoing chemical refining, bleaching, or deodorizing in order to protect the oil’s essential properties (Villarino et al., 2007). Coconut oil is thought to be beneficial to health because it contains high amount of medium-chain triglycerides, which are made mainly of saturated fatty acids with chain length from 6 to 12 carbon atoms (Che Man and Marina, 2006). Medium-chain triglycerides are hydrolyzed faster and more completely than long-chain triglycerides (Adhikari et al., 2010b). In addition, it has been reported that medium-chain triglycerides may reduce the incorporation and storage of dietary fats and oil in adipose tissue (Tsuiji et al., 2001). In 2004, Nevin and Rajamohan reported that VCO obtained by wet process had a beneficial effect in lowering lipid components by reducing total cholesterol in serum and tissues. The polyphenol fraction of VCO was also found to be capable of preventing in vitro LDL oxidation with reduced carbonyl formation.

In this study, zero-trans packet margarines were produced from blends of VCO, palm stearin (PS) and palm oil (PO). The three oils were blended into different weight proportions and their chemical and physical properties as well as crystallization behavior were studied. Then, the fat blends were used as feedstocks for the production of zero-trans experimental margarines. Property changes of the experimental margarines during storage for eight weeks at three different temperatures were characterized and compared with those of commercial margarines in order to select the best formulation for the margarine produced from VCO. In order to maximize the use of VCO, which is widely available in Thailand and other Asian countries, this desired margarine should consist of a maximum weight proportion of VCO, and should be stable (i.e. can withstand a tropical climate) and exhibit physical and textural properties close to those of commercial packet margarines.

**Materials and Methods**

**Materials**  VCO 100% cold press with an iodine value (IV) of 9.4 g I₂/100 g was purchased from a local supermarket (Bangkok, Thailand). Refined, bleached and deodorized PO (IV of 47.1 g I₂/100 g) was kindly supplied by a local palm oil refiner. PS (IV of 38.5 g I₂/100 g) was provided by Moragot Industries PCL (Bangkok, Thailand). Distilled monoglyceride, supplied by Berli Jucker (Bangkok, Thailand), was used as an emulsifier. Two commercial margarines, a trans-packet margarine and an imported zero-trans margarine, were purchased from a supermarket in Bangkok, Thailand. All other reagents and solvents were of analytical or chromatographic grade.

**Trans-fatty acid analysis**  The contents of trans-fatty acids in three pure fat samples (PS, VCO and PO) were analyzed by using AOAC Official method 985.21 (AOAC, 1995).

**Fat blending**  Six fat blends of PS, VCO and PO were prepared. The proportions of the blends are given in Table 1. Two of the fat blends are binary, containing only PS and VCO whereas the rest are ternary, containing PS, VCO and PO. Different properties of the fat blends were characterized as described below. The amount of trans-fatty acids in all fat blends was calculated based on the proportion of the pure fats in each blend. Then, the fat blends were used as fat feedstocks for the production of experimental margarines.

**Preparation of commercial margarine fats**  Two margarine fats were separated from the two commercial margarines: trans- and zero-trans, following a method described by Kim et al. (2008). Briefly, the margarines were melted at 80°C, and the top fat layers were decanted into a separatory funnel and washed five times with warm water. To remove residual moisture, the fats were filtered through an anhydrous sodium sulfate layer with a Whatman filter paper (pore size = 0.45 μm) under vacuum. The anhydrous margarine fats obtained from commercial trans- and zero-trans margarines came from commercial trans- and zero-trans margarines.

<table>
<thead>
<tr>
<th>Blend</th>
<th>Composition (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PSC46</td>
<td>PS/VCO/PO = 40:60:0</td>
</tr>
<tr>
<td>PSC37</td>
<td>PS/VCO/PO = 30:70:0</td>
</tr>
<tr>
<td>PSCP352</td>
<td>PS/VCO/PO = 30:50:20</td>
</tr>
<tr>
<td>PSCP343</td>
<td>PS/VCO/PO = 30:40:30</td>
</tr>
<tr>
<td>PSCP253</td>
<td>PS/VCO/PO = 20:50:30</td>
</tr>
<tr>
<td>PSCP244</td>
<td>PS/VCO/PO = 20:40:40</td>
</tr>
</tbody>
</table>

*Abbreviations: PS, palm stearin; VCO, virgin coconut oil; PO, palm oil.*
were placed in an aluminum pan (30 µL capacity) and hermetically sealed. An empty pan served as reference. The system had an ATWAX capillary column (50 m long, 0.25 mm internal diameter and 0.20 µm film thickness). Compound identification was carried out using external standards of fatty acids methyl esters. Helium was used as a carrier gas with a flow rate of 0.5 mL/min and with a controlled initial pressure of 93.2 kPa at 120°C. N₂ and air were makeup gases. The injection temperature was 210°C, and the oven temperature program was held at 120°C for 3 min before increasing at a rate of 10°C/min to 220°C, holding at this temperature for 30 min, increasing at a rate of 5°C/min to 240°C, followed by holding at 240°C for 30 min. The split ratio was 100:1, the injection volume was 1 µL, and the detector temperature was 280°C. All margarine fats were analyzed after which their chromatograms were acquired. All fatty acid contents were given based on percentage area.

Characterization of solid fat content  SFC of the samples was measured by pulsed-nuclear magnetic resonance (p-NMR) spectrometer (Minispec-mq20, BRUKER, Karlsruhe, Germany). Changes in the SFC as a function of temperature between 15°C and 50°C and melting behavior of the fat blends and the commercial margarine fats were studied using a method for measuring SFC of fat for margarines developed by the “Joint Committee for the Analysis of Fats, Oils, Fatty Products, Related Products and Raw Materials (GA FETT)” as described by Fiebig and Luttke (2003).

Analysis of crystallization and melting profiles  The crystallization and melting profiles of the fat blends and the commercial margarine fats were determined with a Perkin-Elmer differential scanning calorimeter (DSC) (model DSC 8000, PerkinElmer Co., Norwalk, CT) following procedure Cj 1-94 recommended by AOCS (AOCS, 1998). The heat flow of the instrument was calibrated with indium (mp 156.6°C) as a reference standard. A fat sample of 6–8 mg was placed in an aluminum pan (30 µL capacity) and hermetically sealed. An empty pan served as reference. The samples were heated from room temperature to 80°C and held for 10 min to ensure homogeneity and to destroy any crystal memory. Then, the samples were cooled to −60°C at the rate of 5°C/min and held at this temperature for 30 min. This was followed by heating the sample at the rate of 5°C/min to 80°C. The crystallization and melting profiles were generated during the cooling and heating, respectively. The crystallization onset (Tₜ₀) and melting completion temperatures (Tₚ₅) were obtained from the peaks located at the highest temperature of each fat sample. Tₜ₀ and Tₚ₅ were considered to be the temperatures at which the crystallization began and the melting ended, respectively (Kim et al., 2008).

Polymorphic structure analysis  The crystal polymorphic forms of both the experimental fat blends and the commercial margarine fats were determined by an x-ray diffractometer (Rigaku TTRAX III, Rigaku Corporation, Tokyo, Japan). Scans were performed in wide-angle x-ray scattering (WAXS) from 15° to 25° with a scan speed and a step width of 2.7°/min and 0.02°, respectively. The samples were melted at 80°C for 30 min and then poured into rectangular plastic moulds (20 mm × 25 mm × 3 mm). Samples were later left to crystallize at 4°C for 24 h, after which they were analyzed (Kim et al., 2008). Generally, short spacings for the β’ form of fats are identified with two strong spacings at 3.88 and 4.20 Å or three strong spacings at 3.71, 3.97 and 4.27 Å (D’Souza et al., 1990). In addition, a strong short spacing at 4.36 Å has also been reported for the β’ polymorph of palm oil and palm stearin (Yap et al., 1989). In contrast, β polymorph always displays a strong d-spacing at 4.6 Å (D’Souza et al., 1990). In this work, the content of β’ and β structures in the samples was estimated by the relative intensity of the short spacings of β’ form at 4.36 Å and that of β form at 4.6 Å following a method described by Kim et al. (2008).

Crystal morphological study  The crystal morphology of the experimental fat blends and the commercial margarine fats crystallized under static conditions at three different temperatures was observed using a polarized light microscope (Olympus BX51, Olympus Optical Co., Ltd., Tokyo, Japan) equipped with a digital camera (Olympus C-7070, Olympus Optical Co., Ltd., Tokyo, Japan). All fat samples were melted at 80°C for 15 min to totally eliminate the memory effect. 20 µL of each molten sample was placed on a pre-heated glass slide and covered by a cover slip. Then, the prepared slides of each sample were divided into three groups and stored for 24 h at 4°C (a refrigeration temperature), 25°C and 32°C (a room temperature), respectively, using temperature-controlled cabinets. A 10× lens was employed to image the gray scale photographs of the fat crystals.

Margarine processing  Six experimental margarines were produced using the six fat blends of PS/VCO/PO as feedstocks (Table 1). The margarines were named PSC46M, PSC37M, PSCP352M, PSCP343M, PSCP253M and PSCP244M for margarines that were made from the fat blends PSC46, PSC37, PSCP352, PSCP343, PSCP253 and PSCP244, respectively. The margarine formulation (w/ w) used in this study is as followed: lipid phase, 83% (fat blends, 82.5%; distilled monoglyceride, 0.5%) and aqueous phase, 17% (distilled water, 16%; salt, 1%). The addition
of 0.5 wt% of distilled monoacylglycerol as emulsifier gives good stability for a water-in-oil emulsion system, due to its low HLB and low acid value (Saadi et al., 2011). The fat blend was melted in a double-jacket stainless steel vessel at 60°C for 10 min and the emulsifier was mixed in to form an oil phase. The temperature of the sample inside the vessel was controlled by the temperature of the water that located between the jacket. The temperature of the oil phase was reduced to 45°C and the water phase containing salt at room temperature (~32°C) was then added slowly to the oil phase with an agitation rate of 1000 rpm for 10 min to form a good emulsion. The emulsion was then poured into a double insulated bowl of an ice cream maker equipped with a liquid coolant located between the walls where it was mixed and crystallized at a temperature range of 10 − 12°C. For comparison, two newly purchased commercial margarines (a trans-packet margarine (CTM) and a zero-trans margarine (CZTM)) were also melted down and recrystallized using the same procedure. Then, the partially crystallized emulsion was put inside plastic cups (40 mm in diameter and 15 mm in height) and was later allowed to age in a temperature-controlled cabinet set at 25°C for 2 h. After the aging period, each of the six experimental margarines as well as each of the commercial margarines was divided into three groups and stored at the three different test temperatures (at 4, 25°C, and 32°C) for 8 weeks and characterized as followed.

Changes in the SFC of the margarines during storage
The SFC of the margarine samples was followed during storage using the p-NMR. Before being stored for 8 weeks at the three different temperatures mentioned above, the freshly-prepared experimental margarines and commercial margarines were carefully placed inside p-NMR tubes using a spatula and a stainless steel plunger. The SFC measurements were performed once every week. Data were reported as averages of three measurements.

Texture profile analysis (TPA) Changes in textural properties (hardness, adhesiveness and cohesiveness) of all margarine samples were followed during storage for 8 weeks at 4, 25 and 32°C adopting the procedure of TPA described by Bourne (1978). A double compression test was performed using a TA-XT2i Texture Analyzer (Stable Micro Systems, London, England). The temperature inside the room where the test was performed was maintained at 25°C. A 45° conical probe attached to a 5 kg compression load cell was penetrated into the sample at 1.0 mm/s to a depth of 10 mm from the surface and then returned to the initial position at the same speed.

Sensory analysis Overall acceptability of all margarine samples were evaluated and compared using a 5-point hedonic scale (5 for like extremely, 3 for moderate and 1 for dislike extremely) by thirty panelists chosen from postgraduate students and staff of the Department of Food Technology, Silpakorn University. The testing quantity of each sample was approximately 5 mL. The freshly-made margarine samples, which were contained inside plastic cups (40 mm in diameter and 15 mm in height), were stored at 25°C for 4 weeks before the sensory test was performed at room temperature.

Statistical analysis The obtained data was analyzed by Analysis of Variance with Least Significant Difference (ANOVA/LSD) at 95% confidence interval.

Results and Discussion
Fatty acid composition analysis Table 2 shows fatty acid contents of the fat blends and the commercial margarine fats. The chain lengths of fatty acids present in coconut oil, PS and PO range from C12 − C22 (Kim et al., 2008, Winanuwattikulka et al., 2008). Coconut oil is high in Lauric acid (C12) while PS and PO contain high amount of palmitic acid (C16). As a result, all fat blends were high in palmitic acid (22.6 − 35.3%) and lauric acid (17.8 − 33.7%). As the amount of VCO in the fat blends increased, the content of lauric acid increased accordingly with a decrease in palmitic acid content. The amount of stearic acid (C18) was higher in the ternary blends (20.3 − 23.6%) compared to the binary blends (12.6 − 15.0%). This was because there was higher amount of PS and PO together in the former than in the latter. The table also shows that the content of saturated fatty acids was much higher than that of unsaturated fatty acids in all fat blends.

The commercial trans-margarine fat was composed mainly of palmitic, oleic (C18:1) and lauric acids, whereas the fatty acid content of the commercial trans-free margarine fat was dominated by oleic acid, which amounted to more than 57%.

Trans-fatty acid analysis Table 3 shows content of TFA (g/100 g lipid basis) in the pure fats and the fat blends. For the pure fats, PS contained the highest content of total TFA (0.15 g/100 g lipid basis) followed by PO. The major TFA in PS and PO were C18:1 and C18:1,11 respectively. In contrast, VCO contained only a trace amount of TFA (< 0.001 g/100 g).

Total contents of TFA in all fat blends lie in between 0.045 − 0.072 g/100g lipid basis. Generally, the amount of trans-fat present in zero-trans margarines is limited to less than 0.5 g TFA/serving (Anon, 2003). A serving size is set by the FDA at 14 g for margarines. An experimental margarine containing 82.5% fat that is made using the blend PSCP343, which exhibited the highest content of TFA, as a fat feedstock would contain only 0.0083 g TFA/serving. Consequently, all experimental margarines produced later in this
The SFC of all fat blends were higher than 40% whereas the SFC of the margarine fats were 35% and lower. The fat from the zero-trans margarine, CZTMF, exhibited the lowest SFC at all temperatures. At 20°C, the SFC of all samples, except CZTMF, were above 10%, an essential indicator that oiling off due to oil exudation would not occur with those fats (Laia et al., 2000). As the temperature increased from 20 to 25°C, the SFC of CTMF and CZTMF decreased more slowly while the SFC of all the fat blends decreased more rapidly, implying that the fat blends would melt more quickly than the commercial margarine fats.

Table 2. Fatty acid compositions of fat blends (PSC46, PSC37, PSCP352, PSCP343, PSCP253 and PSCP244), commercial trans-margarine fat (CTMF) and commercial zero-trans margarine fat (CZTMF).

<table>
<thead>
<tr>
<th>Fatty acid</th>
<th>CTMF</th>
<th>CZTMF</th>
<th>PSC46</th>
<th>PSC37</th>
<th>PSCP352</th>
<th>PSCP343</th>
<th>PSCP253</th>
<th>PSCP244</th>
</tr>
</thead>
<tbody>
<tr>
<td>Laurie (C12)</td>
<td>10.2 ± 0.23</td>
<td>4.7 ± 0.14</td>
<td>29.1 ± 0.31</td>
<td>33.7 ± 0.51</td>
<td>22.9 ± 0.82</td>
<td>19.0 ± 0.73</td>
<td>24.4 ± 1.41</td>
<td>17.8 ± 0.46</td>
</tr>
<tr>
<td>Myristic (C14)</td>
<td>4.7 ± 0.08</td>
<td>1.7 ± 0.02</td>
<td>12.2 ± 0.03</td>
<td>12.8 ± 0.15</td>
<td>9.5 ± 0.06</td>
<td>8.3 ± 0.03</td>
<td>9.5 ± 0.15</td>
<td>7.7± 0.02</td>
</tr>
<tr>
<td>Palmitic (C16)</td>
<td>31.9 ± 0.01</td>
<td>12.0 ± 0.06</td>
<td>30.0 ± 0.32</td>
<td>22.6 ± 0.12</td>
<td>31.5 ± 0.39</td>
<td>35.3 ± 0.31</td>
<td>29.3 ± 0.74</td>
<td>33.7 ± 0.10</td>
</tr>
<tr>
<td>Stearic (C18)</td>
<td>7.7 ± 0.17</td>
<td>6.6 ± 0.03</td>
<td>15.0 ± 0.16</td>
<td>12.6 ± 0.03</td>
<td>20.3 ± 0.04</td>
<td>23.6 ± 0.47</td>
<td>22.2 ± 1.28</td>
<td>23.6 ± 0.36</td>
</tr>
<tr>
<td>Oleic (C18:1)</td>
<td>27.5 ± 0.47</td>
<td>57.3 ± 0.25</td>
<td>2.6 ± 0.02</td>
<td>2.7 ± 0.01</td>
<td>4.0 ± 0.01</td>
<td>4.7 ± 0.14</td>
<td>4.5 ± 0.21</td>
<td>4.9 ± 0.14</td>
</tr>
<tr>
<td>Linoleic (C18:2)</td>
<td>0.01 ± 0.005</td>
<td>0.01 ± 0.001</td>
<td>0.03 ± 0.004</td>
<td>0.03 ± 0.002</td>
<td>0.05 ± 0.003</td>
<td>0.03 ± 0.027</td>
<td>0.04 ± 0.003</td>
<td>0.04 ± 0.003</td>
</tr>
<tr>
<td>Linolenic (C18:3)</td>
<td>0.09 ± 0.008</td>
<td>2.2 ± 0.03</td>
<td>0.04 ± 0.005</td>
<td>0.04 ± 0.002</td>
<td>0.07 ± 0.002</td>
<td>0.06 ± 0.003</td>
<td>0.07 ± 0.006</td>
<td>0.07 ± 0.006</td>
</tr>
<tr>
<td>Arachidic (C20)</td>
<td>0.21 ± 0.014</td>
<td>0.38 ± 0.014</td>
<td>0.16 ± 0.003</td>
<td>0.04 ± 0.005</td>
<td>0.19 ± 0.002</td>
<td>0.23 ± 0.010</td>
<td>0.05 ± 0.002</td>
<td>0.07 ± 0.002</td>
</tr>
<tr>
<td>Behenic (C22)</td>
<td>0.01 ± 0.005</td>
<td>1.7 ± 0.02</td>
<td>4.7 ± 0.14</td>
<td>5.1 ± 0.15</td>
<td>11.4 ± 0.42</td>
<td>8.8 ± 0.15</td>
<td>10.0 ± 1.89</td>
<td>12.2 ± 0.13</td>
</tr>
<tr>
<td>Others</td>
<td>17.7 ± 0.35</td>
<td>15.1 ± 0.22</td>
<td>11.0 ± 0.21</td>
<td>15.5 ± 0.26</td>
<td>11.4 ± 0.42</td>
<td>8.8 ± 0.15</td>
<td>10.0 ± 1.89</td>
<td>12.2 ± 0.13</td>
</tr>
</tbody>
</table>

For compositions and abbreviations of the fat blends see Table 1. All data are mean values ± standard deviations of duplicate measurements. * * Values with the same letter in each row are not significantly different (P > 0.05).

Table 3. Trans-fatty acid compositions of pure fats and fat blends (PSC46, PSC37, PSCP352, PSCP343, PSCP253 and PSCP244) (g/100 g lipid basis).

<table>
<thead>
<tr>
<th>Trans-fatty acid</th>
<th>Pure Fats</th>
<th>Fat Blends</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PS*</td>
<td>PO</td>
</tr>
<tr>
<td>C16:1</td>
<td>tr</td>
<td>tr</td>
</tr>
<tr>
<td>C18:1n-6</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>C18:1n-9</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>C18:1n-11</td>
<td>0.02</td>
<td>0.04</td>
</tr>
<tr>
<td>C18:2</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>C20:1</td>
<td>0.11</td>
<td>0.03</td>
</tr>
<tr>
<td>C22:1</td>
<td>tr</td>
<td>tr</td>
</tr>
<tr>
<td>Total</td>
<td>0.16</td>
<td>0.09</td>
</tr>
</tbody>
</table>

For compositions and abbreviations of the fat blends see Table 1. tr means the content of trans-fatty acid is less than 0.001 g/100 g lipid basis.

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Characterization of solid fat content SFC is one of the physical parameters related to the quality of margarine including general appearance, oil exudation, organoleptic properties and spreadability (Chu et al., 2002). The plot showing the relationship between SFC and temperature of the fat blends and the margarine fats is given in Figure 1. At 15°C and below, the SFC of all fat blends were higher than 40% whereas the SFC of the margarine fats were 35% and lower. The fat from the zero-trans margarine, CZTMF, exhibited the lowest SFC at all temperatures. At 20°C, the SFC of all samples, except CZTMF, were above 10%, an essential indicator that oiling off due to oil exudation would not occur with those fats (Laia et al., 2000). As the temperature increased from 20 to 25°C, the SFC of CTMF and CZTMF decreased more slowly while the SFC of all the fat blends decreased more rapidly, implying that the fat blends would melt more quickly than the commercial margarine fats. The work using the six fat blends could be categorized as zero-trans margarines.

Figure 1. Solid fat contents (SFC) of fat blends (PSC46, PSC37, PSCP352, PSCP343, PSCP253 and PSCP244), commercial trans-margarine fat (CTMF) and commercial zero-trans margarine fat (CZTMF) measured at different temperatures. For compositions and abbreviations of the fat blends see Table 1.
changes in SFC in the temperature range of 15 – 25°C is related to the cooling effect, which is a desirable mouthfeel property for margarines, and the greater the SFC drop the greater the cooling effect (Hoffmann, 1989). In this regard, the SFC decreases between 15 and 25°C in a declining order were 42.53% (PSC37), 36.92% (PSC46), 33.03% (PSCP352), 29.81% (PSCP253), 27.4% (PSCP343), 26.2% (PSCP244), 11.27% (CTMF) and 6.8% (CZTMF). Accordingly, PSC37 and CZTMF gave the highest and lowest cooling effect, respectively.

Approaching the room temperature of 30 – 32°C in a country with a tropical climate, the SFC of the fat blends, though most still higher, were close to those of the margarine fats. The SFC of PSC37 and PSCP253 were almost the same as that of CTMF. At the body temperature of 37°C, the SFC of all fat samples were lower than 10%. In order to eliminate waxy mouthfeel, a margarine fat should have SFC < 3.5% at temperatures above 33°C (Chrysan, 1996). From Fig. 1, only PSC37, PSCP253 and both margarine fats showed SFC close to 3.5% at around 33°C.

In order to have good spreadability at refrigeration temperature, SFC of fats should be lower than 32% at 10°C (Lida and Ali, 1998). The SFC of the fat blends were higher than 32% at 10°C. However, the aim of this work was to produce zero-trans packet margarines, which should be spreadable at room temperature. The SFC of all fat blends were well below 32% at room temperature. This should give good spreadability to the margarines made from all the blends.

According to Liu et al. (2010), the SFC of a commercially available margarine in Shanghai (China) with acceptable hardness was as high as 75.11% at 10°C. High SFC is not directly related to high hardness in fats as the SFC is not the sole parameter that influences the ultimate strength of the fat crystal network. Apart from the SFC, the mechanical properties of fats can be influenced by other factors, e.g., lipid composition, polymorphism, crystallization behavior and microstructure (Liu et al., 2010). The high SFC values of the fat blends at low temperature range would give the margarines produced from these blends stability and consistency, which is extremely useful for margarines available in tropical regions. In addition, the big drop in SFC of the fat blends when the temperature increased from 5 to 30°C would allow the fats to melt quickly when consumed and the low SFC at the body temperature would leave almost no waxy mouthfeel. The SFC results imply that PSC37 and PSCP253 may be appropriate for the production of margarines that maintain stability, are spreadable at room temperature, give great cooling effect and melt almost completely at body temperature.

**Analysis of crystallization and melting profiles** The DSC thermograms for crystallization and melting of all fat samples are given in Fig. 2. The crystallization thermograms of the fat blends showed 2 – 3 distinct peaks (Fig. 2a), indicating that heterogeneous types of triglycerides were crystallized at different temperatures. The crystallization peaks and T_{CO} were shifted towards low temperatures when the proportion of PS in the fat blends decreased with an increase in either VCO or PO. For the binary blends of PS and VCO, T_{CO} decreased from 23.5°C to 19.5°C as the amount of PS in the blends decreased from 40% (wt) in PSC46 to 30% (wt) in PSC37. A similar trend continued with the ternary blends, e.g. as the quantity of PS in the blends decreased, T_{CO} dropped from 22.8°C (PSCP343) to 21.8°C (PSCP244).

In addition, the number of crystallization peaks appeared to increase as the amount of PS in the fat blend decreased. Out of all samples, T_{CO} of CTMF was the highest (28.6°C). Par-

![Fig. 2. DSC crystallization (a) and melting (b) thermograms of fat blends (PSC46, PSC37, PSCP352, PSCP343, PSCP253 and PSCP244), commercial trans-margarine fat (CTMF) and commercial zero-trans margarine fat (CZTMF). For compositions and abbreviations of the fat blends see Table 1.](image-url)
tial hydrogenation was likely the cause for the high $T_{\text{CO}}$ of CTMF. The crystallization thermogram of CZTFM exhibited 2 peaks, one big located at $-39.5^\circ\text{C}$ and one small located at $19.5^\circ\text{C}$, that were farthest apart. The abundance in unsaturated fatty acids in triglyceride molecules of ingredient oils (rapeseed, sunflower, olive, and palm oils) in CZTFM was the key contribution for the crystallization peak at the very low temperature.

The melting thermograms of the fat blends showed at least 3 distinct peaks. As the amount of PS in the fat blends decreased, resulting in smaller portions of higher melting triglycerides in the blends, the multiple melting peaks and $T_{\text{MC}}$ were moved slightly towards lower temperatures. In addition, when the amount of PS in the fat blends dropped to 20% (wt), the first melting peak on the high temperature end with the peak temperature of $-47.9^\circ\text{C}$ disappeared. The characteristics of the melting thermograms of CTMF and CZTFM were different from those of the fat blends. The thermogram exhibits several broad melting peaks overlapping one another. The lower melting peaks of CZTFM were located at melting temperatures much lower than other samples. The peaks represented the melting of unsaturated triglycerides that were the main triacylglycerol components of the trans-free margarine fat.

Polymorphic structure analysis The polymorphic structures of the fat samples crystallized at 4°C are shown in Table 4. Two types of polymorphic structures, $\beta'$ and $\beta$, were present in all fat blends. $\beta'$ was a predominant polymorph in blends PSC37, PSCP343 and PSCP244. The fat crystals exhibited the same level of $\beta'$ and $\beta$ in blends PSC46, PSCP352 and PSCP253. For binary fat blends, 10% reduction in the amount of PS in the blends from 40% in PSC46 blend (Fig. 1) to 20% (wt), the first melting peak on the high temperature end with the peak temperature of $-39.5^\circ\text{C}$ disappeared. The characteristics of the melting thermograms of CTMF and CZTFM were different from those of the fat blends. The thermogram exhibits several broad melting peaks overlapping one another. The lower melting peaks of CZTFM were located at melting temperatures much lower than other samples. The peaks represented the melting of unsaturated triglycerides that were the main triacylglycerol components of the trans-free margarine fat.

Table 4. Polymorphic form of fat blends (PSC46, PSC37, PSCP352, PSCP343, PSCP253 and PSCP244), commercial trans-margarine fat (CTMF) and commercial zero-trans margarine fat (CZTFM) crystallized at 4°C under static conditions for 24 h.

<table>
<thead>
<tr>
<th>Fat samples</th>
<th>d-spacing (Å)</th>
<th>Polymorphic forms</th>
<th>Level of $\beta'$ and $\beta$ forms*</th>
</tr>
</thead>
<tbody>
<tr>
<td>PSC46</td>
<td>$4.6 s$</td>
<td>3.88 s</td>
<td>$\beta' + \beta$</td>
</tr>
<tr>
<td>PSC37</td>
<td>$4.6 m$</td>
<td>3.88 s</td>
<td>$\beta' + \beta$</td>
</tr>
<tr>
<td>PSCP343</td>
<td>$4.6 m$</td>
<td>3.88 s</td>
<td>$\beta' + \beta$</td>
</tr>
<tr>
<td>PSCP244</td>
<td>$4.6 m$</td>
<td>3.88 s</td>
<td>$\beta' + \beta$</td>
</tr>
<tr>
<td>PSCP352</td>
<td>$4.6 s$</td>
<td>3.88 s</td>
<td>$\beta' + \beta$</td>
</tr>
<tr>
<td>PSCP253</td>
<td>$4.6 s$</td>
<td>3.88 s</td>
<td>$\beta' + \beta$</td>
</tr>
<tr>
<td>CTMF</td>
<td>$4.36 s$</td>
<td>3.88 s</td>
<td>$\beta'$</td>
</tr>
<tr>
<td>CZTFM</td>
<td>$4.36 w$</td>
<td>3.88 s</td>
<td>$\beta'$</td>
</tr>
</tbody>
</table>

$m$ = medium, $s$ = strong, $w$ = weak. *Estimated from $[\beta/\beta'] = ([\text{intensity of short spacing at 4.6 Å}] / [\text{intensity of short spacing at 4.36 Å}])$, that was classified as $\beta' = \beta$ (1.2 $\geq$ $\beta/\beta' > 0.8$), $\beta > \beta'$ (0.8 $\geq$ $\beta/\beta' > 0.4$) or $\beta' > \beta$ (0.4 $\geq$ $\beta/\beta' > 0$) (Kim et al., 2008).
Fig. 3. Crystal morphology of fat blends (PSC46, PSC37, PSCP352, PSCP343, PSCP253 and PSCP244), commercial trans-margarine fat (CTMF) and commercial zero-trans margarine fat (CZTMF) crystallized at 4°C under static conditions for 24 h. For compositions and abbreviations of the fat blends see Table 1.
of CTM at 32°C was likely due to the fact that it contained hydrogenated fats. Textural properties Changes in the hardness of all margarine samples during storage at three different temperatures are shown in Fig. 5 where it was evident that the hardness of the samples was influenced by the storage temperature. At 4°C, PSC46M exhibited the highest hardness at 4 and 8 weeks of storage, possibly due to its highest content in PS, followed by PSC37M, PSCP352M and PSCP253M (Fig. 5a). The hardness of all samples increased substantially during the first 1–2 weeks of storage and this is likely due to the morphology of all fat blends crystallized at 4°C under quiescent conditions for 24 h. Fat crystals in all fat blends, except PSCP343, were radially-oriented spherulites. These spherulites consisted of plate-like polycrystalline crystals radiating and branching from central nuclei. Some degree of crystal aggregation, presumably by van der Waals forces (Berger et al., 1979), is evident in the images, except PSC37. The size of the spherulites in PSC46, PSCP244 and PSCP352 were generally larger than the crystals in PSC37 and PSCP253. In contrast, the crystal morphology for PSCP343 was continuous needle-like with the highest crystal number compared to other fat blends. As the content of PS in the fat blends decreased 10% (wt) from PSC46 to PSC37 and from PSCP343 to PSCP253 with an increase in VCO, the size of crystal aggregates diminished and the portion of liquid oil increased. On the other hand, a 10% increase in VCO while the content of PS remained constant (i.e., from PSCP352 to PSCP343 and from PSCP253 to PSCP244) resulted in higher crystal number and larger crystal size with decreased liquid portion.

The microstructure of crystals in the commercial trans-margarine fat, CTMF, was a mixture of large loosely-packed spherulites and granular texture with some evidence of crystal aggregation, whereas the crystal morphology of the zero-trans margarine, CZTMF, were discontinuous plate-like. Many individual crystals were present in CZTMF with small degree of crystal aggregation. This is in agreement with what was previously observed in the microstructure of a trans-free margarine (Kim et al., 2008).

Solid fat content of margarine products Changes in SFC of the margarine products during storage for 8 weeks at three different temperatures are given in Fig. 4. Apart from a substantial increase and a small drop in SFC during the first week of storage at 4°C (Fig. 4a) and 32°C (Fig. 4b), respectively, the SFC values of all margarines remained relatively constant throughout 8 weeks of storage. This implies that the margarines, both produced in the laboratory and commercially available, were stable with consistent physical characteristics. At any storage week, zero-trans commercial margarine, CZTM, exhibited the lowest SFC values in all three storage temperatures. At 4°C, SFC of all margarines, except CTM and CZTM, were not significantly different from one another (Fig. 4a). As the storage temperature increased to 25°C, SFC measured at any storage week of all margarines decreased noticeably from 4°C, with PSC46M exhibiting the highest SFC throughout 8 weeks of storage (Fig. 4b). At 32°C, SFC of all margarines decreased to below 10% (Fig. 4c). PSC46M and the commercial trans-margarine, CTM, were the formulations with highest SFC at this temperature. The high SFC of PSC46M at all three storage temperatures was likely due to its high PS content whereas the high SFC of CTM at 32°C was likely due to the fact that it contained hydrogenated fats.

Textural properties Changes in the hardness of all margarine samples during storage at three different temperatures are shown in Fig. 5 where it was evident that the hardness of the samples was influenced by the storage temperature. At 4°C, PSC46M exhibited the highest hardness at 4 and 8 weeks of storage, possibly due to its highest content in PS, followed by PSC37M, PSCP352M and PSCP253M (Fig. 5a). The hardness of all samples increased substantially during the first 1–2 weeks of storage and this is likely due to the
Fig. 5. Hardness of experimental margarines (PSC46M, PSC37M, PSCP352M, PSCP343M, PSCP253M and PSCP244M), commercial trans-margarine (CTM) and commercial zero-trans margarine (CZTM) during 8 weeks of storage at 4°C (a), 25°C (b) and 32°C (c). Lower case letters represent significant differences within one margarine sample between 0, 2, 4 and 8 weeks of storage. Capital letters represent significant differences between different margarine samples at the same storage week. Hardness values with the same letter are not significantly different ($P > 0.05$).
decrease in the temperature from the incubation temperature during the margarine manufacturing (25°C for 2 h) to the storage temperature. The increase in the hardness from weeks 0 to 2 of all samples reflects the increase in SFC (Fig. 4). However, the further hardness increase between weeks 2 and 4 (where the SFC had already reached plateaus) of all samples, except CTM and CZTM, indicates again that SFC is not a sole factor to be correlated to the hardness. Further evidence could be seen from the figure that as the hardness at 8 weeks of storage decreased significantly from 37.7 N for PSC46M to 34.0 N for PSC37M and 32.5 N for PSC352M, the SFC of these samples at the sample storage week were not significantly different from one another.

At 25°C, the hardness of all samples decreased dramatically from 4°C. PSCP343M exhibited the highest hardness at 8 weeks possibly due to its high content of PS (30% wt) and high combined content of PS and PO (60% wt). At this storage week, PSC46M showed the same hardness as PSCP352M. The hardness of all margarines, except PSCP343M and PSCP253M, did not change significantly with storage time. At 32°C, the same trend from 25°C continued where PSCP343M remained the sample with the highest hardness at 8 weeks of storage, followed by PSCP352M and PSC46M. Similarly, the hardness of all margarines did not vary significantly with storage time at room temperature.

The hardness of the trans-free margarine, CZTM, was significantly lower than all other margarine samples at all storage temperature. This is in agreement with the changes in SFC results (Fig. 4) where CZTM demonstrated the lowest SFC at all three storage temperatures. The lack in crystal aggregates in the margarine’s microstructure (Fig. 3) and hence interaction between them might have led to a weak crystal network, resulting in its low hardness and stability. On the contrary, the hardness of trans-margarine, CTM, was not significantly different from that of PSCP244M at room temperature and was very close to that of PSC37M at both 25°C and room temperature.

Changes in adhesiveness and cohesiveness of the samples during storage at 25°C are shown in Fig. 6. As the storage time increased from 0 to 8 weeks, the adhesiveness

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Fig. 6. Adhesiveness (a) and cohesiveness (b) of experimental margarines (PSC46M, PSC37M, PSCP352M, PSCP343M, PSCP253M and PSCP244M), commercial trans-margarine (CTM) and commercial zero-trans margarine (CZTM) during 8 weeks of storage at 25°C. Lower case letters represent significant differences within one margarine sample between 0, 2, 4 and 8 weeks of storage. Values with the same letter are not significantly different (P > 0.05).
the blend showed good consistency and demonstrated hardness characteristic close to that of a commercial trans-packet margarine. In addition the margarine received highest score for overall acceptibility.

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**References**


Production of Zero-trans Margarines from Virgin Coconut Oil


