Characterization of Physicochemical and Thermal Properties and Crystallization Behavior of Krabok (*Irvingia Malayan*) and Rambutan Seed Fats

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Abstract: Fatty acid composition, physicochemical and thermal properties and crystallization behavior of fats extracted from the seeds of krabok (*Irvingia Malayan*) and rambutan (*Nephelium lappaceum* L.) trees grown in Thailand were studied and compared with cocoa butter (CB). The krabok seed fat, KSF, consisted of 46.9% lauric and 40.3% myristic acids. It exhibited the highest saponification value and slip melting point but the lowest iodine values. The three fats displayed different crystallization behavior at 25°C. KSF crystallized into a mixture of β'- and pseudo-β' structures with a one-step crystallization curve and high solid fat content (SFC). The fat showed simple DSC crystallization and melting thermograms with one distinct peak. The rambutan seed fat, RSF, consisted of 42.5% arachidic and 33.1% oleic acids. Its crystallization behavior was more similar to CB than KSF, displaying a two-step crystallization curve with SFC lower than that of KSF. RSF solidified into a mixture of β' and pseudo-β' before transforming to β after 24 h. The large spherulitic microstructures were observed in both KSF and RSF. According to these results, the Thai KSF and RSF exhibited physicochemical, thermal characteristics and crystallization behavior that could be suitable for specific applications in several areas of the food, cosmetic and pharmaceutical industries.

Key words: *Irvingia Malayan*, krabok, rambutan, cocoa butter, fat, solid fat content, crystallization

1 INTRODUCTION

Vegetable fats and oils are extensively used as raw material and inputs for industrial food, medicine, and cosmetic production[1]. The possibility of an acute shortage in edible and industrial vegetable fats and oils together with a clear tendency favoring the use of natural vegetable fats for the replacement of those from hydrogenated vegetable oil has encouraged the investigation of edible plants as possible sources of usable fats and oils[1,2]. Krabok(*Irvingia Malayan*) is a large-grown and woody wild almond tree widely distributed in tropical and subtropical areas. It is from the *Irvingia* family, which consists of two species. The other species is *Irvingia gabonensis* or African wild mango, which has been studied extensively. It is a commercial and indigenous fruit tree of West and Central Africa, which has been identified as the most important tree for domestication[3]. The fruits are used as condiment and are highly valued for their food thickening properties. In Thailand, the krabok tree is commonly used for wood and charcoal production, whereas the seeds, after peeling, are consumed by people[4]. In Cambodia, the tree is known as the ‘pauh kijang’, which means ‘mango of the stags’[5]. The most interesting part of the krabok nut seems to be its fat, which is the most abundant component of kernels. Only a few studies have been done on the compositions and properties of krabok seed fat (KSF) and it was reported that KSF is rich in lauric and myristic acids[6], indicating its potential uses as confectionery and cosmetic fat. The nutritional value of KSF was evaluated by Laohawin[6]. Bandelier et al.[7] studied the biochemical and oil composition of the KSF obtained from Cambodia and found that it contained more than 83% of lauric and myristic acids. However, due to the lack of technical information regarding to its properties, especially thermal properties and crystallization behavior, and potential use, KSF has so far been under utilized for oil production.

The rambutan (*Nephelium lappaceum* L.) is a medium-sized evergreen tropical tree growing to a height of 12-20 m. It is believed to be native to the Malay Archipelago, from where it spread to Thailand, Burma, Sri Lanka, India, Vietnam, Philippines and Indonesia. The fruit produced by the tree, also called rambutan, is generally consumed fresh.
2 EXPERIMENTAL PROCEDURES

2.1 Materials

Mature krabok seeds were collected from the northern region of Thailand, and rambutan seeds from Rongrien variety were kindly supplied by Malee Sampran Public Company Limited (Nakhonpathom, Thailand). The seeds were cut open and the seed kernels were removed. The almond-like decorticated seed kernels were crushed by a hand mill and dried in a vacuum oven for 4 h at 60°C. After the process of canning, the residues consist mainly of seeds and peels. Although, the seeds are considered as agro-industrial waste in many countries, but in others, like some Asian countries, they are edible after roasting11. Some studies on the seed have showed that rambutan possesses a relatively high amount of fat (between 17% and 39%) that can be used for manufacturing candles, soaps, and fuels2,30. In one of the most recent studies, Solis-Fuentes et al.1 revealed that rambutan seed fat obtained from RI-104 variety grown in Mexico comprised mainly of oleic and arachidic acids and exhibited potential use for different branches of industries from confectionery to cosmetics. Sirisompong et al.11 reported that, with high level of arachidic acid and low iodine value, the chemical characteristics as well as the physical properties of a fat obtained from a Thai variety of rambutan compared well with those of conventional fats. This would permit the use of the fat, especially where oxidation may be a concern, without its being subjected to hydrogenation.

In this study, fatty acid composition, physicochemical properties and crystallization behavior of the fats extracted from the krabok and rambutan seeds from trees grown in Thailand were investigated for the purpose of evaluating the potentiality of these fruit by-products as sources of natural edible fats with possible industrial use.

2.2 Crude fat extraction and purification

Krabok seed fat (KSF) and rambutan seed fat (RSF) were extracted from the dried and finely ground krabok and rambutan seed kernels, respectively, using the Soxhlet extraction method at 60°C for 6 h with n-Hexane as a solvent. The crude fats were purified employing the method described by Solís-Fuentes and Durán-de-Bazzía31. The purified fats were kept away from light and air at 4°C until further analysis.

2.3 Characterization of fatty acid composition

KSF, RSF and CB were converted into fatty acid methyl esters using AOAC official method 969.3313. The fatty acid methyl esters analysis was performed in a Shimadzu GC with flame ionization detector (GC-FID). The system had an VertiBondTM wax capillary column (50 m long, 0.25 mm internal diameter and 0.20 mm 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 1 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 holding 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. After the fats were analyzed, their chromatograms were acquired and the fatty acid contents were calculated based on percentage of peak area.

2.4 Characterization of physicochemical properties

Iodine value (IV) was analyzed using automatic titrator (Mettler Toledo DL58 titrator). Saponification value and slip melting point were analyzed following Palm Oil Research Institute of Malaysia Test Method no. p3.1 (1995) and no. p4.2 (1995), respectively14. Acid value was analyzed following American Oil Chemists’ Society Official Method Ca 5a-4015.

2.5 Characterization of solid fat content

Changes in the solid fat content as a function of temperature between 15°C and 40°C and the melting behavior of the fats were determined by pulse-nuclear magnetic resonance (p-NMR) spectrometer (Minispec-nq20, BRUKER, Karlsruhe, Germany) following a method for measuring solid fat content of CB and similar fats 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 Luttke36.
2.6 Characterization of crystallization and melting profiles

The crystallization and melting profiles of the fat samples were determined with a Perkin-Elmer differential scanning calorimeter (DSC) (model DSC 8000, PerkinElmer Co., Norwalk, CT) following a procedure employed by Solis-Fuentes et al.\(^1\). The heat flow of the instrument was calibrated with indium (mp 156.6 °C) as a reference standard. A fat sample of 3-5 mg was placed in an aluminum pan (20 μL capacity) and hermetically sealed. An empty pan served as reference. Prior to the analysis of thermal behavior, the samples were heated from 20 °C to 80 °C at 30 °C/min and held for 10 min in order to ensure homogeneity and to destroy any crystal memory. Then, the samples were cooled to −40 °C at the rate of 5 °C/min. The crystallization profile, enthalpy of crystallization, and the phase changes between onset and offset temperatures were recorded. This was followed by heating the sample at the rate of 5 °C/min from −40 °C to 80 °C during which the melting profile, the enthalpy of melting, and the temperatures of the phase changes were recorded. The crystallization onset (T<sub>co</sub>) and melting completion temperatures (T<sub>mc</sub>) were obtained from the peaks located at the highest temperature of each fat sample. T<sub>co</sub> and T<sub>mc</sub> were considered to be the temperatures at which the crystallization began and the melting ended, respectively\(^1\).

2.7 Crystallization behavior under static isothermal condition

The crystallization behavior of KSF and RSF under static conditions at 25 °C was investigated using p-NMR and x-ray diffraction (XRD) techniques. For the p-NMR study, the fat samples, which were contained in p-NMR tubes, were heated to 80 °C for 10 min in a water bath and then were transferred to a cooling bath set below 25 °C. Once the temperature of the samples inside the tubes decreased to 25.5 °C, the tubes were removed from the cooling bath, wiped dry and rapidly put into the p-NMR sample port with the temperature set at 25 °C. The timing then started and the SFC was recorded once per min for 60 min, allowing in-situ observation of the crystallization of the fat samples. Since 25 °C was too high for CB to solidify enough to achieve good SFC reading during the p-NMR measurement, the study of the crystallization behavior of CB using the p-NMR was omitted here.

For the XRD study, each fat sample was put inside an XRD capillary sample holder using a pipette. The sample was then heated to 80 °C for 10 min by dipping in a water bath, after which it was transferred to a temperature-controlled cabinet set at 25 °C and the timing started immediately. The XRD characterization was performed at 0, 1.5, 24 h and 7 days using an x-ray diffractometer (Rigaku TTRAX III, Rigaku Corporation, Tokyo, Japan). Scans were performed in wide angle x-ray scattering from 15 ° to 25 ° 20 with a scan speed and a step width of 2.7 ° 20/min and 0.02 ° 20, respectively.

2.8 Crystal morphology

The crystal morphology of the KSF, RSF and CB crystallized under static conditions at 25 °C was observed by polarized light microscopy (PLM) (Olympus BX51, Olympus Optical Co., Ltd., Tokyo, Japan) equipped with a digital camera a digital camera (Olympus C-7070, Olympus Optical Co., Ltd., Tokyo, Japan). The fat samples were melted at 80 °C for 10 min. A small droplet (about 20 μL) of the melted fats was placed on a glass slide preheated to 80 °C. A pre-heated glass cover slip was carefully placed over the sample to produce a film of uniform thickness. The slides were incubated for 24 h at 25 °C in a temperature-controlled cabinet. A 10× lens was employed to image the gray scale photographs of the fat crystals.

2.9 Statistical analysis

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

3 RESULTS AND DISCUSSION

3.1 Fatty acid composition analysis

Table 1 exhibits the fatty acid contents of KSF, RSF compared with CB, which was high in stearic (35.9%), oleic (32.4%) and palmitic (25.3%) acids. KSF consisted more than 90% of saturated fatty acids. It contained mainly lauric acid (46.7%) and myristic acid (40.3%). The amount of lauric acid in the Thai KSF reported here matched the lauric acid content in coconut and palm kernel oils\(^1\), which are two most important lauric fats for the confectionery industry. Also present are palmitic, stearic, oleic, and behenic acids. This gives KSF a hard consistency with high solid fat content and high melting point as shown in the following sections. The combined amount of lauric and myristic acids found in the Thai KSF (87%) was higher than that of the Cambodian KSF (83%) reported by Bandelier et al.\(^5\) but lower than that of the African wild mango (92%) published by Njoku and Ugwuanyi\(^5\).

Two main fatty acids in RSF were oleic (33.1%) and arachidic (42.5%) acids. Lauric, myristic, palmitic, stearic and behenic acids were also present. The contents of oleic and arachidic acids in the Thai RSF from Rongrien variety reported here were significantly lower and higher, respectively, than the contents of the two fatty acids in the Mexican RSF from RI-104 variety as reported by Solis-Fuentes et al.\(^1\). The high content of arachidic acid, a fatty acid with a long chain and a relatively high melting point, of the Thai RSF would have allowed it to exhibit a harder consistency with higher SFC than the Mexican variety as

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unsaturated fatty acid bonds present in a fat. From the range reported by Joseph CB and RSF. The Iv of KSF given here was well within the saturation and hardness of fats. The higher the Iv, the more different from each other the Iv of CB and RSF 674 3.2 Physicochemical properties can be seen later.

### Table 1 Fatty acid compositions of krabok seed fat (KSF), rambutan seed fat (RSF) and cocoa butter (CB). All data are mean values ± standard deviations of triplicate measurements. *Values with the same letter in each row are not significantly different (p > 0.05).

<table>
<thead>
<tr>
<th>Fatty acid type</th>
<th>Fatty acid content (area%)</th>
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<tbody>
<tr>
<td></td>
<td>CB</td>
</tr>
<tr>
<td>Lauric acid (C12)</td>
<td>–</td>
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<tr>
<td>Myristic acid (C14)</td>
<td>0.083 ± 0.004&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>Palmitic acid (C16)</td>
<td>25.269 ± 0.785&lt;sup&gt;c&lt;/sup&gt;</td>
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<tr>
<td>Stearic acid (C18)</td>
<td>35.872 ± 0.463&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>Oleic acid (C18:1)</td>
<td>32.439 ± 0.161&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>Linoleic acid (C18:2)</td>
<td>2.406 ± 0.003&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>Linolenic acid (C18:3)</td>
<td>0.123 ± 0.001&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>Arachidic acid (C20)</td>
<td>0.890 ± 0.051&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>Behenic acid (C22)</td>
<td>0.135 ± 0.001&lt;sup&gt;c&lt;/sup&gt;</td>
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<tr>
<td>Lignoceric acid (C24)</td>
<td>0.368 ± 0.007&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>Others</td>
<td>2.414 ± 0.104&lt;sup&gt;c&lt;/sup&gt;</td>
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</table>

### Table 2 Physicochemical properties of krabok seed fat (KSF), rambutan seed fat (RSF) and cocoa butter (CB). *Values with the same letter in each row are not significantly different (p > 0.05).

<table>
<thead>
<tr>
<th>Physicochemical properties</th>
<th>CB</th>
<th>KSF</th>
<th>RSF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acid value (% as oleic acid)</td>
<td>2.78 ± 0.028&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.28 ± 0.002&lt;sup&gt;c&lt;/sup&gt;</td>
<td>0.77 ± 0.066&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>Iodine value (g I2/g fat)</td>
<td>34.03 ± 0.467&lt;sup&gt;a&lt;/sup&gt;</td>
<td>9.26 ± 0.215&lt;sup&gt;b&lt;/sup&gt;</td>
<td>32.31 ± 0.771&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>Saponification value (mg KOH/g fat)</td>
<td>190.70 ± 0.534&lt;sup&gt;a&lt;/sup&gt;</td>
<td>223.86 ± 0.253&lt;sup&gt;a&lt;/sup&gt;</td>
<td>199.38 ± 0.972&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>Slip melting point (°C)</td>
<td>31.03 ± 0.058&lt;sup&gt;a&lt;/sup&gt;</td>
<td>38.70 ± 0.000&lt;sup&gt;a&lt;/sup&gt;</td>
<td>38.47 ± 0.058&lt;sup&gt;b&lt;/sup&gt;</td>
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</tbody>
</table>

At 32.31 g I2/g fat, the Iv of the Thai RSF reported here was significantly lower than that of the Mexican variety (47 g I2/g fat). The difference in the rambutan cultivars and the geographical locations where the rambutan trees were planted could have been responsible for the difference of the values.

Saponification value (Spv) is a measurement of the average molecular weight (or chain length) of all the fatty acids present in a fat. Spv decreases when molecular weight increases. KSF exhibited the highest Spv (223.86 mg KOH/g fat) and this was most likely due to a high content of medium-chain fatty acids (lauric and myristic acids) in the fat as discussed earlier. The value was close to the Spv range of African wild mango (212.7 - 219.2 mg KOH/g fat) reported by Joseph<sup>20</sup>. The Spv of RSF from the Thai rambutans (199.38 mg KOH/g fat) and of CB (190.70 mg KOH/g fat) were much lower than that of KSF due to their high contents of long-chain fatty acids such as oleic and arachidic acids for RSF and stearic and oleic acids for CB. The Spv of RSF reported in this work was relatively close to the Spv of the Mexican RSF (186 mg KOH/g fat) given in the lit-
Slip melting point (SMP) of a fat is the temperature at which a column of fat in an open capillary tube softens or becomes sufficiently fluid to slip or run up the tube when it is subjected to a controlled heating. SMP of KSF (38.7°C) and RSF (38.5°C) were higher than CB (31.0°C). The less content of unsaturated fatty acids in KSF and higher content of saturated, long-chain fatty acid (arachidic acid) in RS when compared with CB (see Table 1) must have contributed to the higher SMP of the two former fats.

3.3 Characterization of solid fat content

Solid fat content (SFC) measured at a given temperature represents the percentage of solid fat crystallized at that particular temperature. A plot of SFC versus temperature also provides information on the melting behavior of fats. Figure 1 shows SFC of KSF, RSF, and CB measured at different temperatures between 15-40°C. It can be seen from the figure that SFC of KSF was the highest at all temperatures. The low content of unsaturated fatty acids contained in the fat (Table 1) was the key contribution for its high SFC. SFC of CB was the lowest at temperatures above 15°C due to its high content of unsaturated fatty acids (~35%) whereas SFC of RSF, which was high in both unsaturated fatty acids (~33%) and long-chain saturated fatty acids (especially arachidic acid) was in between those of the former two fats.

At temperature range 15-30°C, SFC of KSF remained relatively unchanged as the temperature increased while SFC of CB dropped dramatically by 98.7% and SFC of RSF decreased slowly by 34.8%. The fast drop in SFC of CB with temperature and its low SFC as the temperature approached a body temperature are well-known characteristics. The low content of unsaturated fatty acids, recorded by Solís-Fuentes et al.10, suggests that heterogeneous types of triglycerides were crystallized in KSF. At a body temperature, the SFC of the Cambodian KSF decreased within the same temperature range as reported by Bandelier et al.7. However, the Cambodian KSF melted completely at around 35°C whereas the complete melting of Thai KSF occurred just above 40°C. Though not as high as KSF’s, SFC of RSF was much higher than CB at room temperature (~30°C). At a body temperature, the SFS of both KSF and RSF were still high above 20%. This would make them unattractive for consumption if they were to be used as a sole fat ingredient in a confectionery product due to the waxy mouthfeel they could generate. Hence, the fats’ triacylglycerol composition/structure should be modified by one or more of various modification methods such as blending, fractionation and chemical/enzymatic interesterification, etc. before use.

3.4 Analysis of crystallization and melting profiles

The DSC thermograms for crystallization of KSF, RSF, and CB are given in Fig. 2(a) and the temperature of phase transition points for the fat samples were summarized in Table 3. The crystallization of KSF showed a simple solidification profile with only one sharp peak at 14.23°C (T1) whilst the crystallization thermogram of RSF and CB exhibited 3-4 peaks that appeared non-distinct, indicating that heterogeneous types of triglycerides were crystallized at different temperatures. The crystallization onset temperature, Tm, was highest for RSF (28.13°C), possibly a result of its high arachidic acid content, followed by KSF (24.61°C) and CB (19.10°C). The crystallization enthalpies in a decreasing order were 111.1, 83.27 and 72.81 J/g for KSF, RSF, and CB, respectively. RSF had a major thermal transition at 26.83°C (T1) and minor transitions at 16.6°C (T2), 6.47°C (T3) and 0.95°C (T4). CB exhibited a broad main peak at 14.58°C (T1), which was located at a lower temperature than that of RSF, with a shoulder on the high-temperature side at 17.76°C (T2). Tm for RSF reported here was lower than that of the Mexican RSF published by Solís-Fuentes et al.10. In addition, a sharp peak representing a thermal transition at a very low temperature of ~18.1°C, indicating a group of triacylglycerols with an abundance of unsaturated fatty acids, recorded by Solís-Fuentes et al.10 was not observed here. This might have been the result of the difference in the cultivars of rambutan seeds used in the two studies and the geographical areas where the rambutan trees were planted.

The DSC thermograms for melting of the fat samples are given in Fig. 2(b). The melting completion temperatures, Tm, for KSF (42.22°C) and RSF (41.55°C) were almost the same and were much higher than Tm of CB (29.64°C). KSF had only one sharp melting peak at 39.88°C (T1), suggesting that the fat contained a group of triacylglycerols with similar phase behavior. In addition, the sharp DSC melting

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**Fig. 1** Solid fat content measured at 15-40°C of krabok seed fat (KSF), rambutan seed fat (RSF) and cocoa butter (CB).

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profile where the melting completed at 42.2°C reflected what was observed earlier with the SFC study when the SFC of KSF decreased rapidly at the temperatures above 30°C and came down to almost zero once the temperature reached just above 40°C (Fig. 1). Both RSF and CB showed three or four overlapped peaks with shoulders on both sides. The peaks corresponded to the melting of different groups of triacylglycerols that had difference fatty acid compositions. The melting enthalpies in a decreasing order were 131.66, 97.98 and 87.71 J/g for KSF, RSF and CB, respectively.

3.5 Static crystallization behavior

Figure 3 displays crystallization curves of KSF and RSF which followed changes in SFC of the fat samples during static isothermal crystallization at 25°C for 60 min.

![Figure 3](image)

**Table 3** Temperature of phase transition points (T) and crystallization and melting enthalpies (ΔH) for krabok seed fat (KSF), rambutan seed fat (RSF) and cocoa butter (CB). T<sub>CO</sub> and T<sub>MC</sub> represent crystallization onset and melting completion temperatures, respectively. 1, 2, 3 and 4 are points of phase transition, based on Figure 2 for DSC thermograms of crystallization and melting.

<table>
<thead>
<tr>
<th>Sample</th>
<th>ΔH (J/g)</th>
<th>Transition point temperature (°C)</th>
</tr>
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<tbody>
<tr>
<td></td>
<td></td>
<td>T&lt;sub&gt;CO&lt;/sub&gt;</td>
</tr>
<tr>
<td>Crystallization</td>
<td></td>
<td></td>
</tr>
<tr>
<td>KSF</td>
<td>111.61</td>
<td>24.61</td>
</tr>
<tr>
<td>RSF</td>
<td>83.27</td>
<td>28.13</td>
</tr>
<tr>
<td>CB</td>
<td>72.81</td>
<td>19.10</td>
</tr>
<tr>
<td>Melting</td>
<td></td>
<td></td>
</tr>
<tr>
<td>KSF</td>
<td>131.66</td>
<td>39.88</td>
</tr>
<tr>
<td>RSF</td>
<td>97.98</td>
<td>9.42</td>
</tr>
<tr>
<td>CB</td>
<td>87.71</td>
<td>17.49</td>
</tr>
</tbody>
</table>
static isothermal crystallization at 25°C for 60 min. Both samples started to solidify before the crystallization temperature was reached with RSF demonstrating a higher SFC at the starting point of the crystallization time. The crystallization of KSF then developed rapidly with its SFC surpassing that of RSF within 1 min and the crystallization of the fat continued until the SFC attained a plateau at ~45 min, suggesting that the equilibrium had been reached. It can be seen from the figure that the crystallization of KSF was a one-step process. This was possibly due to the fact that KSF was comprised of a group of triglycerides with an abundance of saturated fatty acids that began to crystallize at approximately the same time. On the contrary, the crystallization of RSF, which contained more complex mixtures of triglycerides, was clearly divided into two parts with different slopes, suggesting that the crystallization of the fat was a two-step process. The two-step crystallization curves have been observed before with vegetable fats\textsuperscript{21, 22}. The change in the slope of the crystallization curve could be related to either the formation of different polymorphic forms of the fats, or the crystallization of different fractions\textsuperscript{22}. The SFC of RSF reached a plateau at around 40 min with an SFC value that was ~35% lower than that of KSF.

Changes in the polymorphic structure of KSF, RSF and CB during static isothermal crystallization at 25°C for 7 days was demonstrated in Fig. 4. KSF began to crystallize before the temperature decreased to 25°C (Fig. 4a). At t = 0, the fat crystallized into a mixture of polymorphs with four diffraction peaks located at 3.84(1), 4.04(2), 4.24(3) and 4.41(4) Å. The peaks at 3.84 and 4.24 Å corresponded to β’ structure\textsuperscript{23}. The 4.04 Å peak was close to peak range of β (3.70-4.00 Å) reported by Ghotra et al.\textsuperscript{24}. The peak at 4.41 Å matched one of the diffraction peaks of pseudo-β’ structure reported by D’Souza et al.\textsuperscript{25} and O’Brien\textsuperscript{26}. During 7 days of crystallization, the diffraction profiles of KSF did not display any significant change with the four diffraction peaks remaining, indicating that the fat’s structure was a mixture of β’ and pseudo-β’ throughout the crystallization time.

RSF also began solidification before the crystallization temperature was reached (Fig. 4b). The fat crystallized into a mixture of polymorphs with diffraction peaks at 3.85 (1), 4.15 (2), 4.24 (3) and 4.55 Å (4). The diffraction pattern remained the same for at least 24 h. The peaks at 3.85 and 4.24 Å corresponded to β’ structure\textsuperscript{27} while the 4.15 Å peak could be related to either α structure\textsuperscript{27} or pseudo-β’ structure\textsuperscript{23}. However, considering that fats usually crystallize into α structure at a low temperature before transforming to a more stable polymorph, it was more likely that the diffraction peak at 4.15 Å of RSF crystallized at 25°C for 24 h corresponded to pseudo-β’ structure. The diffraction peak at 4.55 Å corresponded to β structure\textsuperscript{28}. At 7 days, the diffraction profile showed one dominating diffraction peak at 4.60 Å, a typical diffraction pattern of β structure\textsuperscript{27}. This suggested that polymorphic transition had taken place between 1 and 7 days of the crystallization time. The fact that the polymorphic structure of RSF remained unchanged during the first 1.5 h implies that the two-step crystallization curve observed earlier with RSF during the SFC study (Fig. 3) was more likely related to the crystallization of different fractions than the formation of different polymorphic forms of the fat.

CB did not crystallized immediately as the temperature descended to 25°C (Fig. 4c). At 1.5 h of crystallization, the fat had solidified into form IV in β’ structure with two diffraction peaks at 4.15(5) and 4.35 Å (6). At 24 h, the fat structure was still in β’ structure. After 7 days, CB had transformed into β structure with four typical diffraction peaks at 3.67(1), 3.75(2), 3.87(3), 3.98(4) and 4.58 Å (7), corresponding to a stable form V of the fat\textsuperscript{29}.

It can be seen here that the crystallization behavior of the three fats were quite different from one another. However, the crystallization behavior of RSF was more similar to CB than KSF. Both RSF and CB exhibited polymorphic transition during crystallization and after 7 days had transformed into β structure. The phase transformation did not occur with KSF during the experiment and after 7 days the fat was mostly still in β’ structure, indicat-
ing that $\beta'$ was probably the most stable structure of the fat.

3.6 Morphology study

The microstructure of fat crystal networks has a great effect on macroscopic properties\(^\text{30}\). The PLM micrographs of the fat samples obtained after static crystallization at 25°C for 48 h are given in Fig. 5. The solid phase appears white or gray while the liquid phase appears black. The microstructure of CB crystals was loosely-packed spherulites consisting of needle-like crystals radiating and branching outward from central nuclei (Fig. 5a). The crystal size of the fat ranged from 15 to 60 μm. Some degree of crystal aggregation, presumably by van der Waals forces\(^\text{31}\), is evident in the figure. The microstructure of KSF crystals was densely-packed spherulites with near-perfect spherulitic shape and smooth appearance that strongly aggregated to one another (Fig. 5b). The crystal size of KSF was apparently much larger than that of CB. The largest crystal in the image was as large as ~375 μm. Finally, the microstructure of RSF crystals was very similar to KSF but with a slightly smaller average crystal size (Fig. 5c). A small extent of crystal aggregation had also been observed.

4 CONCLUSION

From the results obtained in this study, KSF exhibited the highest saponification value and slip melting point but the lowest iodine values. KSF, RSF and CB displayed different crystallization behavior at 25°C. KSF displayed a one-step crystallization curve and simple DSC crystallization and melting thermograms. It started melting rapidly around 30°C and completed just after 40°C. The crystallization behavior of RSF was more similar to CB than KSF with a two-step crystallization curve. The amount of lauric acid in KSF situated well within the range of lauric acid content in coconut and palm kernel oils. This would give it potential to be used as a starting material for manufacturing lauric-fat cocoa butter replacer. According to these results, the Thai KSF and RSF have physicochemical and thermal characteristics and crystallization behavior that may be useful for specific applications in several segments of industry, from confectionery to cosmetic and pharmaceutical.

REFERENCES


Characterization of Krabok and Rambutan Seed Fats


