Tripalmitin and monoacylglycerols as modifiers in the crystallisation of palm oil

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1. Introduction

The fatty acid composition of palm oil is characteristic and unique, containing approximately the same amount of saturated and unsaturated fatty acids, particularly palmitic and oleic acids. Another relevant factor is the significant amount of saturated fatty acids (10–16%) located in the sn-2 position of the triacylglycerols, these being determinant with respect to the crystallisation properties. The triacylglycerols present are composed of 4.0–10.5% of tri-saturated, 41–59% of disaturated–monounsaturated, 32–54% of monosaturated–disaturated and 3.0–12% of triunsaturated (O’Brien, 2004).

The types of nucleation involved in fat crystallisation are divided into primary and secondary nucleation, the first being subdivided into homogeneous and heterogeneous. Primary nucleation occurs not only at the beginning of the crystallisation process, but also parallel to secondary nucleation, being controlled by a sufficient amount of thermodynamic forces, such as subcooling or supersaturation. Most natural fats have sufficient amounts of minority lipids to influence this process. The secondary nucleation process is linked to crystal growth from the surface of previously formed structures, or parts of these, which may give rise to a crystalline network. A fat crystal network is formed by their aggregation, due to the attraction exerted by Van der Waal’s forces. This union continues to grow until a three-dimensional network is formed. The crystals start to join up in the presence of small already-formed structures, until they become crystal structures of great volume, while the processes of nucleation and growth continue. A consequence of the simultaneous processes of crystallisation and aggregation is that even with low proportions of crystallised fat, a continuous network is formed. This process leads to the formation of solid bridges between crystals (sintering) and aggregated particles. The number, size and shape of the particles and the dimensions of the clusters will define the microstructure, which will determine the mechanical properties of the fat (Bois-telle, 1988; De Graef, Dewettink, Verbeke, & Foubert, 2006; Foubert, Dewettink, Van de Walk, Dijkstra, & Quinn, 2007).

In a crystallisation process, the induction time may be defined as the time required to detect the formation of the first nucleus in a subcooled or supersaturated system. This period includes the actual time required for the nucleation, plus the time required to detect crystallisation using an experimental technique. Since subcooling is the temperature to which the triacylglycerol is cooled below the equilibrium temperature and leads to an increased nucleation rate and shorter nucleation time (Metin & Hartel, 2005), one may consider that the induction time usually increases with an increase in crystallisation temperature and decrease in sample melting point.
Monoacylglycerols assume an important role in the crystallisation process. In some cases, when they are present at high levels or low temperatures, they generally contribute to the crystallisation process by increasing both the number of crystals and the nucleation rate. On the other hand, when they are present at low levels or higher temperatures, they will slow the crystallisation process down in a lipid material (Foubert, Vanhoutee, & Dewettinck, 2004).

Triacylglycerols levels in binary mixtures affect their crystallisation behaviour. Both the thermal behaviour observed by DSC and the polymorphism value by X-ray diffraction have changed for different fractions of tripalmitin blended with 1,3-dipalmitoyl-2-oleoyl-glycerol (POP) and 1,2-dioleoyl-3-palmitoyl-glycerol (POO) (Mihara, Ishiguro, Fukano, Taniuchi, & Ogino, 2007).

The lipid composition and crystallisation conditions influence the crystal format, and different polymorphic forms and crystal morphologies are possible. The crystals are aggregated into larger structures forming a network, which characterises the fat microstructural level. The type of polymorph characteristic of a fat or oil is dependent on the distribution of fatty acids in the triacylglycerol molecule, and the degree of randomisation is particularly important. In turn the microstructure concept includes information about the state, quantity, shape, size, spatial relationship and interaction amongst all the components of the crystalline network, and has an enormous influence on the macroscopic properties of the fats (Marangoni & Hartel, 1998; Ribeiro et al., 2009; Shi, Liang, & Hartel, 2005).

Although there are explanations about the mechanisms that determine the crystal type formed, there is little information about the way the presence of some compounds modifies crystal polymorphism. Knowledge of this effect could make it possible to control palm oil crystallisation, leading to its application in a huge variety of products and processes. The objective of this study was to make a complete characterisation of the changes caused in the crystallisation behaviour of refined palm oil by the addition of monoacylglycerols with different fatty acid compositions and two different levels of tripalmitin. The characterisation was made considering the thermogram and isothermal crystallisation, the kinetics and morphology of crystal formation and the polymorphic changes that occurred.

2. Materials and methods

2.1. Materials

Refined, bleached and deodorised palm oil (Po) were provided by national industry. Tripalmitin (PPP), 99% purity, was provided by Sigma–Aldrich (St. Louis, MO). Monoacylglycerols of fully hydrogenated palm oil (MP), 90% of theoretical purity and monoacylglycerols of behenic acid (MBe), 90% of theoretical purity, were used as commercial samples.

2.2. Sample preparation

2.2.1. Addition of acylglycerols

Four palm oil samples were prepared by adding tripalmitin (two different levels) and monoacylglycerols (behenic acid and full hydrogenated palm oil) to a Po sample.

Two different levels of PPP were added (5.7% and 11.4% of Po sample mass), resulting in final tripalmitin contents of 13.6% (PoTP1) and 17.8% (PoTP2). The palm oil samples were previously melted, tripalmitin was weighed on an analytical balance and added to the tubes with palm oil. The systems were shaken in shaker tubes for 30 s, heated at 100°C for 30 min and shaken again for 30 s at around 100°C, to ensure complete homogenisation.

Following the above procedure, 1.01% (m/m) of MP or MBe was added, resulting in PoMP and PoMBe samples, respectively, each one with 1.0% of monoacylglycerols regarding the final mass.

2.3. Analytical methodology

2.3.1. Triacylglycerol composition

Triacylglycerol levels were measured based on AOCS CE 5-86 (2004) methodology, determined by an Agilent capillary gas chromatography system, Series 6850, with flame ionisation detector (FID), and an Agilent DB-17 capillary column (50% phenyl–methylpolysiloxane; length 15 m, internal diameter 0.25 mm and 0.15 µm film thickness). Flow rate was 1.0 ml/min, linear velocity of 40 cm/s, with a detector temperature of 375°C, injector temperature of 360°C, oven temperature from 250 to 350°C (5°C/min), followed by 350°C for 20 min, carrier gas of helium; injected volume of 1.0 µl with 1:100 split. Retention times were determined comparing with commercial standards, samples and others vegetable oils (palm oil, soybean oil, and palm kernel oil) previously identified and quantified in our laboratory. All fractions of triacylglycerols in palm oil were quantified based on relative peak area, in duplicate. The results were compared with those obtained following the procedure of Antoniosi Filho, Mendes, and Lanças (1995) and with a literature compilation (Andrikopoulos, 2002).

2.3.2. Fatty acid composition of the monoacylglycerols

Fatty acid composition was determined in duplicate by an Agilent capillary gas chromatography system, Series 6850, FID detector, with an Agilent DB-23 capillary column (50% cyanopropylmethylpolysiloxane; length 60 m, internal diameter 0.25 mm and 0.2 µm film thickness). Flow rate was 1.0 ml/min, linear velocity of 24 cm/s, with a detector temperature of 280°C, injector temperature of 250°C, oven temperature: 110°C for 5 min, 110–215°C (5°C/min), 215°C for 34 min, helium carrier gas; injected volume of 1.0 µl, 1:50 split. Methylation reaction was done using NH4Cl in methanol solution. In fatty acid methyl esters (FAME) separation saturated salt solution and petroleum ether were used according to the methodology proposed by Hartman and Lago (1973). FAME in petroleum ether were transferred into vials and analysis was done in duplicate. Individual components were identified by comparison with commercial FAMES standards, and other FAMES from vegetable oils (palm oil, soybean oil, and palm kernel oil) prepared, identified and quantified in laboratory previously. Fatty acids were quantified based on relative peak areas.

2.3.3. Isothermal crystallisation

The samples were melted in an oven and kept in an incubator for 15 min at 100°C to ensure destruction of the crystalline forms. After removing from the oven, the samples were placed in a dry static thermal bath with the temperature controlled by a Duratech tcon Peltier system (temperature range from –5 to 70°C) at a temperature of 70°C for 1 h (Campos, 2005). After this period, they were subjected to a temperature of 25°C and readings of the solids contents taken every 60 s, using low-resolution magnetic pulsed nuclear resonance equipment (NMR) (Minispeq mq 20, Bruker; Silberstreifen, Rheinstetten, Germany), until the solids level became stable.

2.3.4. Differential scanning calorimetry

The equipment used was a Perkin–Elmer Delta Series Model DSC 7 differential scanning calorimeter (DSC) of the power compensation type (Waltham, MA). The samples were previously melted and weighed (about 3–10 mg) in aluminium pans, and covers were sealed into place. An empty sealed aluminium pan was used as reference in the other DSC oven. A baseline was obtained with an empty sealed aluminium pan prior to analysis of samples.
The samples were subjected to the following temperature program: heated to 80 °C and maintained at isothermal conditions for 10 min, cooling to a temperature of −40 °C at a rate of 10 °C/min. DSC values reported are the average of three scans. The manufacturer’s software (Pyris Manager 2.04/windows) was used in thermal analysis.

2.3.5. Polarisated light microscopy

The samples were melted at 70 °C and a drop transferred onto a glass slide with the aid of a capillary tube. The drop was covered with a pre-heated cover slip before transferring to an incubator at 25 °C and maintaining at this temperature for a period of 20 h. After this period, the slides were transferred to a plate at a temperature of 25 °C (Mettler Toledo, FP82 Microscope Hot Stage). With the aid of a polarised light microscope (Olympus, model BX 50) connected to a digital video camera (Media Cybernetics), images were taken from three different visual fields at a magnification of ×40, and then a single image selected for the analysis (Gamboa & Gioielli, 2006). The Image-Pro Plus software, Version 4.5.1.22 (Media Cybernetics) was used to take the images and carry out the quantitative analysis of the results. The analysis parameter chosen was the maximum diameter of the crystal (greatest length on a given axis).

2.3.6. X-ray diffraction

The crystalline polymorphic form of palm oil was determined according to the AOCS Cd 2-95 (2004) method. The tests were performed in a Philips (PW1710) diffractometer; Bragg_Bretano geometry (θ/2θ); Cu Kα radiation (λ = 1.54056 Å, at 40 kV and 30 mA). The measurements were performed with a 0.02° step in 2θ, with an acquisition time of 2 s, over the range from 5° to 40° (2θ scale). Diffraction was performed at a temperature of 20 °C, sufficient to ensure crystallinity of the samples. The crystalline forms were identified from their characteristic short spacing, calculated using the Bragg Law:

\[ \lambda = 2d \sin \theta \]  

where \( \lambda \) is the wavelength of the X-ray emitted, \( d \) is the short spacing and \( \theta \) is the angle of diffraction. The α-form is characterised by a single line of diffraction at 4.15 Å. The β'-form is characterised by two lines of diffraction at 3.8 and 4.2 Å or 4.27, 3.97 and 3.71 Å or 3.9 and 4.3 Å. The β-form is associated with a number of diffraction lines, predominantly at 4.6 Å, and lines of lower intensity, including those at 3.9 and 3.8 Å. The sub-β-form may be characterised by a strong peak for a short spacing of 4.73 Å or three intermediate peaks at 4.5, 3.9 and 3.6 Å (AOCS, 2004; Cerdeira, Martini, Candal, & Herrera, 2006; D’Souza, deMan, & deMan, 1990; Yap, de Man, & de Man, 1989). The β- and β'-form contents in the samples were estimated by the relative intensity of the short spacing (AOCS, 2004; Che Man, Shamsi, Yusoff, & Jinap, 2003; Szydlouska-Czerniak, Karlovits, Lach, & Szlyk, 2005).

2.3.7. Statistical analysis

DSC data were statistically analysed by one-way analysis of variance (ANOVA) with Statistica (V.6) Software (Statsoft Inc., Tulsa, OK) Software. Tukey test was applied to determine significant differences between means, at a level of p < 0.05.

3. Results and discussion

3.1. Triacylglycerol composition

The triacylglycerol composition of the palm oil was 9.7 ± 0.22, 50.2 ± 0.6, 35.7 ± 0.49 and 4.3% ± 0.14 of trisaturated, disaturated–monounsaturated, monosaturated–diunsaturated and triunsaturated fractions, respectively. The tripalmitin content was 8.5% ± 0.11.

3.2. Fatty acid characterisation of the monoacylglycerols

The monoacylglycerol samples were characterised in relation to their fatty acid compositions. The primary fatty acids of the MP sample were C16:0 and C18:0, in proportions of 45.4 ± 0.05 and 53.6% ± 0.05, respectively. In turn, the MBe sample contained the fatty acids C18:0, C20:0 and C:22:0, with respective percentages of 3.6 ± 0.01, 6.9 ± 0.01 and 85.5% ± 0.02.

3.3. Crystallisation kinetics

As can be seen in Fig. 1, the induction time was reduced from 33 to 15 and 12 min, respectively, for Po, PoTp1 and PoTp2, suggesting an increase in the crystallisation rate of the samples with added tripalmitin.

The crystallisation behaviour of palm oil was changed by the addition of tripalmitin, a triacylglycerol present in significant amounts in some oils and in the stearin fraction of some fractionated oils, causing anticipation of its crystallisation when subjected to an isothermal condition.

The addition of 1% of monoacylglycerol to palm oil showed a significant effect in reducing the induction time, as shown in Fig. 1. The induction times decreased from 33 to 19 and 13 min, respectively, for PoMp and PoMBe. The addition of MBe to Po showed a greater decrease in induction time than when the same proportion of MP was added.

Monoacylglycerols act as crystallisation inducers, serving as a nucleation seed and consequently facilitating aggregation of the triacylglycerol molecules, thus reducing the induction process time. The presence of these partial acylglycerols did not lead to significant changes in the final solids content after isothermal crystallisation, which is in agreement with the results obtained by Wright, Hartel, Narine, and Marangoni (2000), who found that acceleration of the crystallisation speed by the presence of minor compounds did not necessarily affect the final solid fat content in an isothermal process.

In a study of the interaction of partial acylglycerols and triacylglycerols in milk fat, Foubert et al. (2004) reported two mechanisms of interaction with the triacylglycerol crystals. The first resulted in slower crystal growth, due to competition in binding with the triacylglycerols. The second form involved organisation in a micellar structure of partial acylglycerols, acting as nucleation facilitators, as described by Savage and Dimick (1995) and Skoda and Van de Tempel (1967), reducing the induction time and increasing the number of crystalline nuclei.

The addition of higher levels of monostearin to milk fat accelerated the crystallisation process at lower temperatures, while lower levels associated with higher temperatures delayed the crystallisation process. Distearin provoked a general delay in the crystallisation process. On the other hand, higher levels of monoolein and diolein increased the crystal growth speed, resulting in a less pronounced effect on the induction time (Foubert et al., 2004).

In a study carried out by Niiya, Maruyama, Imamura, Okada, and Matsumoto (1973) with hydrogenated fat, increases in the crystallisation rate, melting point and solid fat content were reported with the addition of saturated monoacylglycerols, such as monopalmitin, monostearin and monobehenin, the effect of the latter predominating over the others in causing rises in the melting point and solids content.

Monoacylglycerol behenic acids are probably more effective as crystallisation inducers, due to the presence of a longer fatty acid chain than those found in high proportions in the monoacylglycerols of the fully hydrogenated palm oil (palmitic and stearic acids),
leading to greater stability at the crystallisation seed-forming temperature.

3.4. Thermal behaviour

The results of one-way analysis of variance (ANOVA) indicated that, for the Po sample, the addition of tripalmitin and monoacylglycerols changed significantly the beginning of the crystallisation process \( (T_{\text{onset}}) \), the temperature at which the exothermal effect is maximum \( (T_{\text{peak}}) \) and the energy released by the crystallisation process (enthalpy) on the stearin fraction. No significant differences were observed comparing PoTp1 and PoMp, with respect to \( T_{\text{onset}} \). In the same way, PoTp1 and PoMbe did not show significant differences concerning \( T_{\text{peak}} \).

Fig. 2 shows two distinct exothermic peaks during the crystallisation process of the Po sample. The first, located in the region of higher temperatures, between 31 and 15 °C in the different thermograms, represented the crystallisation phase rich in saturated triacylglycerols, the stearin fraction. The second, between 10 and –12 °C, represented the crystallisation process of the phase rich in unsaturated triacylglycerols, the olein fraction, which corroborates the observations of Tan and Che Man (2000), who described the formation of two distinct peaks in the DSC analysis of palm oil.

Acceleration of the crystallisation process in the samples with added tripalmitin and monoacylglycerols may be observed by the displacement of the \( T_{\text{onset}} \) and the \( T_{\text{peak}} \), referring to stearin in the region of higher temperatures. As can be seen in Table 1, the start of crystallisation of the Po was early in proportion to the addition of tripalmitin. The presence of MBe resulted in a greater change in the Po crystallisation temperature, by 2.9 °C, whereas with MP it was only by 1.6 °C.

Increasing the crystallisation temperature by the addition of PPP is in agreement with the results of studies by Che Man, Haryati, Ghazali, and Asbi (1999) on the thermal behaviour of crude palm oil and its derivatives, in which the crystallisation peaks of the compounds containing more saturated triacylglycerols moved...
to the region of higher temperatures. According to Toro-Vazquez, Briceno-Montelongo, Dibildox-Alvarado, Charo-Alonso, and Reyes-Hernandez (2000), who studied the crystallisation kinetics of palm stearin in sesame oil, the tripalmitin was primarily responsible for increasing the crystallisation temperature of this blend.

Samples with added tripalmitin led to the release of more heat during the crystallisation of the phase rich in saturated triacylglycerols. On the other hand, the addition of monoacylglycerols in spite of increasing the crystallisation temperature produced a lower increase in the release of energy during the crystallisation process relative to tripalmitin (Table 1). A great increase in the release of heat during the crystallisation process may be detrimental, since it may result in elevated temperatures that will cause the dissolution of already-formed crystals. Wassell and Young (2007) mentioned the addition of small amounts (1–2%) of saturated triacylglycerols as a cheap and effective alternative to induce the start of the crystallisation process.

3.5. Crystalline morphology and microstructure

The minimum and maximum values for maximum crystal diameter at 25 °C were 53 and 128, 55 and 142, 56 and 118, 7 and 99, and 25 and 51 μm, respectively, for Po, PoTp1, PoTp2, PoMp and PoMBe.

It can be seen that the minimum values for the crystal diameter of Po, PoTp1 and PoTp2 were very close to 50 μm, indicating that raising the PPP level did not cause an increase in the smallest crystal diameter formed in palm oil. Higher PPP levels led to the formation of larger amounts of crystals with relatively homogeneous size and form. A small number of clusters can be observed in PoTp2 (Fig. 3).

It can be seen from the Po, PoMp and PoMBe samples that the addition of monoacylglycerols induced the formation of large numbers of small crystalline nuclei, in agreement with that described by Foucart et al. (2004) who reported an increase in the amount of crystallisation seed and in the number of crystals formed and a decrease in the induction period, due to the influence of existing partial acylglycerols. The minimum diameter values, 7 and 25 μm, were much lower than those obtained for Po in the absence of monoacylglycerols.

Monoacylglycerols play the role of crystallisation seeds, dispersed in the palm oil. Triacylglycerol molecules are adsorbed onto the surface of these structures and then the crystallisation process begins. A large number of seeds results in smaller crystals, since the triacylglycerols are distributed during their adsorption and crystallisation.

As seen in Fig. 3, the addition of monoacylglycerols of behenic acid resulted in the formation of a structured network composed of clusters of homogeneous crystals. However, the presence of palm-based monoacylglycerols, while increasing the amount of crystals, did not lead to the formation of a structured network, showing great diversity in their diameter.

The crystallisation occurring from the formation of a large number of small crystalline nuclei could be one of the causes of the lower energy release during this process, since the samples showing lower exothermic peaks during the process possessed the smallest crystal diameters. The energy released during the formation of larger crystals seems to be greater than that released during the formation of smaller crystals, even when in significantly larger numbers.

The addition of saturated monoacylglycerols leads to the formation of a greater number of crystallisation seeds, possibly more stable to the effect of temperature. During the crystallisation process, a crystalline network is formed that allows for greater interaction between triacylglycerol molecules, between which intermolecular attractive forces such as the Van der Waal’s forces can act, which may promote greater intermolecular attraction, leading to a decrease in system solubility, more evident at high temperatures, contributing to the crystallisation process.

3.6. Avrami model

The Avrami model is the one most commonly used to study the crystallisation of fats and may be used to assess the crystallisation kinetics and suggest the nature of crystal growth. The model takes into account that crystallisation occurs by nucleation and by crystal growth and is based on the isothermal transformation conditions, random spatial growth and the kinetics of the system, in which the growth speed of the new phase depends solely on temperature. The Avrami equation is presented in the following way:

$$\frac{SFC}{SFC_{\text{max}}} = 1 - e^{-kt^n}$$

where \( n \) is the Avrami exponent (dimensionless), \( k \) is the Avrami constant, \( SFC \) is the solids content at a given time and \( SFC_{\text{max}} \) is the maximum level of solids at a given temperature.

The half life of crystallisation, \( t_{1/2} \), reflects the magnitude of \( k \) and \( n \) according to the equation:

$$t_{1/2} = \left( \frac{\ln 2}{k} \right)^{1/n}$$

The constant \( k \) represents the rate of crystallisation, while the exponent \( n \), known as the crystallisation index, indicates the mechanism of crystal growth. The parameter \( n \) is a combination function of a time-dependent nucleation and number of potential growth dimensions (Marangoni, 2005).

Nucleation may be sporadic or instantaneous and crystal growth may be one, two- or three-dimensional, characterising the formation of needles, disks or spherulites, respectively, as the crystalline forms. Values of \( n = 3 \) correspond to an instantaneous or sporadic nucleation spherulite form or to a sporadic nucleation disk form, while values of \( n = 2 \) correspond to the sporadic growth of needle-like forms or the instantaneous nucleation of disk-like growth. Although \( n \) should be a whole number, fractional values are commonly obtained. This event is primarily related to the formation of crystals with similar morphology from different types of nucleation (sporadic or instantaneous). Fractional values of the exponent \( n \) may be explained by the simultaneous development of crystals with different morphologies (Marangoni, 2005).

The parameters of the Avrami model were calculated based on the results from isothermal crystallisation at 25 °C, considering the time interval occurring when the induction period ends, up to 10 min after stabilisation of the solid fat content.

### Table 1

Crystallisation temperatures and exothermic peaks of refined palm oil and its blends with tripalmitin and monoacylglycerols.

<table>
<thead>
<tr>
<th></th>
<th>Po</th>
<th>PoTp1</th>
<th>PoTp2</th>
<th>PoMp</th>
<th>PoMBe</th>
</tr>
</thead>
<tbody>
<tr>
<td>T&lt;sub&gt;onset&lt;/sub&gt; (°C)</td>
<td>24.37 ± 0.31</td>
<td>25.83 ± 0.06</td>
<td>29.71 ± 0.14</td>
<td>26.00 ± 0.44</td>
<td>27.3 ± 0.36</td>
</tr>
<tr>
<td>T&lt;sub&gt;peak&lt;/sub&gt; (°C)</td>
<td>20.17 ± 0.81</td>
<td>24.80 ± 0.00</td>
<td>27.41 ± 0.19</td>
<td>23.63 ± 0.35</td>
<td>25.01 ± 0.21</td>
</tr>
<tr>
<td>Area (J/g)</td>
<td>3.99 ± 0.42</td>
<td>19.3 ± 0.03</td>
<td>23.08 ± 0.38</td>
<td>8.73 ± 0.23</td>
<td>13.10 ± 0.26</td>
</tr>
</tbody>
</table>
From the $k$-values reported in Table 2, it can be observed that the crystallisation rates increase with the percentage of PPP. Of the samples with added monoacylglycerols, PoMBe showed higher crystallisation rates than PoMp, confirming the greater effectiveness of the monoacylglycerols of behenic acid as accelerators of the crystallisation process, as compared to palm-based monoacylglycerols. Both the samples with added tripalmitin and with added monoacylglycerols showed higher rates of crystallisation than Po.

These results agree with those found for the value of the half life of crystallisation.

From the exponent $n$, observed in Table 2, a tendency for crystal formation of the spherulite type for Po can be noticed. The addition of 1% of palm-based monoacylglycerols did not change the crystal morphology, since crystals of the spherulite type continued to form. Although the $n$-value obtained for PoTp2 was 2.4, Fig. 3 shows the formation of spherulites. For PoTp2 and PoMBe, the $n$-values suggest a transition from two-dimensional growth, disc type, to three-dimensional growth, spherulite type.

### 3.7. Crystalline polymorphism

From the X-ray diffractograms in Fig. 4, the absence of peaks for a short spacing of 4.6 Å and the presence of an intense peak showing crystals with a short spacing of 4.2 Å can be seen for Po, where crystals with a short spacing of 3.8 Å can also be observed. This configuration characterises the absence of $\beta$-crystals and the

<table>
<thead>
<tr>
<th>$k$ (min$^{-1}$)</th>
<th>Po</th>
<th>PoTp1</th>
<th>PoTp2</th>
<th>PoMP</th>
<th>PoMBe</th>
</tr>
</thead>
<tbody>
<tr>
<td>$n$</td>
<td>3.9</td>
<td>3.0</td>
<td>2.4</td>
<td>4.1</td>
<td>2.6</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.96</td>
<td>0.96</td>
<td>0.90</td>
<td>0.81</td>
<td>0.81</td>
</tr>
<tr>
<td>$t_{1/2}$</td>
<td>48.8</td>
<td>24.4</td>
<td>16.5</td>
<td>24.8</td>
<td>18.0</td>
</tr>
</tbody>
</table>

Table 2

Avrami model parameters for the crystallisation of refined palm oil and its blends with tripalmitin and monoacylglycerols at 25 °C.

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Fig. 3. Microscopic images under polarised light at 25 °C of refined palm oil, refined palm oil with added tripalmitin and refined palm oil with added monoacylglycerols: Po; PoTp1; Po2Tp2; PoMp; PoMBe. The bar represents 200 μm.
strong presence of β-crystals. In a similar way, Braipson-Danthine and Gibon (2007) demonstrated the diffraction lines of the β-form for palm oil at 20 °C, with peaks of low intensity suggesting short spacings of 4.32 and 4.12 Å and peaks of high intensity in the short spacings of 3.88 and 4.20 Å, close to those obtained in the present paper.

The addition of tripalmitin induced the formation of polymorphic β-form crystals, and the amount of β-crystals formed was in proportion to the addition of tripalmitin, as can be seen from the increase in intensity of the diffraction peak for a short spacing of 4.6 Å, characteristic of PoTp1 to PoTp2.

The addition of monoacylglycerols also led to a change in the polymorphic form of the crystals present in palm oil. The presence of MP led to the formation of β-type crystals. When MBe was added, peaks for β-crystals appeared and a sub-β transitional form could also be observed, indicated by short spacings of, respectively, 4.6 and 3.9 Å. Adding 1% of fully hydrogenated palm-based monoacylglycerols also caused the formation of β-crystals, despite coexisting with a higher content of β'-crystals, since a relatively intense peak for a short spacing of 4.2 Å can be observed.

The decreasing intensity of the peaks related to the β-form and simultaneous increase in the intensity of the β peaks and appearance and increase in intensity of peaks related to a transition of the sub-β form, indicated by, respectively, short spacings of 4.5 and 3.9 Å, shows the effect of PPP in facilitating the transition to β.

Mazzanti, Guthrie, Sirota, Marangoni, and Idziak (2004) reported that the formation of the β-phase was largely dependent on a previously formed α-phase. The polar lipids (acylglycerols) act as crystallisation sites for the induction of crystallisation in the initial α-phase. From this previously formed α-stage, the triacylglycerols could switch to a β-phase, due to increased stability of the crystalline arrangement. However, the absence of polar lipids allows for freer accommodation of the triacylglycerol molecules in the β-form, inducing a quick transition from the α to the β'-form.

Smith, Furó, and Smith (2007) described the action of partial acylglycerols in the modification of crystal morphology, by binding them to a crystalline face and preventing deposition of triacylglycerol molecules on that surface, reducing crystalline growth in this region. Wright and Marangoni (2003) also stated that when impurities were present in a fat crystal, they generally modified the growth of certain faces, changing the morphology of the crystalline structures. Even so, the authors found no changes in the crystalline morphology of milk fat due to the removal of minor compounds or the addition of diacylglycerols.

Timms (1984) relates the β'-form to the asymmetry of the triacylglycerol molecule in the presence of saturated and unsaturated fatty acids. Similarly, the β-form is related to the symmetry of triacylglycerols, both in the occupancy of the 1,3 positions and in the occupancy of all three positions by fatty acids of similar structures. This statement confirms the increase in the polymorphic β-form and the decline in β' with the addition of tripalmitin, a completely symmetrical triacylglycerol.

Monoacylglycerols of fully hydrogenated palm oil favoured the formation of β-crystals without leading to the removal of β'-crystals, which makes it an important inducer of the crystallisation process of fats in the food industry. Nevertheless, the addition of tripalmitin and monoacylglycerols of behenic acid as accelerators of the crystallisation process of palm oil, leading to β-crystal formation, may be very important in the chocolate industry, where this type of crystal is desired.

4. Conclusions

The palm oil crystallisation process may be changed by adding tripalmitin and monoacylglycerols. The addition of tripalmitin heightened the speed of crystallisation, the increase in solids content, the release of thermal energy, the increase in size of the triacylglycerol crystals and the formation of β-crystals. In turn, the addition of monoacylglycerols accelerated the crystallisation of palm oil by increasing the number of crystallisation seeds, reducing the size of the crystals formed and favouring the formation of β-crystals, without changing the solid fat content at the end of the crystallisation process.

The addition of saturated monoacylglycerols and triacylglycerols affected the crystallisation of palm oil, and by controlling these modifications, its application in specific processes could become possible. Alteration of its polymorphism, favouring the production of β-crystals instead of the β'-type, could make its application in the chocolate industry possible, decreasing production costs without modifying the characteristics of the final product. Higher crystallisation rates decrease process costs and would make it possible to use this oil in the production of food that requires high rates of crystallisation, such as candy coatings and cookie fillings, conserving the desired palm oil characteristics such as its plasticity.

References


