Research Article

Crystallization behaviour of binary fat blends containing shea stearin as hard fat

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Filling fats are used in bakery and confectionery applications. These fats are made up of complex mixtures of triacylglycerols (TAG). The crystallization, melting behaviour and polymorphic stability of fat blends are determined by the behaviour of the TAGs that they contain. Filling functionalities are influenced by their fat composition but also by the processing conditions used for crystallization. In this study, the crystallization behaviour of fat blends, all based on shea stearin as hard fat (which is high in 1,3-distearoyl-2-oleoyl glycerol (SOS)) combined with either sunflower oil, shea olein or rapeseed oil, were investigated by means of pulsed nuclear magnetic resonance (pNMR), differential scanning calorimetry (DSC) and X-ray diffraction (XRD). Blends containing either 30 or 40% shea stearin combined with one of the soft fats were selected as they met the criteria required for filling fats. Under static isothermal conditions (at 10°C, 15°C or 20°C), a two-step crystallization was observed for those blends, which can be explained by polymorphic transitions from α-form into more stable forms. All the selected blends exhibited different crystallization mechanisms according to the TAG composition of the liquid phase and their complementarity with TAG from the solid phase.

Practical applications: Results of this research are useful for the fat industry as they could help to develop new filling fats, based on shea stearin, with a reduced content of saturated fats, while maintaining the desired physical properties of such specific products.

Keywords: Filling fats / Isothermal / Polymorphism / SAFA / Shea butter

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1 Introduction

Filling fats are mainly used in the bakery and confectionery industries. The fats for such products must present specific physical properties. They hold other ingredients in place, providing a continuous fat phase, mostly solid at room temperature, but melting at mouth temperature, releasing flavours and aroma without an undesirable waxy feeling in the mouth [1, 2]. Solid fat content (SFC) should be high enough at room temperature in order to prevent fat migration leading to detrimental effects on the surrounding matrix, such as chocolate. Partial hydrogenation of vegetable oils has been used in filled confectionery for producing fats with the desired physical properties. This process creates fats with significant functional benefits for the product. However, trans fatty acids are formed, which have been shown to have unfavourable effects on blood cholesterol levels, increasing the risk of developing coronary heart diseases (CHD) [3]. For these reasons, many regulations have come into force across the world to reduce the consumption of these trans fatty acids. In many cases, filling fats containing partially hydrogenated oils have been replaced by blends of palm mid fractions (rich in 1,3-dipalmitoyl-2-oleoyl glycerol...
(POP)). In addition to nutritional improvements, the fats present a steeper melting profile giving some cool-melting mouth-feel. Nowadays, extensive work is going on in many countries to reduce the levels of saturated fats in the diet. Indeed, some studies in human health have demonstrated that their intake increases the plasma level of low-density-lipoprotein (LDL) cholesterol compared to high-density-lipoprotein (HDL) cholesterol [4], although other recent papers suggest that saturated fats may not be a problem [5]. However, the development of confectionery fillings needs solid or semi-solid fats to provide a certain degree of structure in the product and the triacylglycerols (TAGs) which have melting points above room temperature are those that contain saturated fatty acids or trans fatty acids [6]. Stanley (2009) [7] has shown that stearic acid, in spite of being saturated, does not have any effect on the cholesterol blood levels. Indeed, stearic acid is transformed very quickly into oleic acid in the liver. The latter, being unsaturated, increases HDL cholesterol and diminishes LDL cholesterol. Stearic acid is considered as physiologically neutral for all those reasons [7]. Nevertheless, the position of the stearic acid group on the TAG molecule plays also an important role. It should be esterified in the 1- or 3-position (as in cocoa butter) to be digested and released as free stearic acid [4].

In this context, the aim of this research was to explore the crystallization and polymorphic behaviour of some fat blends containing shea stearin (which is high in 1,3-distearoyl-2-oleoyl glycerol (SOS)) in order to develop new filling fats with a reduced content of saturated fats, while maintaining their desired physical properties.

2 Materials and methods

Industrial samples of shea stearin, shea olein, high oleic high stearic sunflower oil and rapeseed oil were kindly supplied by Loders Croklaan B.V. (Wormerveer, The Netherlands).

Three binary blends, all based on shea stearin as hard fat were prepared at composition intervals of 10% with 0% to 100% shea stearin content.

2.1 Fatty acid profile determination

Fatty acid methyl esters (FAME) were prepared by a base-catalyzed transesterification method based on AOCS Ce 2-66. Fat (20 μL) was melted and 0.5 M sodium hydroxide in anhydrous methanol (0.4 mL) was added. The solution was incubated for 6 min at 80°C. Boron trifluoride (20% solution in methanol) (0.4 mL) was added and incubated for an additional 1 min. Methyl esters were dissolved in iso-octane (100 μL) and saturated sodium chloride solution was added (0.4 mL). The mixture was settled for 1 min and the upper layer was diluted with iso-octane (130 μL) and 0.5 μL of the upper layer was injected. The mixture was analyzed by GC (Focus GC, Interscience, NL) using a fused silica capillary column CP-Sil (50 m × 0.25 mm × 0.2 μm film thickness). The injector and detector temperature was 245°C. The carrier gas was hydrogen (100 kPa) and the column temperature was 210°C.

2.2 TAG determination

The composition of TAGs was determined by HR-GC using a Thermo Scientific TraceGC Ultra gas chromatography system (Interscience, NL) equipped with a Thermo TriPlus autosampler, cold on column (CoC) injector and flame ionization detector. A capillary column, CP-TAP CB of 25 m of length, 0.25 mm internal diameter and 0.10 μm film thickness (Agilent Technologies, NL) was used. The elution of TAGs was carried out by using a temperature gradient (300–350°C at 7°C/min, hold at 350°C for 8 min), while the detector temperature was set at 360°C. The sample injection volume was 1.0 μL, hydrogen was used as a carrier gas and the column head pressure was regulated by applying a constant flow rate of 2.4 mL/min. The gas chromatography method was validated and peaks identified using the Cocoa Butter Equivalent Reference Material (Loders Croklaan B.V.) and pure TAGs (POS, SOS and POP). Integration of the chromatographic peaks was performed using the manufacturer’s software (EZChrom Elite, Agilent).

2.3 Solid fat content determination by p-NMR

The SFC was determined using a pulsed nuclear magnetic resonance (pNMR) spectrometer (Minispec-mq20, Bruker, Karlsruhe, Germany). Automatic calibration was made daily using three standards (Bruker, Karlsruhe, Germany) containing, respectively, 0.0, 31.3 and 74.8% of solids.

2.3.1 Melting profiles

Solid fat content determination was performed according to the IUPAC 2.150 (a) non-tempered serial method and IUPAC 2.150 (b) tempered serial method [8]. Data are reported as averages of two independent measurements.

2.3.2 Isothermal crystallization

Filled NMR tubes were put 30 min in an oven at 80°C to fully melt and erase the crystal history. Tubes were then transferred in a water bath coupled with a temperature regulator to reach the isothermal temperature (10, 15 or 20°C). SFC measurements were done after 2, 5, 8, 10, 12, 15, 20, 30, 45, 60, 90, 120, 150, 180 and 250 min at the isothermal temperature. All the measurements were performed in duplicate.
2.4 Differential scanning calorimetry (DSC)

2.4.1 Isothermal crystallization curves by DSC via stop-and-return technique

Samples were analysed by DSC using the stop-and-return technique as described by Foubert et al. [9]. Analyses were carried out using a Q1000 DSC (TA Instruments, New Castle, DE). Fats were hermetically sealed in aluminum hermetic pans. An empty pan was used as a reference. Calibration was made with indium (m.p. 156.6°C) and n-dodecane (m.p. –9.56°C) standards. Nitrogen was used to purge the system in order to prevent condensation in the cells.

The following time-temperature program was applied: holding for 10 min at 80°C to ensure the complete melting of the sample and erase its history; cooling at –10°C/min to the isothermal crystallization temperature which was either 10, 15 or 20°C; holding for the required crystallization time at this temperature and further heating at 5°C/min to 80°C.

2.5 X-ray diffraction spectroscopy (XRD)

The polymorphic forms of the fat crystals in the samples were determined by XRD spectroscopy using a D8 Advance Diffractometer (Bruker, Germany) equipped with a X-ray generator Kristalloflex K780 (Bruker, Germany) (λ Cu =1.54178 Å, 40 kV, 30 mA), and a temperature control unit (TCU 110 system, Anton Paar, Austria) connected to a water bath. This system allows adjustments of the temperature of the thermostated diffractometer chamber TTK 540 (Anton Paar, Graz, Austria).

2.5.1 Isothermal crystallization

The temperature program applied on the samples in the X-ray diffractometer was the following: holding for 10 min at 80°C to ensure the complete melting of the sample; cooling at –10°C/min to the isothermal crystallisation temperature: 10, 15 or 20°C and holding for 4 h at this temperature. X-ray measurements were performed every 30 s during the isothermal period, in the 2θ range 15°–27° (short spacings region) using a Vantec detector (Bruker, Germany). The diffraction pattern was analysed using EVA Diffrac.suite and EVA Diffrac.plus softwares (Bruker, Germany).

3 Results

3.1 SFC melting profiles

Three binary blends all based on shea stearin as hard fat (at composition intervals of 10 ± 0.1% (w/w), from 0 to 100% shea stearin content) have been prepared and characterised by pNMR. All the mixtures were submitted to non-tempered method (Fig. 1A–C), and tempering 40 h at 26°C (Fig. 1D–F). Curves corresponding to blends containing more than 57% of saturated fatty acid (SAFA) have been represented using dashed lines (Fig. 1A–F). As expected, the amount of solid fat increased with the concentration of shea stearin; this is true for all the binary blends. According to the NMR profiles, non-tempered blends made of shea stearin and rapeseed oil or sunflower oil are ‘not ideal’: the curves intersect (Fig. 1A and C). This is due to the fact that the shea stearin crystallises in a less stable polymorph than in the presence of higher amount of liquid oil. After tempering, the curves are not crossing anymore since the shea stearin has had timed to stabilise into a more stable polymorph (β). After tempering, the behaviour of the three binary blends is ‘monotectic’ as indicated by the isosolid diagrams (Fig. 2A–C).

3.2 Blend selection

The blend selection for the rest of the study was based on four criteria all linked to industrial final application as filling fats: (i) a steep melting profile; (ii) a low solid fat content at 35°C; (iii) a saturated fatty acids level lower than 57% (commercial reference); and (iv) a sufficient level of SFC at 20°C (close to 50%) [10].

The solid fat contents considered for the blend selection were the tempered ones.

According to the four criteria required for filling fats, just listed, two different proportions of binary blends were selected: blends containing 40 or 30% of shea stearin mixed either with sunflower oil or shea olein.

Blends containing 30% shea stearin were selected due to their low SFC at 35°C (around 1%) even if their SFC at 20°C were slightly low (22–24%). For this reason, blends containing 40% of shea stearin were also considered due to their higher SFC at 20°C (28–34%), despite the fact that their SFC at 35°C might be somewhat too high (around 6% each). At 37°C, they were almost completely melted (1.5%). In view of those results, the four selected binary blends were made of shea stearin/sunflower oil (30/70 and 40/60) and shea stearin/shea olein (30/70 and 40/60).

All of them presented a notably steep melting profile between 25°C and 35–37°C. Regarding the SAFA contents, blends made of shea olein contained more saturated fat (around 46 and 49%) compared to same proportions using sunflower oil as soft fat (around 38 and 42%) (Table 1). Those contents are significantly reduced compared to the commercial reference (57%). Among the blends made of rapeseed oil, none of them met all the required criteria. However, the blend made of 40% shea stearin and 60% rapeseed oil has also been studied in order to validate some hypothesis.
3.3 Isothermal crystallisation behaviour of binary blends containing 30% of shea stearin

3.3.1 Blend containing sunflower oil as soft fat

The NMR isothermal crystallisation curves obtained at 10, 15 and 20°C are presented Fig. 3A–C, respectively (plain lines).

This blend made of 30% shea stearin mixed with 70% sunflower oil presented two-step crystallisation behaviour for all the temperatures. A two-step crystallisation can be due to a sequential crystallisation of high-melting components followed by low-melting components or to a sequential crystallisation of two different polymorphs (α to β'). The two-step phenomenon was somewhat less clear at 10°C as a large proportion of the fat already crystallised during the
cooling (SFC content is not 0 at the beginning of the isothermal period). To better characterise the crystallisation behaviour of the blend, DSC stop and return experiments were conducted as described by Foubert et al. [9]. This technique allows the monitoring of the degree of crystallisation as a function of isothermal time, despite the fact that some crystallization had occurred before the isothermal temperature was reached. Results obtained by this technique for the three isothermal temperatures (10, 15 and 20°C) are presented in Fig. 4A–C. At 10°C, at the beginning of the isothermal period, a first low melting peak appeared then it tended to decrease and eventually disappeared at the benefit of a higher melting peak (Fig. 4A). This higher melting peak continued to grow even after disappearance of the first peak, indicating an increasing amount of crystals. The lower melting peak appeared at around 12°C and the second peak appeared at around 25°C. At 15°C, at the beginning of the crystallization a small broad peak was detected, afterwards the curves evolved into a well-resolved growing peak at around 25–27°C (Fig. 4B). At 20°C, a similar behaviour was observed (Fig. 4C).

To better understand the crystallisation behaviour of this blend, isothermal XRD experiments were conducted to monitor the polymorphic behaviour of the blend during the whole isothermal period (4 h). Results are presented as a function of time (from 0 to 240 min) in Fig. 5 and 5bis (Supporting Information). At 10°C, the first crystallization step was characterised by an interplanar distance (short spacing) at \( d = 4.2 \, \text{Å} \), corresponding to \( \alpha \)-form, which was then converted to \( \beta' \)-form (short spacings at \( d = 4.36, 4.30, 4.17, 3.88 \) and 3.80 Å). At the end of the isothermal period (240 min), \( \beta' \) and traces of \( \beta \) (short spacings at \( d = 5.3, 4.6, 4.37, 4.30, 4.17, 3.89 \) and 3.80 Å) were present (Fig. 5A). At 15°C, similar trends were observed. This blend crystallised first into \( \alpha \) which evolved into \( \beta' \). After 4 h at 15°C, a blend of \( \beta' \) and a small amount of \( \beta \) were observed (Fig. 5B). At 20°C, a very small amount of \( \alpha \) crystallised first, then it transformed into more stable forms; a mixture of \( \beta' \) and \( \beta \) was detected after 4 h at 20°C (Fig. 5C).

### 3.3.2 Blend containing shea olein as soft fat

The NMR crystallisation curves obtained for this second blend at 10, 15 and 20°C are presented in Fig. 3A–C, respectively (dashed lines). The crystallisation rate of this blend was lower compared to the previous blend with sunflower oil (Fig. 3A–C, plain lines); different shapes of the crystallisation curves were observed. The effect of the crystallisation temperature was even more pronounced in this case. Moreover, no true ‘plateau’ (indicating stable SFC) reached after 4 h of isothermal conditions whatever the temperature; this is especially true for 20°C. Again, higher temperature decreases the driving force of crystallisation.

DSC stop and return experiments were conducted as for the previous blend at 10, 15 and 20°C; results are presented in Fig. 4D–F.

At 10°C, at the beginning of the isothermal period, a low melting peak was present together with a small higher melting peak (observed round 22°C), which increased during the isothermal period (Fig. 4D). At 15 and 20°C a small broad peak was first observed (Fig. 4E and F). Afterwards it evolved into better-resolved, higher-melting peak (around 27°C), which then grew indicating an increasing amount of crystals. After 2 h, a shoulder was observed at temperatures even higher than 30°C (Fig. 4E). At 20°C, the small peak observed at the

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**Figure 2.** (A–C) Isosolid diagrams constructed from NMR data (after tempering 40 h at 26°C); binary blend made of shea stearin and sunflower oil (A), binary blend made of shea stearin and shea olein (B), and binary blend made of shea stearin and rapeseed oil (C).
beginning of the isothermal period remained constant during more than 2 h. It corresponds to the broad ‘plateau’ observed in the NMR curve (Fig. 3C).

Isothermal XRD experiments were performed to better characterise and understand the crystallisation behaviour of the blend. Results are presented in Fig. 5D–F and 5bis d–f (Supporting Information). It is obvious that the crystallisation kinetic was slower than the previous blend and that temperature had a higher impact (Fig. 5F vs. C). At 10°C, the crystallisation temperature decreased, short spacings at \( d = 4.17 \text{Å} \), then as time increased, short spacings at \( d = 4.69 \text{Å} \), \( d = 4.53 \text{Å} \), \( d = 4.34 \text{Å} \) and \( d = 3.87 \text{Å} \) were added to the first one, indicating the presence of the \( \gamma \)-form of SOS TAG [11] (Fig. 5D). At the end of the isothermal period (4 h), a blend of \( \gamma \) and \( \beta \)’ were detected. At 15°C, the \( \alpha \)-form was detected at the beginning of the isothermal period and it stayed longer compared to the previous blend containing sunflower oil instead of shea olein (Fig. 5E vs. B), in accordance with the NMR crystallisation curves. At 20°C, only \( \alpha \) was present during the whole ‘plateau’ observed in the NMR curve (more than 2 h); moreover the amount was very low as indicated by the very low intensity in the diffraction pattern. It then evolved into \( \beta \)’ (Fig. 5F). The two-step crystallisation observed by pNMR corresponds to polymorphic transitions from \( \alpha \)-form into more stable forms (\( \gamma + \beta \)’).

3.4 Isothermal crystallisation behaviour of binary blends containing 40% of shea stearin

The NMR crystallisation curves obtained at 10, 15 and 20°C, for the three blends containing 40% shea stearin as hard fat combined with either sunflower oil, shea olein or rapeseed oil, are presented in Fig. 6D–F, respectively.

It is obvious that the blend made of rapeseed oil as soft fat presented a higher crystallisation rate at every temperature. Moreover, the final SFC (after 4 h of isothermal period) of this binary mixture was lower, linked to its lower SAFA content.

XRD results confirmed that the kinetic of the polymorphic transformation was different within the three blends (Fig. 7A–I and 7bis a–i (Supporting Information)). The binary blend made of shea stearin mixed with shea olein crystallised the slowest.

This is further explored in more detail hereafter with binary blends containing either shea olein or rapeseed oil as soft fat (Fig. 8). At 10°C both blends crystallised first in the \( \alpha \)-form. However, after 10 min the polymorphic state of those blends was totally different. The \( \gamma \)-form of SOS was observed in the blend containing rapeseed oil. Moreover after 4 h, this blend was stabilised in a well-resolved \( \beta \)-2 form. This was not the case for the blend containing shea olein, which is richer in SOO.

4 Discussion

Regarding the isothermal crystallisation behaviour of the three types of binary blends, it is clear that whatever the blend, the higher the temperature, the slower the crystallisation occurs, as would be expected. Higher temperatures led to an increase in induction time and a decrease of the crystallisation rate resulting in a longer required isothermal time to get a constant SFC. As can be noticed, the higher the crystallisation temperature, the lower the SFC after 250 min. This is logical as higher crystallisation temperature decreases the driving force of crystallisation. According to the XRD results, the two-step crystallisation observed by pNMR and DSC can be explained by initial crystallisation of the \( \alpha \)-form followed by polymorphic transitions from the \( \alpha \)-form into more stable forms. The temperature effect could be

| Table 1. Fatty acid composition of the raw fats and key binary blends (% GC) |
|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|
|                    | Shea stearin      | Sunflower oil     | Shea olein        | Rapeseed oil      | 30% SheaSt/70% sun | 30% SheaSt/70% SheaOl | 40% SheaSt/60% sun |
| C12:0              | 0                 | 0.45              | 0.7               | 0.2               | 0.31              | 0.49              | 0.27               | 0.42               |
| C14:0              | 0                 | 0.2               | 0.3               | 0.2               | 0.14              | 0.21              | 0.12               | 0.18               |
| C16:0              | 2.9               | 6.9               | 7.1               | 4.6               | 5.7               | 5.84              | 5.3                | 5.42               |
| C18:0              | 60.9              | 15                | 28.4              | 2                 | 28.77             | 38.15             | 33.36              | 41.4               |
| C18:1              | 31.3              | 68.6              | 52.7              | 62.2              | 57.41             | 46.28             | 53.68              | 44.14              |
| C18:2              | 2.7               | 4.9               | 8.3               | 18.2              | 4.24              | 6.62              | 4.02               | 6.06               |
| C18:3              | 0.1               | 0.1               | 0.2               | 9.7               | 0.1               | 0.17              | 0.1                | 0.16               |
| C20:0              | 1.8               | 1.15              | 1.2               | 0.5               | 1.35              | 1.38              | 1.41               | 1.44               |
| C20:1              | 0                 | 0.1               | 0.4               | 1.1               | 0.07              | 0.28              | 0.06               | 0.24               |
| C22:0              | 0.2               | 1.8               | 0.1               | 0.3               | 1.32              | 0.13              | 1.16               | 0.14               |
| C24:0              | 0.1               | 0.3               | 0.1               | 0.1               | 0.24              | 0.1               | 0.22               | 0.1                |
| SAFAs              | 65.9              | 29.95             | 38.1              | 8                 | 37.9              | 46.4              | 41.9               | 49.2               |
| MUFA               | 31.3              | 68.85             | 53.3              | 63.8              | 57.6              | 46.7              | 53.8               | 44.5               |
| PUFA               | 2.7               | 5                 | 8.5               | 28                | 4.3               | 6.8               | 4.08               | 6.2                |
Figure 3. (A–C) pNMR isothermal crystallisation curves obtained at 10°C (A), 15°C (B) and 20°C (C) for binary blend made of 30% shea stearin and 70% sunflower oil (plain lines) and binary blend made of 30% shea stearin and 70% shea olein (dashed lines) and corresponding XRD pattern collected at the end of the isothermal period (4h). A1, B1, C1: 30% shea stearin/70% sunflower oil; A2, B2, C2: 30% shea stearin/70% shea olein.
explained by the lower driving force at 20°C leading to slower crystallisation which favours the stable polymorphic form [12].

The crystallisation rate of the blend containing shea olein as soft fat was lower compared to the other blends, whatever the proportion of hard versus soft fat (Figs. 3 and 6). According to all these data, the crystallisation behaviour of the selected binary blends depended on the soft fat involved, especially regarding the kinetics and the polymorphic behaviour.

Regarding the binary blends containing 30% shea stearin: these binary blends are mainly made of three different TAGs, which are SOS, SOO and OOO (Table 2). Their SOS contents are similar, however, the OOO content is higher in the blend made of sunflower oil, while its SOO content is lower. For a same temperature and cooling rate, the
Figure 5. (A–F) XRD diffraction pattern collected during the isothermal period (4 h) at 10°C (A and D), 15°C (B and E) and 20°C (C and F) for binary blend made of 30% shea stearin and 70% sunflower oil (A–C) and binary blend made of 30% shea stearin and 70% shea olein (D–F). For each picture, data are presented from bottom to top as a function of isothermal time (from 0 to 240 min).
crystallisation rate of the blends was influenced by their liquid fractions. One one hand, higher amount of OOO is supposed to increase the TAGs mobility and enhance polymorphic transitions. On the other hand, a higher SOO content could have an impact on the SOS crystallisation if there were a specific interaction between the two TAG.

In order to validate this hypothesis, new blends with similar SOS content were considered. The main TAGs

Figure 6. (A–C) pNMR isothermal crystallisation curves obtained at 10°C (A), 15°C (B) and 20°C (C) for binary blend made of 40% shea stearin combined with 60% of either sunflower oil or shea olein or rapeseed oil.
Figure 7. (A–I) XRD diffraction pattern collected during the isothermal period (4 h) at 10°C (A, D and G), 15°C (B, E and H) and 20°C (C, F and I) for binary blend made of 40% shea stearin and 60% sunflower oil (A–C), binary blend made of 40% shea stearin and 60% shea olein (D–F) and binary blend made of 40% shea stearin and 60% rapeseed oil (G–I). Data are presented from bottom to top as a function of isothermal time (from 0 to 240 min).
present in the three new binary blends, all containing 40% shea stearin, were also SOS, SOO and OOO (Table 2). The soft fat was either sunflower oil, shea olein or rapeseed oil (even though none of the blends involving rapeseed oil met all four criteria regarding fillings fats). In this way, different proportions of OOO and SOO were present in the three new blends. Their SOS contents were similar; the SOO content was the lowest in the blend made of rapeseed oil and the highest in the blend containing shea olein.

It is clear from all the results that the crystallisation rate varied as hypothesised according to the soft fat involved. The amount and quality of liquid fractions of those blends was of great importance. Higher amount of unsaturated TAGs (such as OOO) increases the TAGs mobility and enhances polymorphic transitions. For a same temperature and cooling rate, when a higher amount of liquid oil is present, TAGs can rearrange themselves more easily into the fat crystal network, leading to more stable polymorphic forms [13]. On the other hand, a higher SOO content had an impact on SOS crystallisation, as hypothesised. SOO could interact with SOS rich crystal faces (poisoning effect) and slow crystal growth accordingly. According to Zang et al. [14] SOS and sn-OOS are immiscible, revealing a monotectic mixing property. This could explain the different behaviour of the binary blend made of shea stearin and shea olein as soft fat, as this blend contains the highest amount of SOO.

Table 2. Composition of the raw fats and the key binary fat blends, in terms of main TAGs (% by GC)

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<th>Soft fat</th>
<th>Shea stearin</th>
<th>Sunflower oil</th>
<th>Shea olein</th>
<th>Rapeseed oil</th>
<th>30% Shea stearin</th>
<th>40% Shea stearin</th>
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5 Conclusions

In this study, the polymorphic and crystallisation behaviour of binary fat blends made of shea stearin combined with either sunflower oil, shea olein or rapeseed oil, were investigated. In view of all the results, the evaluated binary blends made of shea stearin/sunflower oil (30/70 and 40/60) and shea stearin/shea olein (30/70 and 40/60) could be used as confectionery and/or bakery fats with reduced SAFA contents (up to 35% reduction compared to the commercial reference). However, using DSC, pNMR and XRD data, it can be concluded that different behaviour exists resulting from the different soft fats: the crystallisation rate varied according to the soft fat involved.

Moreover, among three binary blends, two different systems have been highlighted. On one hand, in binary blends made of sunflower or rapeseed oils and shea stearin the soft fats mainly act as a solvent and, in this way, increase the mobility of solid TAGs. Liquid oil increases the mobility of TAGs, leading to easier rearrangements within the fat crystal network. On the other hand, shea olein and shea stearin behave as a mixed system where TAGs such as SOO and SOS interact during crystallisation leading to lower crystallisation rate and slower polymorphic transformations, indicating that this type of blend needs tempering in order to avoid post-crystallisation in the applications.

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