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Feature

Physical characterisation of silica-treated shea stearin

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Summary

Shea stearin is widely used in cocoa butter equivalents to provide enhanced solidity and crystallization characteristics to chocolate. Although it is predominantly composed of triacylglycerols, a small amount of diacylglycerols is also naturally present in the fat. This can affect its crystallization. To determine the extent of these effects shea stearin and shea stearin that has been treated with silica to remove diacylglycerol have been compared.

Introduction

Shea stearin (SHs) is produced by fractionation of shea butter obtained from the West African *Vitellaria paradoxa* (also called *Butyrospermum parkii)* tree. One of its major uses is as a component of cocoa butter equivalents (CBEs). In terms of its triacylglycerol (TAG) content, shea stearin is rich in 1,3-distearoyl-2-oleoylglycerol (StOSt)[1]. When used in CBEs it is usually blended with the mid-fraction of palm oil which is rich in 1,3-dipalmitoyl-2-oleoylglycerol (POP). Together, POP and StOSt are able to match the physical characteristics of cocoa butter and so function as fats that are equivalent in this respect to cocoa butter.

As is the case with almost all naturally occurring oils and fats, shea butter contains some diacylglycerol (DAG) as well as TAG. During the fractionation process this partitions between the low-melting olein fraction and the high-melting stearin fraction. The degree of partition is largely dependent on the type of fractionation carried out. Shea butter is often solvent fractionated to obtain a stearin fraction that is rich in StOSt triglycerides without there being significant inclusion of the softer TAGs that conventionally form part of the olein fraction. When the solvent used is acetone then the relative polarity of DAGs is such that most of these go into the olein fraction. However, a small amount still remains in the stearin.

The effects of DAG on the crystallization of both cocoa butter [1] and CBEs (containing shea stearin) [2] has been studied in the past but not its effect on the physical characteristics of shea stearin alone. IOI Loders Croklaan is a global producer of both shea stearin and CBEs such as the Coberine™ range. In recognizing the importance of understanding these effects, they sponsored research at Loughborough University in the UK. The results of this were published by Ray et al. [3] and this article is a distillation of that paper.

TAGs such as those found in cocoa butter and shea stearin show very complex crystallization behaviour and this is complicated further by the presence of DAGs. It is important, therefore, particularly in terms of cocoa butter equivalent production and formulation to understand the effects that DAGs have on shea stearin. The physical characteristics that are perhaps most important in this respect are the melting characteristics (as defined by solid fat content and differential scanning calorimetry (DSC)), the crystallization characteristics (as defined by DSC) and the crystal forms (as defined by the more traditional methods of microscopy and X-ray diffraction as well as more modern techniques such as confocal Raman microscopy).

[1] The abbreviations for fatty acids used in this article are: P = palmitic; St = stearic; O = oleic; L = linoleic

Composition of shea stearin

The shea stearin (SHs) used in this study was provided by IOI Loders Croklaan Europe. This was then silica treated to remove DAG and other polar material. The silica treatment involved first dissolving SHs in hexane (1 : 4 w/v) and then mixing this (1 : 3 w/w) with silica gel-60 (from Sigma-Aldrich) for 5-10 minutes. The silica gel was then filtered off and the hexane removed by rotary evaporation to leave silica-treated shea stearin (SiSHs). Both SHs and SiSHs were analysed by high-resolution GC (to determine the TAG composition) and by HPLC (to give a breakdown of the DAGs present). The major TAG present was StOSt (73.4% in SHs and 74.2% in SiSHs). None of the other TAGs present differed by more than 0.4% between the two fats. SHs contained 0.7% total DAG, mainly 1,3-StO, 1,2-OL and 1,2-StO; SiSHs was free from DAG.

Solid fat content

The melting characteristics of the two fats as measured by their solid fat contents (as determined by pulsed NMR using IUPAC 2.150b stabilisation) were almost identical although SiSHs had a slightly higher level of solid fat at 40°C (8% compared to 7.1% in untreated SHs). DAG has the effect of reducing solid fat content so this higher level could be due to the removal of DAG in SiSHs.

Non-isothermal DSC

After holding at 80°C for 5 minutes to erase crystal memory the two samples were first cooled to –20°C at 5°C/min and then heated to 60°C at 5°C/min. The resulting cooling and heating curves are shown in **Figure 1**. Silica-treated shea stearin starts to crystallize slightly before untreated shea stearin (as can be seen by an earlier onset and a small shoulder in Figure 1A). This shoulder is probably

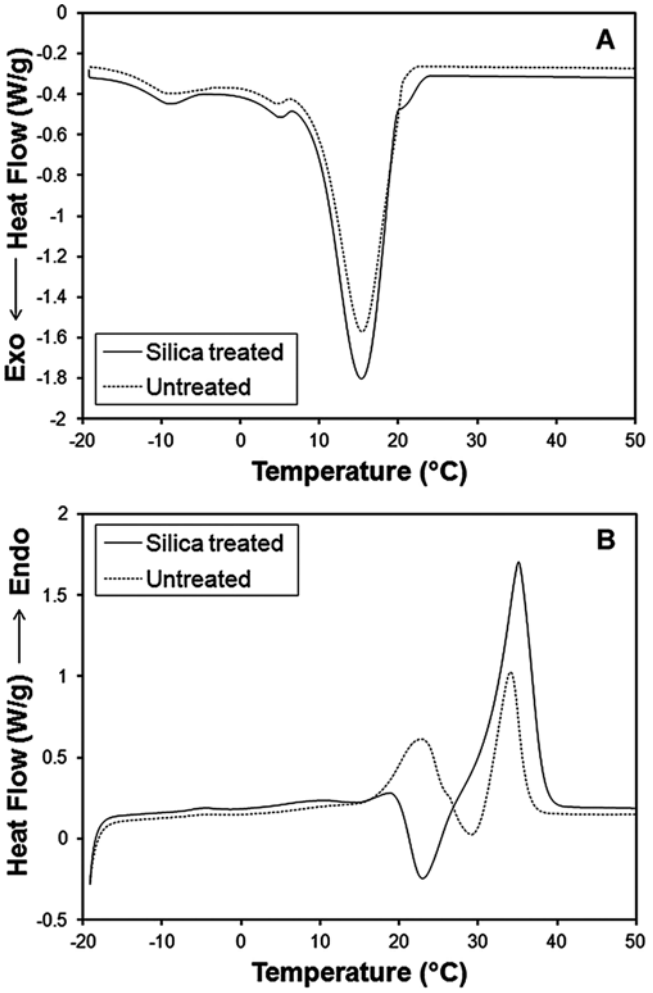


Figure 1. Non-isothermal DSC (A) cooling thermograms and (B) heating thermograms

trisaturated TAG crystallizing before the main SOS peak. Cebula and Smith [2] found that DAGs inhibited the crystallization of trisaturated TAG and so, clearly, removing these from SiSHs has allowed the trisaturated TAG to crystallize first. The main peak in SiSHs is sharper (narrower) than that for SHs again suggesting that DAG has an inhibitory effect on crystallization.

Compared to the relative similarities of the two peaks in the cooling thermograms, the heating thermograms are distinctly different. Both samples have two main melting peaks coupled with a significant exothermic event which is most probably due to a polymorphic change from an unstable to a stable crystal form. This is more obvious in the silica-treated sample and it occurs at a lower temperature suggesting that the absence of DAG allows this transition to occur more quickly (or at a lower temperature). Conversely the presence of DAG again shows an inhibitory effect on (re)crystallization. Considering the relatively low level of DAG (0.7%) in the untreated sample the effects that this is having on polymorphic change and melting is really quite marked.

Isothermal DSC[2]

Isothermal DSC crystallisation at 20°C shows a sharp peak for SiSHs peaking after about 8 minutes and with an induction time of 4.51 minutes compared with a much broader peak for SHs peaking after about 17 minutes and with an induction time of 6.85 minutes again demonstrating the difficulty of getting stable nuclei when DAG is present. Fitting the Avrami equation to the isothermal DSC data using linear regression (with correlation coefficients greater than 0.98) gave Avrami indices for SHs of 2.91 and for SiSHs of 2.89. An Avrami index of 3 is consistent with spherulitic growth. The crystallisation rate constant, k, which relates to both nucleation and the overall rate of crystallisation was very low (0.12×10^{-2} min^{-1}) for SHs compared to SiSHs (1.27×10^{-2} min^{-1}), yet again showing the inhibiting effect of DAG.

Stop and return DSC

The melting profiles of the two fats after holding for various times at 20°C were measured using 'stop and return' DSC, a technique fully described by Foubert et al [4]. The profiles are shown in **Figure 2**. These show three distinct melting peaks (22, 29, 34–35°C) which are probably related to three different polymorphic forms. Rousset and Rappaz [5] defined three polymorphs for StOSt (the main TAG in SHs) whose melting points correspond to these three peak temperatures (22.4°C for α, 28.8°C for δ, 35.5°C for γ). The melting point of the β′ form of StOSt is 36.5°C and so the high-melting peak could be γ or a mixture of γ and β′. In SHs both α and δ polymorphs were seen up to 5 minutes and then, after 7 minutes, the γ form appeared. By 15 minutes the α and δ polymorphs had disappeared leaving the γ form alone to grow. In SiSHs the α and δ forms were present up to 3 minutes and then had completely transformed to γ or a mixture of γ and β′ after 7 minutes. By the end of

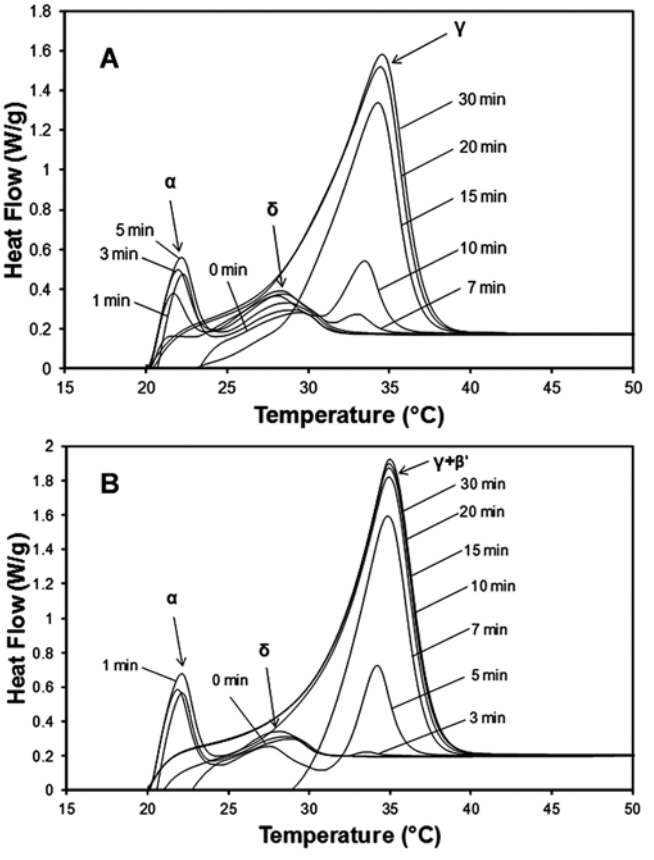


Figure 2. Melting profiles of (A) SHs and (B) SiSHs after 'stop-and-return' DSC in which isothermal crystallization at 20°C was interrupted after 1, 2, 3, 5, 7, 10, 15, 20 and 30 minutes

[2] The isothermal DSC curves are shown in the original paper (Ray et al. [3])

the crystallization time the enthalpies suggest that SHs is in the γ form while SiSHs also contains the β′ form.

X-ray diffraction[3]

The polymorphic forms suggested by isothermal DSC were validated by X-ray diffraction (XRD) by comparison to literature patterns for pure StOSt and POSt. After erasing any crystal memory and cooling to 20°C, XRD patterns were measured every minute for 30 minutes over 2Θ values between 15° and 30°. With the SHs sample, there was initially a broad peak at 4.16 Å which could correspond to a mixture of α and δ. After 6 minutes this transformed into three peaks corresponding to the γ form. This continued for the first 30 minutes but, then, after 7 days, peaks corresponding to a mixture of β′ and β were seen. In the case of the silica-treated sample the situation was much the same up to 30 minutes when as well as three peaks corresponding to the γ form, three further peaks were apparent which corresponded to the β′ form of StOSt. After 7 days there was again a mixture of β′ and β but the relative intensities were such that SiSHs contained more of the β form than did untreated SHs.

Microstructure

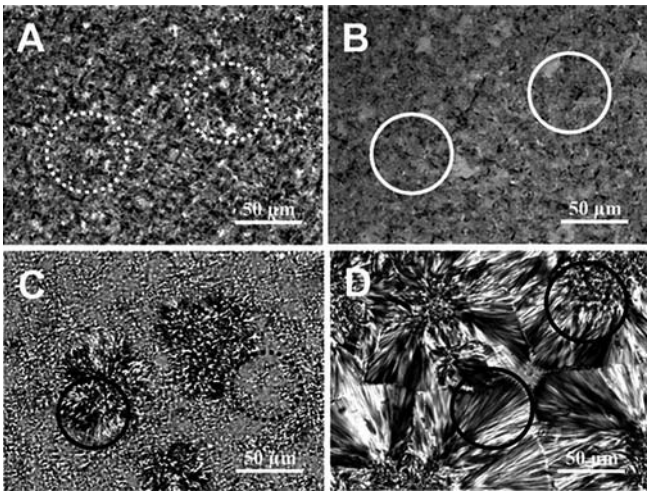
Polarised light microscopy (PLM) was used to visualize differences in texture, crystal growth and polymorphism (**Figure 3**). The samples were melted to 80°C and then cooled at 50°C/min to 20°C where PLM images were taken after 2 minutes and 30 minutes. Subsequently, the samples were kept in an incubator at 20°C and PLM images taken after 1 day and 7 days. The different polymorphic forms (identified by Raman spectroscopy – see below) are indicated by circles on the microstructure. White dashed circles represent the α form; white solid circles represent the γ form; black dashed circles represent the β′ form; black solid circles represent the β form. Both samples crystallized quite quickly and showed similar granular networks after 2 minutes. After 30 minutes SHs showed a slight change whereas SiSHs showed two different crystal morphologies – one a dense structure of very small crystals, the other pale spherulitic crystals. After 1 day feathery spherulitic crystals had begun to appear; there were more of these in SiSHs than in SHs. After 7 days these feathery spherulitic crystals were the only crystals present in each sample.

Raman spectroscopy

The same microscope slides as were used in the PLM work were studied via Raman spectroscopy with Raman spectra being acquired from samples taken within the circled regions of **Figure 3**. The full description of each of the vibrations identified in the four polymorphs (α, γ, β′ and β) is beyond the scope of this summary article and interested readers are directed to the original paper [3] for this more detailed information. What we can say, though, is that Raman spectroscopy enabled these four polymorphic forms to be clearly identified in the samples taken from the microscope slides. The δ form identified by DSC and XRD techniques could not be identified by Raman spectroscopy, possibly because this technique could not resolve it from the other forms.

To summarise the polymorphic transformations seen by Raman spectroscopy:

I – Untreated shea stearin



II – Silica-treated shea stearin

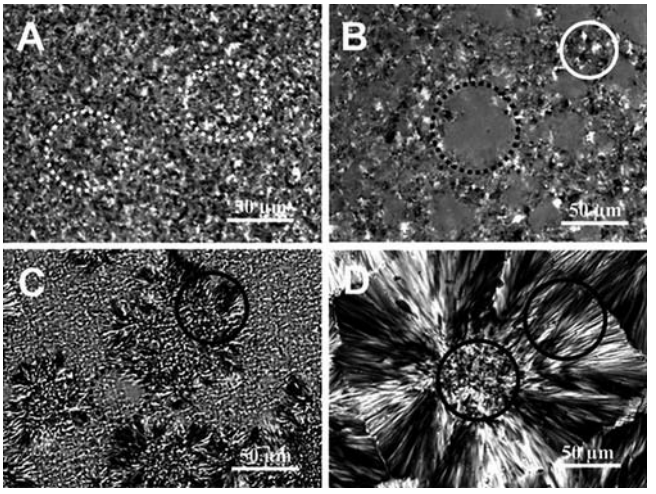


Figure 3. Microstructure of (I) shea stearin and (II) silica-treated shea stearin samples under polarized light after crystallizing at 20°C for (A) 2 min, (B) 30 min, (C) 1 day and (D) 7 days.

- After 2 minutes at 20°C both samples had crystallized in the α form
- After 30 minutes, SHs was mainly in the γ form, but SiSHs showed the presence of some β′ crystals.
- After 1 day the γ form had disappeared and both samples were mainly in the β′ form along with some β crystals that had started to grow.
- After 7 days both samples had completely transformed into large β crystals.

Conclusions

What does all of this information mean in practical terms? Firstly, this study has generated a large wealth of basic physical and morphological data not just on the effects of silica treatment but also on the basic morphology of shea stearin when crystallized under particular conditions. At the practical level, as opposed to the fundamental science of this work, it is clear that the silica treatment of shea stearin and the consequent removal of DAG changes the way in which the fat crystallizes. Although there are some aspects of this work which show little or no differences between the treated

[3] The X-ray diffraction patterns are shown in the original paper (Ray et al. [3])

and untreated shea stearin, where there are differences they are predominantly along the lines of silica-treated shea stearin either crystallizing more quickly or transforming to a higher polymorphic form more quickly. This could have consequences for the use of shea stearin in confectionery products, particularly as a component of CBEs.

Arguably, removing DAG from shea stearin will make chocolate easier to temper and faster to crystallize (although this would need to be proven in practice). However, there are points to bear in mind in saying this. Firstly, it is unusual for shea stearin to be used on its own; it is usually blended with other fats such as palm mid-fraction, particularly in CBEs, and so the effect of silica-treatment will be diluted – and may even be swamped by the effects of DAG being present in the other components. Secondly, the DAG level in shea butter before fractionation can vary, depending on the origin of the oil and how the oil has been stored. While the DAG will still preferentially partition into the olein fraction the amount left in the stearin will also vary. Thirdly, and very importantly, these results give us a small-scale guide as to what could be achieved if DAG (and other polar material) were removed industrially by silica treatment of shea stearin. Carrying out silica treatment of oils on an industrial scale, though, is not a trivial undertaking. In this work the oil was dissolved in hexane and then stirred with the silica and filtered off. This could be done industrially in a similar way but would be expensive because of the need for solvent recovery, operating in a flameproof environment and the economic necessity to recover and regenerate the silica after use. Nevertheless, the potential improvements that could be made in terms of crystallization do, perhaps, give a target for future process developments. Silica treatment is not, however, the only way of removing DAG from oils such as shea stearin. The use of enzymes to achieve this has also been suggested and patented [6].

References

[1] Wähnelt S. et al., *Fat. Sci. Technol.* **1991**, *93* 174–178.
[2] Cebula D. J. and Smith K. W., *J. Am. Oil Chem. Soc.* **1992**, *69*, 992–998.
[3] Ray J. et al., *Eur. J. Lipid Sci. Technol.* **2013**, *115*, 1094–1106.
[4] Foubert I. et al., *Thermochim. Acta* **2008**, *471*, 7–13.
[5] Rousset P., Rappaz M., *J. Am. Oil Chem. Soc.* **1996**, *73*, 1051–1057.
[6] Kristensen et al., *Eur. Pat. 1862554 B1*