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ScienceDirect
Food Chemistry 103 (2007) 477–485
Food Chemistry
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Effects of variation in the palm stearin: Palm olein ratio on the crystallisation of a low-*trans* shortening

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Received 12 April 2006; received in revised form 22 June 2006; accepted 22 August 2006

Abstract

Changes in the rheological properties during crystallisation and in the crystal size and morphology of blends containing rapeseed oil with varying percentages of palm stearin (POs) and palm olein (POf) have been studied. The crystals formed from all three blends were studied by confocal laser scanning microscopy, light microscopy and environmental scanning electron microscopy, which revealed the development of clusters of 3–5 individual elementary "spherulites" in the early stages of crystallisation. The saturated triacylglycerol content of the solid crystals separated at the onset of crystallisation was much greater than that in the total fat. Fat blends with a higher content of palm stearin had a more rapid nucleation rate when observed by light microscopy, and this caused an earlier change in the rheological properties of the fat during crystallisation. Using a low torque amplitude (0.005 Pa, which was within the linear viscoelastic region of all samples studied) and a frequency of 1 Hz, the viscoelastic properties of melted fat during cooling were studied. All samples, prior to crystallisation, showed weak viscoelastic liquid behaviour (G'', loss modulus $>G'$, storage modulus). After crystallisation, a more "solid like" behaviour was observed (G' similar to or greater than G''). The blend having the highest concentration of POs was found to have the earliest onset of crystallisation (27% w/w POs; 12 mins, 22% w/w POs; 13.5 mins, 17% w/w POs, 15 mins, respectively). However, there were no significant differences in the time to the point when G' became greater than G' among the three blends.

Keywords: Crystallisation; Fat; Palm olein; Palm stearin; Rheology; Shortening

1. Introduction

Shortenings are fats that are added to bakery products, and the crystallisation behaviour, crystal properties and melting profile are important for their application in food products. Shortenings are required to display a plastic behaviour across a range of temperatures (Danthine & Deroanne, 2003). Hydrogenated fats have commonly been used in shortenings but concern about the nutritional effects of *trans*-unsaturated fatty acids in the diet has encouraged the food industry to develop shortenings with components that are low in these fatty acids. The solid fat content of the fat blend is a major factor that determines the texture of the fat but the fat crystal polymorph and the microstructure of the network of crystalline particles also determine the mechanical properties of the fat (Marangoni & Hartel, 1998; Marangoni & Narine, 2002). Lipid composition and crystallisation conditions influence the microstructure, crystal habit and interaction between the crystals (Chawla, deMan, & Smith, 1990; Heertje, 1993; Juriaanse & Heertje, 1988). Smaller and finer β′ crystals can stabilise more air and more liquid component than larger and coarser β crystals (Podmore, 2002). The shape and size of the fat crystals and crystal aggregates found in a shortening are affected by the polymorph present, to differing extents in different fats (Berger, Jewel, & Pollitt, 1979; Kellens, Meeussen, & Reynaers, 1992). Viscosity measurements are commonly used to monitor changes in

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doi:10.1016/j.foodchem.2006.08.034

fat rheology due to crystallisation, but the application of shear can destroy some of the delicate interactions present in fat systems and, consequently, a controlled stress rheometer was used for the present studies.

The aim of this study was to determine the effect of variation in palm stearin: palm olein ratio on the rheology and crystallisation behaviour of low *trans* shortenings. The effect of changes in palm olein and palm stearin content on the crystallisation and physical properties of three blends, which varied in the ratio of palm stearin to palm olein, was studied.

2. Materials and methods

2.1. Blend preparation

Rapeseed oil (Rp), refined, bleached and deodorized (RBD) palm olein, with iodine value of 47 (POf), and RBD palm stearin, with iodine value of 35 (POs) were supplied by Loders Croklaan BV, Wormerveer, The Netherlands.

Three blends were prepared for study with compositions: (i) 56% w/w Rp, 27% w/w POs, 17% w/w POf (ii) 56% w/w Rp, 22% w/w POs, 22% w/w POf and (iii) 56% w/w Rp, 17% w/w POs, 27% w/w POf.

Each fat blend (80 g) was melted in a jacketed glass vessel at 80 °C with stirring at 50 rpm for 2 h. Then, melted sample was loaded onto the rheometer and held at 80 °C for 5 min prior to measurement.

2.2. Rheological measurements

Rheological properties were measured using a controlled stress Rheometer (RTI Ltd.). A 30 mm diameter flat plate was selected with a gap of 2 mm (to prevent "particle bridging"). The linear viscoelastic region (LVR) of all three blends was first assessed by applying an oscillatory amplitude sweep. A torque of 0.005 Pa was chosen as it was found to be within the LVR of each sample. The temperature of both upper and lower plates was controlled at 80 °C for 30 min prior to measurement. The storage modulus (G') and loss modulus (G'') were determined every 1.5 mins at a frequency of 1 Hz for each sample during crystallisation using cooling water at 20 °C.

2.3. Separation of solid crystals

Samples (≈0.5 ml) were removed by pipette, either from the jacketed glass vessel or from the rheometer plate, when the fat temperature reached 35 °C, at the onset of crystallisation and at the end of the rheological measurement and transferred to 99% isobutanol (5 ml) kept at the same temperature. The sedimentation of solid crystals was observed and the liquid phase was removed using a Pasteur pipette. The solid phase was resuspended in isobutanol, 3 times, to ensure complete removal of the liquid oil, since this can obscure the original solid crystalline matrix (Chawla et al., 1990). The suspension of solid crystals in isobutanol was then used for light microscopy (LM), confocal laser scanning microscopy (CLSM) and environmental scanning electron microscopy (ESEM).

2.4. Crystal morphology

2.4.1. Light microscopy (LM)

Samples were taken at 35 °C from either the bulk material or from the rheometer after application of "low" shear. The resulting structures were examined by phase contrast light microscopy. A Nikon Microphot-SA (Nikon, Japan) light microscope, equipped with a photometer (Roper Scientific), was used. The images were acquired by Image-Pro Plus software version 4.5.

2.4.2. Confocal laser scanning microscopy (CLSM)

Nile Blue solution in ethanol (0.02 ml, 1% w/v) was applied to the melted fat at 80 °C before crystallisation and the separation of solid crystals. Five drops of the solid crystals suspension were transferred to the sample holder and covered. The sample holder was then placed onto the microscope. The CLSM used was an inverted confocal microscope Leica TCS SP5 (Leica-Microsystems) with an argon/argon krypton (Ar/ArKr) mixed gas laser (excitation wavelength 488 nm) and viewed under a 40× objective lens. Each image was taken in 50 sections. The photomicrographs were acquired using Leica confocal software.

2.4.3. Environmental scanning electron microscopy (ESEM)

The solid crystal suspension was transferred from the isobutanol dispersion onto a metal sample holder using a Pasteur pipette. Solvent was evaporated from the crystals at room temperature. Samples were placed in a chamber at 5 °C and examined at an accelerating electron voltage of 20 keV, emission current of 270 μA and pressure of 4.31 Torr. The ESEM used was the FEI Quanta 600 FEG environmental scanning electron microscope equipped with an Oxford INCA energy and wavelength dispersive X-ray system.

2.5. Lipid composition

Analysis of fatty acid composition (FAC) of each blend and of solid crystals separated at the onset of crystallisation after washing with isobutanol for 24 h, was performed using GC. Fatty acid methyl esters (FAMEs) were prepared by a base-catalysed transesterification, as described by Christie (2003). FAMEs were analysed on a Hewlett-Packard model 5890 instrument with autosampler, equipped with a flame-ionization detector (FID) and a Hewlett-Packard electronic integrator, model 3390 A. A fused silica capillary column, Chromapak CP7488 (50.0 m length, 250 μm internal diameter and 0.20 μm film thickness) was used. Hydrogen, at 40.0 ml/min, was used as a carrier gas, and nitrogen at 50.0 ml/min was used as the make up gas. The FID and injector were maintained at

250 °C and 220 °C, respectively. The initial column temperature was held at 100 °C for 1 min, then the temperature was programmed to 200 °C at 4 °C/min and held at this temperature for 4 min. FAME peaks were identified by comparison with the standard FAME mixture, containing 20% each of palmitic (16:0), stearic (18:0), oleic (18:1), linoleic (18:2) and linolenic (18:3) acids. Concentrations were calculated as an area percentage.

The triacylglycerol (TAG) composition was also determined by GC according to AOCS official Method Ce 5–86. The temperatures of the FID and injector were 370 °C and 360 °C, respectively. The temperature of the column was initially held at 280 °C for 1 min, then increased at a rate of 3 °C/min to 350 °C and maintained at this temperature for 15 min.

FAMEs and TAG composition of the blends, blend components, and their crystals separated at the onset of crystallisation and at the crossover point ($G' > G''$) were analyzed in triplicate.

2.6. Equilibrium solids measurements

Equilibrium solids contents (N values) were determined using a Bruker Minispec 120 pulse NMR spectrometer. Each fat was treated by melting in an oven at 80 °C. Samples of the fat were placed into tubes and held for 30 min in a water bath at 60 °C. The tubes were transferred to a water bath at 0 °C for 1 h before being placed in a bath at the measuring temperature (20, 25, 30, 35 and 40 °C). After a further 30 min at the measuring temperature, the solid fat content was determined.

Peroxide values were determined by AOCS official method Cd 8–53.

3. Results and discussion

3.1. Composition of blends studied

Increasing the concentration of palm olein and decreasing the content of palm stearin in the blend by 10% increased the total unsaturated fatty acid content and decreased the total saturated fatty acid content by 0.6–0.7% (Table 1).

The main triacylglycerols in the 3 blends were PPO/POP, PPP, OOO and POO (Table 2). Both POs and POf contributed to the content of tripalmitin (PPP, C48). POP and PPO were not separated from each other but the sum of these triacylglycerols represented a concentration of 23–25%. Blend I contained tripalmitin (PPP) at a level of 17.4% while blend III, which contained the highest content of palm olein, contained 13.6%. The higher content of PPP and other high melting triacylglycerols in blend I was reflected in a higher solid fat content between 20 and 40 °C (Table 3).

3.2. Preheating prior to studies of crystallisation kinetics

It is known that fats need to be thoroughly melted to destroy all crystal nuclei if kinetic studies of crystallisation are to be performed. When the blend containing 56% Rp, 22% POs, 22% POf was heated at 80 °C for various periods of time prior to cooling in the rheometer, the time for onset of crystallisation (shown by an increase in G') increased from 12 min to 13.5 min when the heating time at 80 °C was increased from 90 min to 120 min (Fig. 1). This indicated that a longer heating time was required to destroy all residual crystal nuclei. However, a further increase in heating, while causing a more rapid onset of crystallisation (10.5 min), caused the peroxide value of the samples to increase significantly (Fig. 2). This suggested that the oxidation of unsaturated fatty acids was responsible for the reduction in time to onset. Consequently, a pre-heating time of 120 min was used for subsequent studies.

3.3. Preparation of crystals for microscopic studies

Previous studies of crystals formed from crystallising fats have involved suspending the crystals in isobutanol prior to microscopy (Heertje, Leunis, van Zeyl, & Berends, 1987; Mazzanti, Guthrie, Sirota, Marangoni, & Idziak,

Table 1
Comparison of fatty acid composition between the original bulk fat and crystals separated at the onset of crystallisation

Fatty acid	Low *trans* shortenings					
	I (27% POs)		II (22% POs)		III (17% POs)	
	Original	Crystals	Original	Crystals	Original	Crystals
Saturated						
14:0 (M)	0.54 ± 0.00	1.05 ± 0.51	0.54 ± 0.01	0.86 ± 0.01	0.55 ± 0.01	0.79 ± 0.01
16:0 (P)	27.2 ± 0.03	55.6 ± 0.01	26.8 ± 0.17	44.4 ± 0.13	26.6 ± 0.06	41.0 ± 0.05
18:0 (S)	3.18 ± 0.01	4.74 ± 0.01	3.24 ± 0.07	4.44 ± 0.01	3.23 ± 0.03	4.02 ± 0.01
Total	31.0 ± 0.04	61.4 ± 001	30.6 ± 0.25	49.7 ± 0.15	30.4 ± 0.10	45.8 ± 0.07
Unsaturated						
18:1 (O)	44.6 ± 0.08	27.4 ± 0.01	45.0 ± 0.32	35.4 ± 0.10	45.2 ± 0.09	37.6 ± 0.09
18:2 (L)	13.7 ± 0.01	8.06 ± 0.01	13.9 ± 0.09	10.6 ± 0.04	13.8 ± 0.03	11.5 ± 0.01
18:3 (Ln)	5.54 ± 0.01	3.12 ± 0.01	5.57 ± 0.05	4.28 ± 0.01	5.53 ± 0.02	4.72 ± 0.01
Total	63.9 ± 0.10	38.6 ± 0.01	64.4 ± 0.46	50.3 ± 0.15	64.6 ± 0.14	53.8 ± 0.11

Table 2
Triacylglycerol composition of low *trans* blends and crystals separated at the onset of crystallisation and at the crossover point ($G' = G''$)

TAG	Triacylglycerol composition (%)								
	27% POs			22% POs			17% POs		
	Original	Crystal		Original	Crystal		Original	Crystal	
	Blend	Onset	Transition	Blend	Onset	Transition	Blend	Onset	Transition
C48	18.6 ± 1.7	57.5 ± 0.3	23.4 ± 0.2	16.1 ± 3.1	55.5 ± 0.1	23.3 ± 1.1	14.7 ± 1.3	53.8 ± 0.5	29.1 ± 0.7
C50	33.1 ± 2.9	28.3 ± 0.2	27.7 ± 0.3	35.1 ± 4.5	26.7 ± 0.2	28.4 ± 1.0	32.0 ± 2.3	26.8 ± 0.1	29.4 ± 0.8
C52	19.4 ± 1.7	4.9 ± 0.1	17.2 ± 1.0	20.5 ± 2.2	6.3 ± 0.1	18.3 ± 0.9	20.1 ± 0.9	6.4 ± 0.1	16.8 ± 1.0
C54	24.4 ± 2.6	4.1 ± 0.1	28.0 ± 0.3	22.6 ± 2.6	6.7 ± 0.1	26.5 ± 1.0	25.3 ± 2.9	8.2 ± 0.5	20.8 ± 1.1
Total	95.5 ± 8.9	94.7 ± 0.6	96.3 ± 1.73	94.2 ± 12.4	95.3 ± 0.4	96.5 ± 4.0	92.1 ± 7.4	95.1 ± 1.2	96.0 ± 2.6

Table 3
Solid fat content within the temperature range 20–40 °C of the low *trans* shortenings

Temperature (°C)	Solid fat content (%)		
	Blend I (27% POs)	Blend II (22% POs)	Blend III (17% POs)
20	19.7	18.2	18.1
25	16.3	15.2	14.5
30	12.8	11.9	11
35	10	8.6	8.4
40	7.8	6.9	6.1

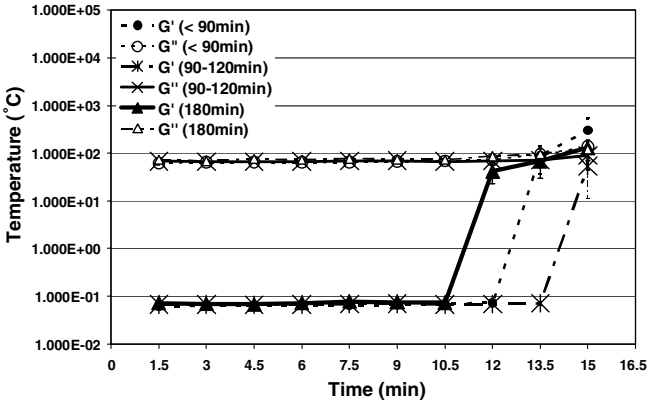

Fig. 1. Storage (G') and loss (G'') modulus of a fat blend (56% w/w Rp, 22% w/w POs, 22% w/w POf) as a function of cooling time (15 min).

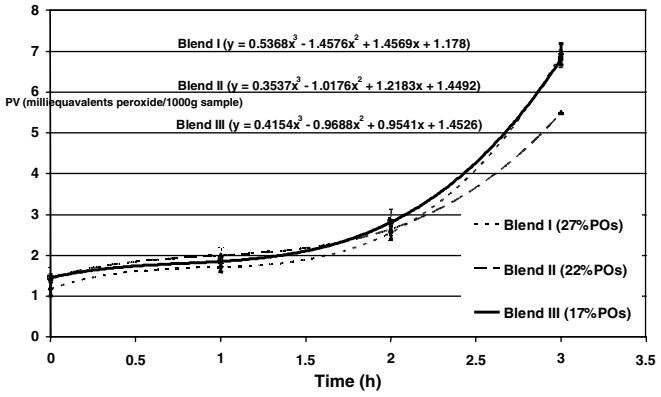

Fig. 2. Peroxide value (milliequivalents peroxide/1000 g sample) of fat blends heated at 80 °C for various times.

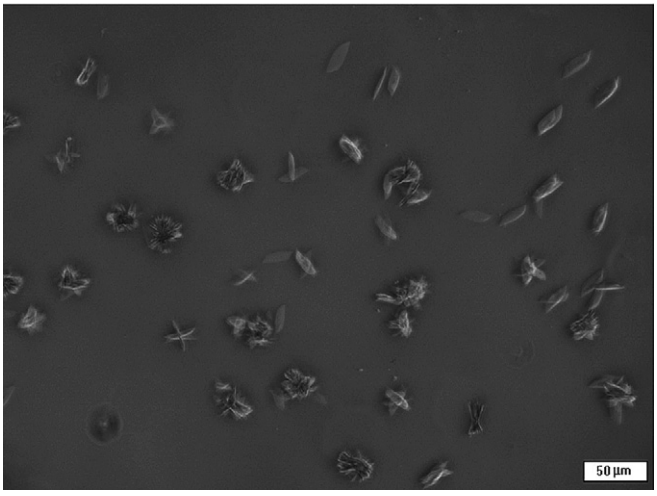

Fig. 3a. Blend II (22% POs) in isobutanol at 35 °C for 5 min.

2003). The isobutanol removes the oil, allowing clearer microscopic studies. It is important that sufficient time is allowed for oil to be removed, but without allowing changes in the crystals to occur. The effect of suspension in isobutanol for various times was studied. Comparison of the size of the crystals after suspension in isobutanol for different times showed that the crystal diameter was in the range 20–50 µm but that the crystals appeared to cluster at longer suspension periods (Figs. 3a–3e). As the lipid crystals agglomerated, the oil was expressed and the clusters became denser and aged (Mazzanti et al., 2003). After 24 h suspension in isobutanol, agglomeration of crystals was extensive and much of the liquid oil had been extracted.

Heertje et al. (1987) suggested that the optimal deoiling time of fatty products with large crystals, and with no water content at 15 °C, was between 22 and 30 h. In this study, it was found that 24 h was the optimal deoiling time for the fat blends examined. Liquid oil was not trapped in the spherulites after this time and changes to their dimensions were minimal.

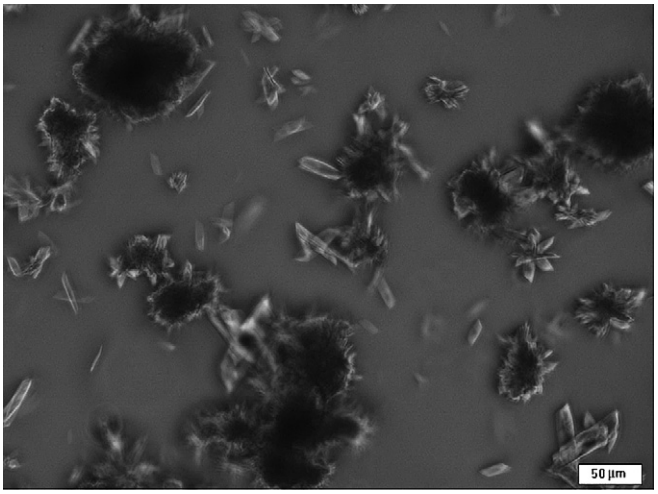

Fig. 3b. Blend II (22% POs) in isobutanol at 35 °C for 15 min.

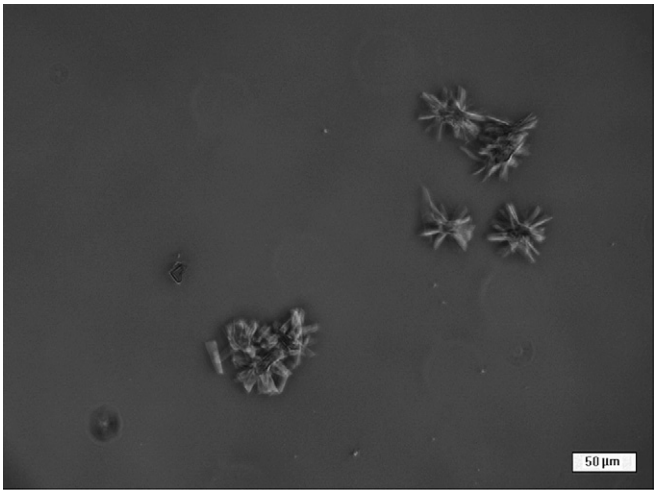

Fig. 3c. Blend II (22% POs) in isobutanol at 35 °C for 30 min.

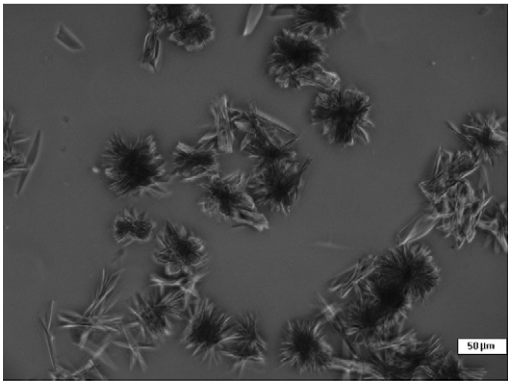

Fig. 3d. Blend II (22% POs) in isobutanol at 35 °C for 1 h.

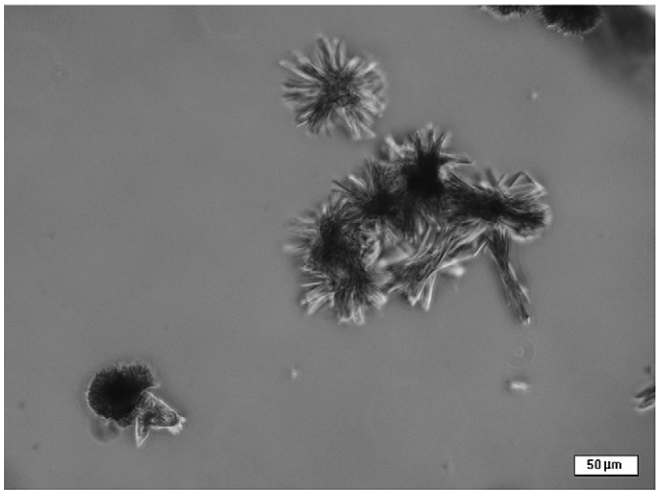

Fig. 3e. Blend II (22% POs) in isobutanol at 35 °C for 24 h.

3.4. Crystal morphology

The more rapid nucleation in blends containing increasing palm stearin content was confirmed by removing a sample from the rheometer at 35 °C before crystallisation, and allowing the sample to solidify on a microscope slide at room temperature (Figs. 4a–4c). The degree of nucleation was higher, observed as a greater number of crystals, in the blend having the higher palm stearin content. ESEM showed that the crystals were spherulites that had formed small clusters. The size of individual spherulites ranged from 20 to 50 µm, and the crystals varied in density of the needles within the spherulites (Figs. 5 and 6). No clear differences in size and shape of the spherulites formed from the three blends were observed.

The importance of the high melting triacylglycerols on the formation of crystals at the early stages of crystallisation was confirmed by taking samples from the rheometer immediately after G' had started to increase (onset of crystallisation) and separating the crystals from each fat blend. FAME analysis of the fat crystals showed that the concentration of saturated fatty acids was at least 50% greater in the crystals at onset of crystallisation than in the original bulk fat, with a corresponding reduction in

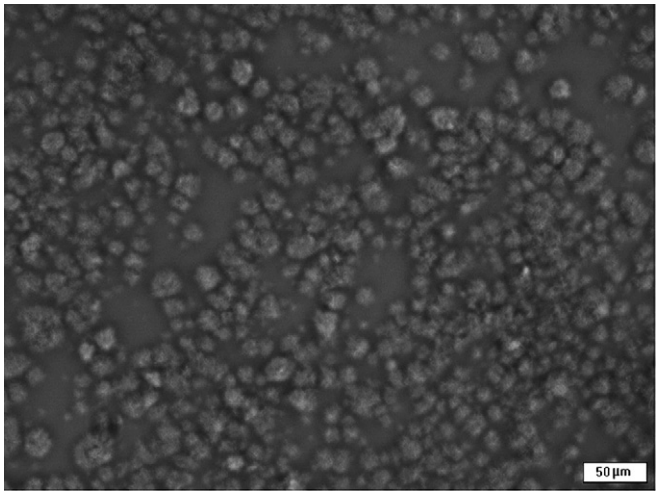

Fig. 4a. Blend I (27% POs) at 35 °C before suspension in isobutanol.

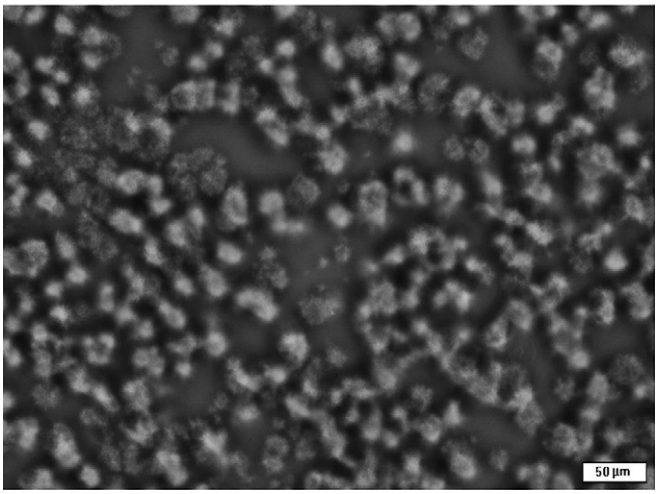

Fig. 4b. Blend II (22% POs) at 35 °C before suspension in isobutanol.

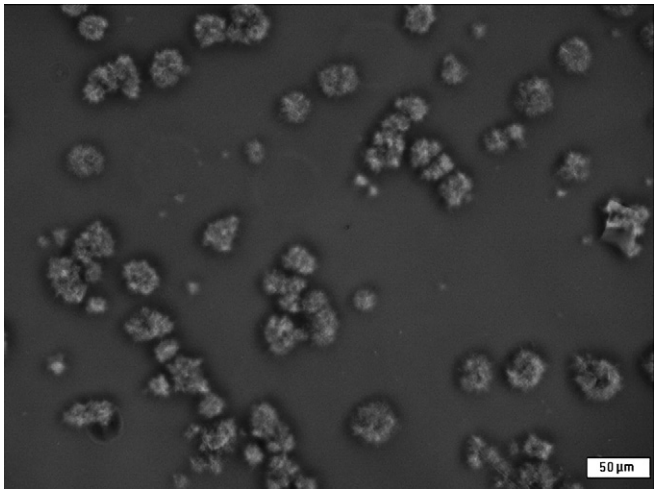

Fig. 4c. Blend III (17% POs) at 35 °C before suspension in isobutanol.

the unsaturated fatty acids of the crystals (Table 1). A study by deMan, D'Sousa, deMan, and Blackman (1992) also showed an increase in the C16:0 and C18:0 and a reduction in C18:1 and C18:2 in separated crystals washed with isopropanol compared to the original shortenings. Analysis of the TAGs in the crystals separated at the onset of crystallisation confirmed that the C48 TAGs, which mainly contained PPP, had increased significantly compared with those in the bulk fat, and there was a corresponding decrease in the C50 and C54 TAGSs which mainly contained low-melting unsaturated fatty acids (Table 2). The difference in composition between the blend and the crystals at the onset of crystallisation was rather similar for all of the three blends, with the blends containing 27%, 22% and 17% POs containing 18.6, 16.1 and 14.7% C48 TAGs, respectively, and the respective crystals containing 57.5%, 55.5% and 53.8% C48 TAGs. Hence the crystals formed in the early stages of crystallisation are dominated by the high melting trisaturated TAGs.

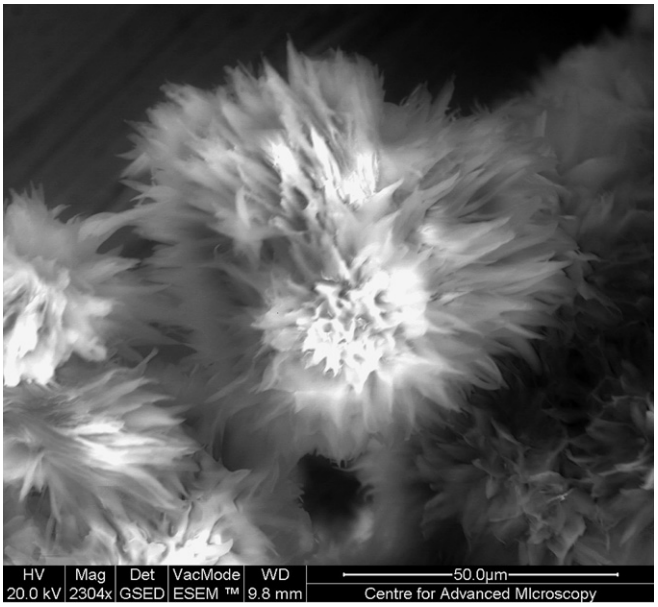

Fig. 5. Typical ESEM image, showing spherulites of crystals of blend II (22% POs) separated from the bulk material at the onset of crystallisation and suspended in isobutanol for 24 h at 35 °C.

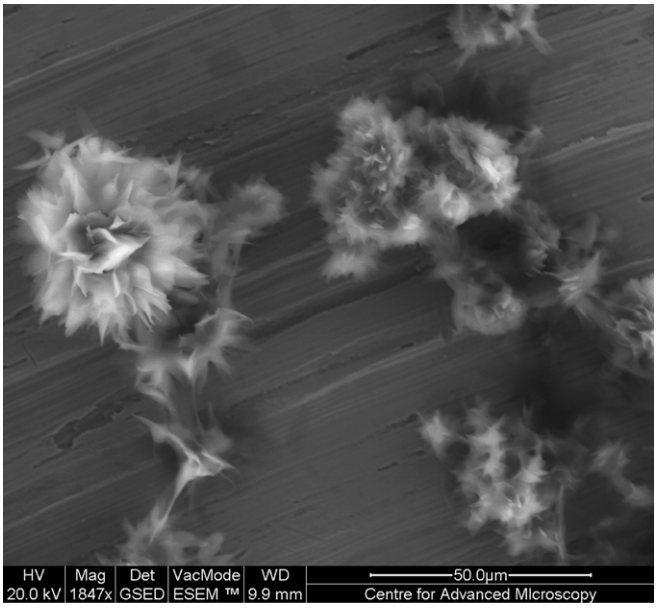

Fig. 6. Typical ESEM image, showing spherulites of crystals of blend II (22% POs) from the rheometer plate removed at the onset of crystallisation and suspended in isobutanol.

A study of model lipid systems by Shi, Liang, and Hartel (2005) also confirmed that there is little difference in crystal morphology and in the state of aggregation within the same high melting lipid classes. A lipid mixture, rich in PPP, PPO and POP, formed needles and regular spherulites whereas, in a mixture containing POS, POP and SOS, the needle-like elementary crystals grew into irregular spherulites and flocs (Shi et al., 2005).

CLSM and ESEM images of crystals from the current blends separated at the onset of crystallisation showed that 3–5 spherulites had aggregated together via links between needle-like filaments (Figs. 7 and 8). These were not artifacts from the long suspension in isobutanol, since ESEM pictures of crystals after suspension in isobutanol for 30 min were shown to also exist as clusters of spherulites (Figs. 9 and 10). This may be important for the application of fats as shortenings for bakery products because clusters of spherulites can trap more air in the batter and optimise their resulting textures.

3.5. Crystallisation and rheology

All three blends were cooled from the melt using circulating water (initially at 20 °C). All temperature profiles were found to be essentially the same (Fig. 11). Initial cooling was rapid (0–5 min) with a temperature drop of about 45 °C. This was associated with a slight rise in the temperature of the cooling water used (about 7–8 °C). After this point, the cooling rate slowed significantly until after about 12 min, at which point the cooling rate settled to a steady 0.4 °C/min for the next 15 min. For the remainder of the experiment (27–30 min), the rate fell to about 0.1 °C/min as the fat samples equilibrated with the temperature of the coolant.

All three sample blends showed similar rheological profiles on cooling. Figs. 12–14 show that each had two regions of behaviour, with an initial weak viscoelastic liquid response ($G'' > G'$), followed by the more "solid like" behaviour after the onset of crystallisation (Ferry, 1980). When the fats started to crystallise there was a sharp increase in the storage modulus (G'). The time to the onset of crystallisation increased progressively from 12 to 15 min, as the palm olein content of the blend increased and the palm stearin content decreased (27% w/w POs; 12 min (Fig. 12), 22% w/w POs; 13.5 min (Fig. 13), 17% w/w POs, 15 min (Fig. 14)). The increase in time to the onset of crystallisation with increasing palm olein content was thought to be due to the effect of the high melting triacylglycerols on the initial nucleation of the fat. This formation of embryonic crystals, which are rich in the high-melting TAGs has previously been suggested by D'Souza, deMan, and deMan, (1991).

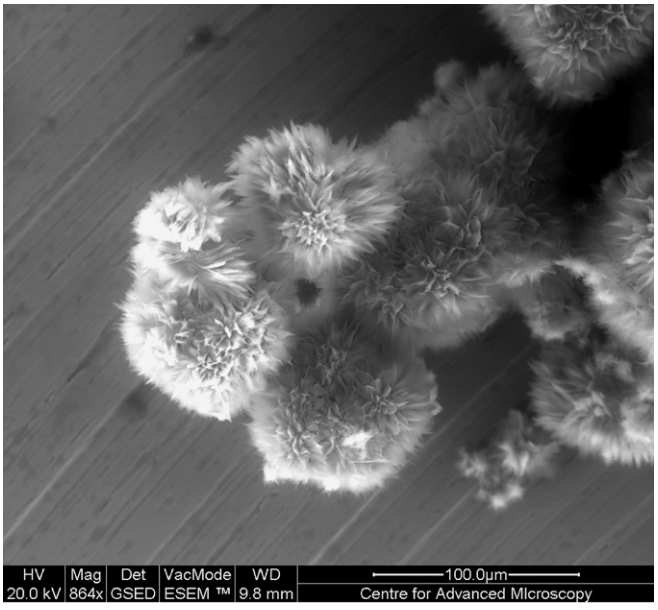

Fig. 7. ESEM image showing aggregated crystals of blend II (22% POs) separated from the bulk material in the early stages of crystallisation and suspended in isobutanol for 24 h.

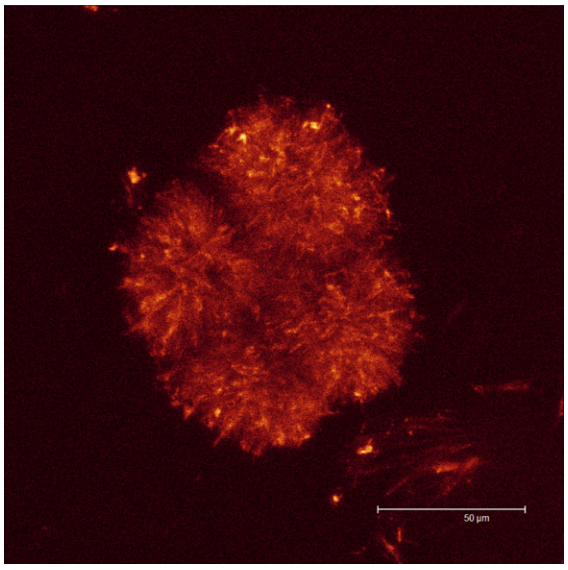

Fig. 8. CLSM image of a cluster of crystals of blend II (22% POs) separated at the onset of crystallisation at 35 °C.

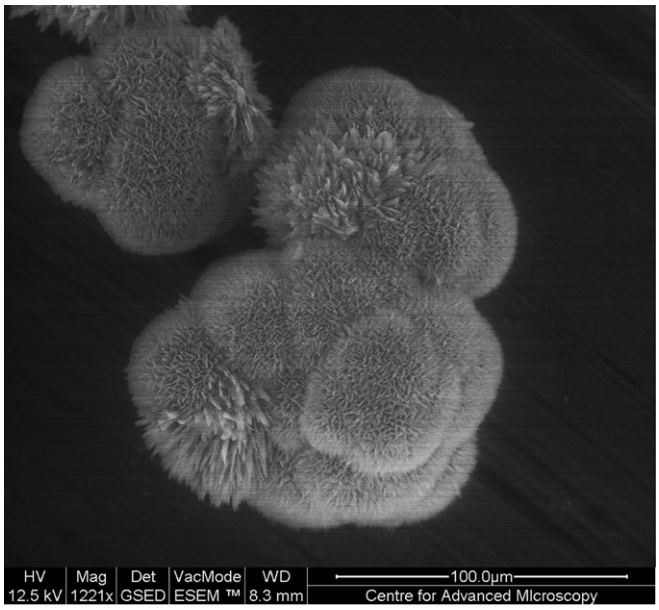

Fig. 9. ESEM image, showing clusters of solid crystals of blend II (22% POs) from the rheometer plate at the onset of crystallisation after a 30 min suspension in isobutanol.

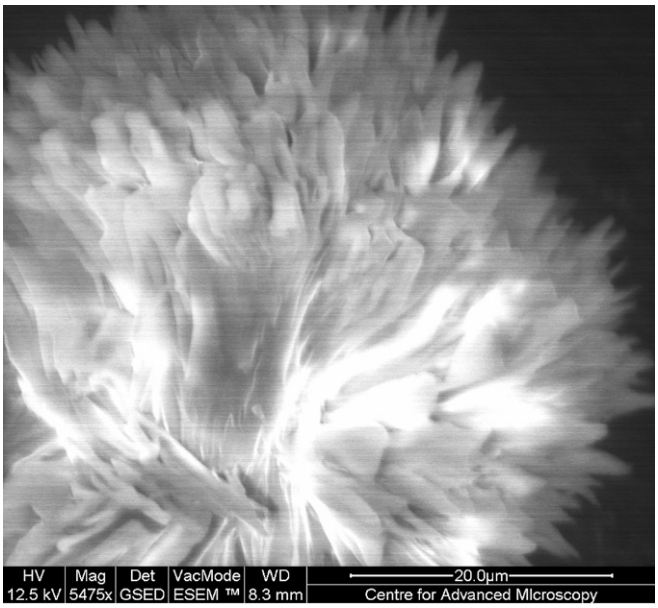

Fig. 10. ESEM image, showing filaments of spherulite of blend II (22% POs) removed from the rheometer plate at the onset of crystallisation and suspended in isobutanol for 30 min.

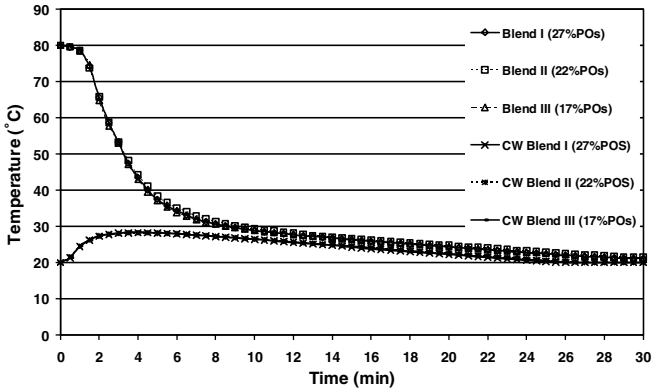

Fig. 11. Cooling profile of fat blends (CW = cooling water temperature, blend = temperature of fat blend).

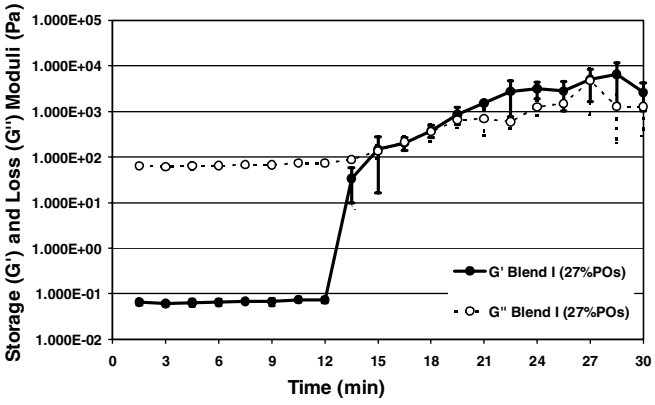

Fig. 12. Storage (G') and loss (G'') modulus of blend I (27% w/w POs) as a function of cooling time (30 min).

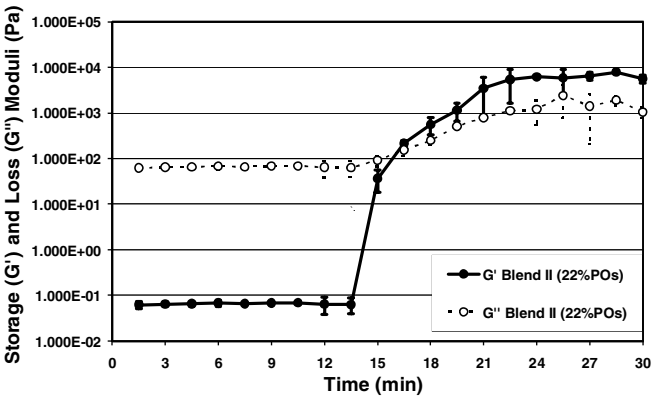

Fig. 13. Storage (G') and loss (G'') modulus of blend II (22% w/w POs) as a function of cooling time (30 min).

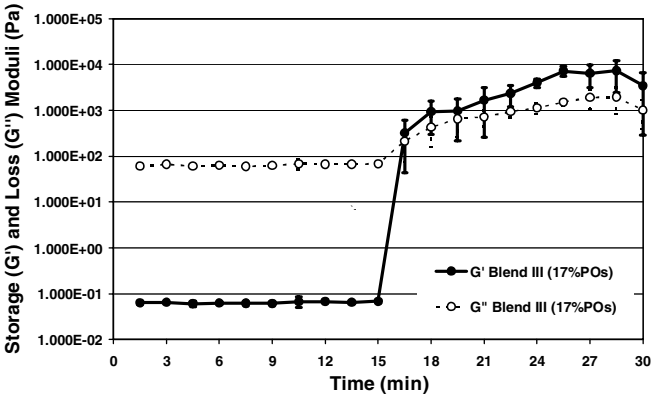

Fig. 14. Storage (G') and loss (G'') modulus of blend III (17% w/w POs) as a function of cooling time (30 min).

As crystallisation of the fat blends proceeded, agglomerates of spherulites were formed as discussed above. The growth of such structures in mixed triacylglycerol systems has previous been reported by Narine and Marangoni (1999), who suggested that the textural properties resulted from a combination of "strong" and "weak" regions. Shi et al. (2005) further developed the concept that fat crystal network characteristics were derived from spherulites of well ordered needle like crystals, linked together by liquid or semi-solid bridging lipids. This forms a three-dimensional network with the oil present as the liquid phase (Narine & Marangoni, 1999).

As the fats continued to crystallise after the onset of crystallisation, the storage modulus (G') continued to increase until G' became greater than the loss modulus (G''). However, the absolute final values of both the storage and the loss moduli and the loss tangent (the ratio of "liquid like" to "solid like" behaviour) were essentially the same for all the blends studied.

The storage modulus (G') exceeded loss modulus (G'') at a time of about 16.5 min for the blends containing 22% or 27% palm olein, while the moduli (G' and G'') were about equal, between 15 and 18 min, for the blend containing

17% palm olein. This implied that all the final structures formed were similar; this was supported by the microscopic study which showed no major differences in crystal size or morphology.

In conclusion, the rheological measurements show that the lipids present in the melt crystallise from the less structured ''liquid'' phase into crystals which then grow into larger crystalline structures. These then form networks by either direct aggregation of the spherulites or weak networks via ''other cross-linking material'' in the liquid phase, as shown by ESEM (Fig. 9). However the extent of such ''structuring'' seems to be heavily dependent, not only on the dynamic shearing conditions during crystallisation, but also on the triacylglycerol composition. In any given mixture, the nature of the ''liquid phase'', as well as the crystal size, packing density, polymorphic type and crystal shape, may all play a part in determining the development of the network (Johansson & Bergensthl, 1995; Marangoni & Hartel, 1998). Formation of aggregates seems to be heavily dependent on the volume-fraction of the spherulites present. Once a ''critical'' volume fraction has been obtained, no further increase in cluster size is possible and only a strengthening of network linkages is observed (Marangoni, 2002).

Whereas the composition of the crystals precipitated during the early stages of crystallisation were rich in trisaturated TAGs, those precipitated when G' became greater than G'' were rather similar to the original bulk fat (Table 2). It appears that most of the TAGs had already crystallised at that point.

4. Conclusions

Increasing the palm stearin content and reducing the palm olein content in the fat blends caused a decrease in time to the onset of crystallisation, due to the effect of the high melting triacylglycerols in the stearin component. This was confirmed by the increase in saturated TAGs in the crystals at the onset of crystallisation compared to those in the original molten fat. However, when crystallisation had proceeded to such an extent that G' became greater than G'', no significant differences in the rheological profile of the three blends were evident and the TAGs composition of the crystals reflected that of the original bulk fat.

The crystals separated from the fats at the onset of crystallisation showed needle-like crystals that grew into each other to form spherulites. These spherulites then aggregated to form small clusters. These clusters linked together via the liquid or semi-solid bridges in the amorphous liquid oil to form a three dimensional network which gives rise to the elastic textural properties of fats (Heertje, 1993). However, the size and shape of the spherulites formed from the three blends studied were similar, which is consistent with the similar TAG compositions of the crystals formed in the early stages of crystallisation.

Acknowledgement

We are grateful to IOI Loders Croklaan, Wormerveer, The Netherlands, for funding this research.

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