

Effects of composition on fat rheology and crystallisation

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Abstract

The crystallisation behaviour of three fat blends, comprising a commercial shortening, a blend of fats with a very low *trans* fatty acid content (“low-*trans*”) and a blend including hardened rapeseed oil with a relatively high *trans* fatty acid content (“high-*trans*”) was studied. Molten fats were lowered to a temperature of 31 °C and stirred for 0, 15, 30, 45 and 60 min. Samples were removed and their rheological properties studied, using a controlled stress rheometer, employing a frequency sweep procedure. Effects of the progressive crystallisation at 31 °C on the melting profile of fat samples removed from the stirred vessel and solidified at –20 °C were also studied by differential scanning calorimetry (DSC).

The rheological profiles obtained suggested that all of the fats studied had weak viscoelastic “liquid” structures when melted, but these changed to structures perceived by the rheometer as weak viscoelastic “gels” in the early stages of crystallisation (G' (storage modulus) > G'' (loss modulus) over most of the measured frequency range). These subsequently developed into weak viscoelastic semi-solids, showing frequency dependent behaviour on further crystallisation. These changes in behaviour were interpreted as changes from a small number of larger crystals “cross-linking” in a liquid matrix to a larger number of smaller crystals packed with a “slip plane” of liquid oil between them.

The rate of crystallisation of the three fats was in the order high *trans* > low-*trans* > commercial shortening. Changes in the DSC melting profile due to fractionation of triacylglycerols during the crystallisation at 31 °C were evident for all three fats.

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1. Introduction

The application of fat blends as shortenings in bakery products depends on their crystallisation and melting properties. However, the crystal size, shape and alignment, the degree of formation of mixed crystals and the ability of crystals to flocculate into a network which increases firmness are also important (Opfer, 1975). The melting behaviour is determined by the composition and by the polymorphs that are present. The shape and size of the 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). Smaller and finer β' crystals can stabilise more air and more liquid

component than larger and coarser β crystals (Podmore, 2002). Viscosity measurements are commonly used to monitor changes in 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 compare the rheology during crystallisation of three fats differing in composition but with similar melting profiles, and any effects of the crystallisation on subsequent melting of the fats after solidification.

2. Materials and methods

2.1. Materials

Rapeseed oil (Rp); refined, bleached and deodorised (rbd) palm olein with iodine value of 47 (POf); rbd palm stearin

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Table 1
Fatty acid composition (%) of rapeseed oil (Rp), palm stearin (POs IV35) and palm olein (POf IV47)

Fatty acid composition (%)			
Fatty acid	Blend components		
	Rp	POs IV35	POf IV47
Saturated			
C14:0 (M)		1.26 ± 0.005	1.17 ± 0.01
C16:0 (P)	5.35 ± 0.55	58.9 ± 0.189	50.1 ± 0.25
C18:0 (S)	1.60 ± 0.05	5.44 ± 0.090	5.33 ± 0.02
Total	6.95 ± 0.60	65.6 ± 0.284	56.6 ± 0.28
Unsaturated			
C18:1 (O)	60.4 ± 0.285	27.4 ± 0.11	34.3 ± 0.25
C18:2 (L)	19.1 ± 0.128	6.10 ± 0.09	7.97 ± 0.06
C18:3 (Ln)	9.69 ± 0.106	0.22 ± 0.11	0.29 ± 0.01
Total	89.2 ± 0.52	33.7 ± 0.31	42.5 ± 0.32

with iodine value of 35 (POs) were used as components of the low *trans* blend. Their fatty acid and triacylglycerol compositions are presented in Tables 1 and 2, respectively. Soybean oil, hardened to a slip melting point of 65 °C (BO65), and rapeseed oil, hardened to slip melting point of 38 °C (Rp38), were used as components of the high *trans* blend. All materials were supplied by Loders Crokiaan BV (Wormerveer, The Netherlands).

Fat blends prepared for study were (a) a low *trans* blend (“low-*trans*”): 56% Rp, 22% Pof, 22% POs (b) *trans* containing blend (“high-*trans*”): 66% Rp, 30% Rp38, 4% BO65 and (c) a commercial vegetable shortening, purchased from a local retail outlet (for comparison).

2.2. Crystallisation

Each fat blend (250 g) was stirred with a mechanical stirrer at a rate of 30 rpm for 30 min in a jacketed glass vessel at 87 °C. The melted oil was cooled under the same con-

Table 2
Triacylglycerol composition (%) of rapeseed oil (Rp), palm stearin (POs IV35) and palm olein (POf IV47)

TAG	Triacylglycerol composition (%)		
	Rp	POS IV35	POf IV47
C48			
PPP	–	41.3	12.4
MPO	–	2.29	1.73
C50			
PPS/PSP	–	5.90	4.82
PPO/POP	–	36.6	40.5
PPL	–	4.73	8.43
C52			
POS	–	–	5.95
POO	6.83	–	15.5
POL	4.42	–	4.57
C54			
OOO	27.9	–	–
OOL/OLL	16.8	–	–
LLL	7.40	–	–

trolled cooling conditions using circulating water at 20 °C until the temperature of the melted oil reached 34 °C. Then the temperature of the cooling water was raised to 22 °C until the oil temperature reached 33 °C, when it was raised to 25 °C until the oil reached 32 °C and finally to 29.8 °C in order to maintain the oil temperature at 31 °C, at which point small samples were removed at 0, 15, 30, 45 and 60 min for rheological measurements ($n = 6$ for each). A second sample was removed at each time point and frozen at –20 °C for subsequent DSC analysis of its melting profile. The effect of stirring was also investigated by stirring at 60 rpm and studying the crystallisation as described above.

2.3. Rheology

Rheological measurements were obtained using a controlled stress Rheometer (RTI Ltd.). A 20 mm diameter flat plate was selected with a gap of 2 mm (to prevent “particle bridging”). The temperature of the sample was held at 31 ± 0.1 °C. Initial stress amplitude sweeps were carried out on all of the test blends to determine the region of linear viscoelastic behaviour for each. An initial test torque of 0.005 Pa was found to produce response within the linear viscoelastic region (LVR) of each test sample. The frequency sweep within the LVR was then performed quickly by loading a small sample (about 2 ml) from the crystallisation vessel onto the rheometer plate. A frequency range of 0.1–10 Hz was used. No significant differences were observed between sweeps carried out from 0.1 to 10 Hz and those from 10 to 0.1 Hz (data not shown). This suggested that the time taken for the measurement did not change the overall data profile. As all samples continued to develop crystalline structures when held at 31 °C, each sample was then taken out at each time point to perform the rheological measurement as a function of time at torque of 0.005 Pa and frequency of 1 Hz for 30 min. The storage modulus (G') and loss modulus (G'') were determined as a function of frequency for each sample.

2.4. Thermal analysis by DSC

The DSC melting profile was determined for each sample from the crystallisation vessel at least in duplicate. The melting profile was recorded with a Perkin–Elmer DSC-7 with nitrogen as the purge gas at a flow rate of about 30 ml/min. Indium, with a melting point of 156.6 °C, was used to calibrate the instrument. Samples of 12 and 20 mg were loaded to the middle of the aluminium pans using small spatula and hermetically sealed. Samples were then inserted into the instrument at 15 °C and heated immediately from 15 to 60 °C with a heating rate of 5 °C/min.

2.5. Fatty acid analysis

The fatty acid composition of each fat blend was determined by AOAC methods 969.33 and 963.22 (Reading Scientific Services Ltd., Reading UK).

2.6. Equilibrium solids measurements

Equilibrium solids contents (N values) were determined by pulse NMR using a Bruker Minispec NMS 120 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, 30 and 35 °C). After a further 30 min at the measuring temperature, the solid fat content was determined.

3. Results and discussion

3.1. Composition

The three fats represented low, medium and high *trans* fats (Table 3). The fats were selected to have similar equilibrium solids contents in the temperature range 20–35 °C (Table 4). In the low-*trans* fat, the high melting triacylglycerols were rich in 16:0 (26.7%) but, in the high *trans* fat, a low 16:0 (8.9%) and higher 18:0 content contributed to the high melting triacylglycerols. The commercial fat was intermediate in *trans* 18:1 content, and in 16:0 content with the 18:0 a little lower than in the high *trans* fat. The fats used in preparing the blends suggested the presence of tripalmitin and dipalmitoyloleylglycerol in the low-*trans* blend with tristearin from the hardened bean oil, and distearoylaidylglycerol, stearoyldielaidylglycerol and trielaidylglycerol from the hardened rapeseed oil in the high *trans* blend contributing importantly to the high melting triacylglycerols.

3.2. Crystallisation and rheology

The commercial fat and the low-*trans* blend cooled to 31 °C in less than 12 min. However, the “high-*trans*” fat sample formed some crystals more rapidly during cooling which caused a marked increase in viscosity during cooling,

Table 3
Fatty acid composition (%) of commercial fat, low-*trans* and high *trans* samples

Fatty acid (%)	Commercial fat	Low <i>trans</i>	High <i>trans</i>
12:0	0.1	0.1	0.1
14:0	0.3	0.5	0.2
16:0	14.9	26.7	8.9
16:1	0.2	0.2	0.1
18:0	6.2	3.3	7.7
18:1 (<i>trans</i>)	5.2	0.1	13.0
18:1 (<i>cis</i>)	49.3	48.7	49.1
18:2 (<i>trans</i>)	0.1	0.1	0.5
18:2 (<i>cis</i>)	14.2	14.0	13.0
18:3 (<i>trans</i>)	0.1	0.2	0.2
18:3 (<i>alpha</i>)	6.1	4.1	4.9
20:0	1.2	0.5	0.6
22:0	0.3	0.8	1.0
22:1	0.6	0.2	0.3
Total (%)	98.8	99.5	99.6

Table 4
Equilibrium solids contents (N values) of commercial fat, low *trans* and high *trans* samples

Temperature (°C)	N (%) for commercial fat	N (%) for low <i>trans</i>	N (%) for High <i>trans</i>
20	17.9	18.5	18.6
30	12.1	11.2	9.8
35	7.4	8.6	5.9

and cloudiness around the wall of the jacketed glass vessel at about 6.0–6.3 min. This is thought to be the result of crystallisation of tristearin from the hardened soybean oil (BO65) and distearoylaidylglycerol from the hardened rapeseed oil. Latent heat of crystallisation was released and this retarded the cooling, so the fat took longer to reach 31 °C (this took nearly 20 min. Fig. 1).

Fully melted fats showed a weak viscoelastic liquid structure with the loss modulus (G'') higher than the storage modulus (G') throughout the measured frequency range (Fig. 2). Any residual structure was so weak that it was lost soon after the lowest frequency of 0.1 Hz was applied. At the higher frequency values, the $\tan \delta$ values were about 1000. Both moduli showed the characteristic frequency dependency associated with essentially “liquid” behaviour (Ferry, 1980).

It was noted that all fat samples studied continued to develop their crystalline structure at 31 °C. Structure development depended on both the time held at 31 °C and the stirring rate employed in the crystallisation vessel (for example see Fig. 3). This implied that the “starting point” of any measurement of structural development was highly dependent on the total amount of energy supplied in the mixing process, i.e., dependent on the total work done on the sample prior to the rheological measurement. In fact, the gradients of the change in G' and G'' with time, measured for both stirring rates, were similar (slight increase in G' with time and G'' essentially constant). The essential difference for the two stirring rates was the time at which the “cross-over” of the moduli occurred ($\tan \sigma = 1$). The material stirred at the higher rate (60 rpm) showed mainly “liquid” behaviour over most of the measured timescale.

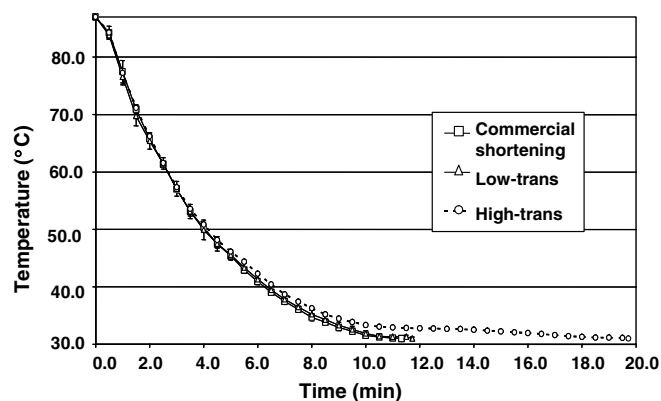


Fig. 1. Cooling curves of 3 fats studied.

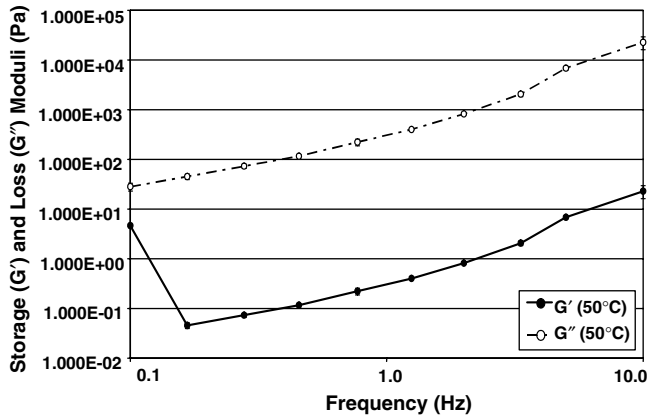


Fig. 2. Frequency sweep curve, showing rheology of fully melted commercial shortening at 50 °C.

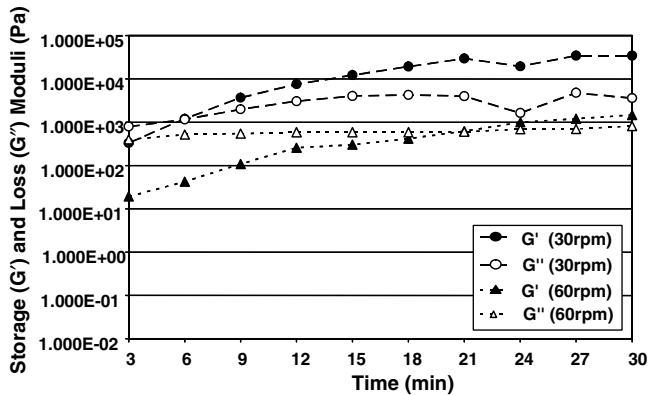


Fig. 3. Typical changes observed for the storage and loss moduli at 1 Hz as a function of time after sampling. Commercial fat samples held at 31 °C and stirred for 45 min at 30 and 60 rpm, respectively.

This more heavily “worked” material would in this sense be considered as indicating a “less developed” version of the same structure. Because of this, all subsequent rheological measurements on the fat samples were carried out on a strictly timed basis to allow comparison of the three different fat blends.

As crystallisation of the commercial shortening proceeded, small crystals developed as a dispersion in the liquid oil. During the first 15 min of stirring at 31 °C, the storage modulus (G') was greater than the loss modulus (G'') over most of the measured frequency range, with a reduced dependence on frequency which, according to Ferry (1980), is a characteristic of a weak viscoelastic “gel” system (Fig. 4). After 30 min of stirring, the material reverted to a profile characteristic of a weak viscoelastic liquid ($G'' > G'$, Fig. 5), with any remaining structure showing a marked sensitivity to increasing frequency. It appears that, initially, the rheological behaviour was dominated by the presence of relatively few crystals but, after a longer period of stirring, the weak viscoelastic “liquid” behaviour developed and this may be the result of more liquid “slip planes” between a larger number of small solid crystals,

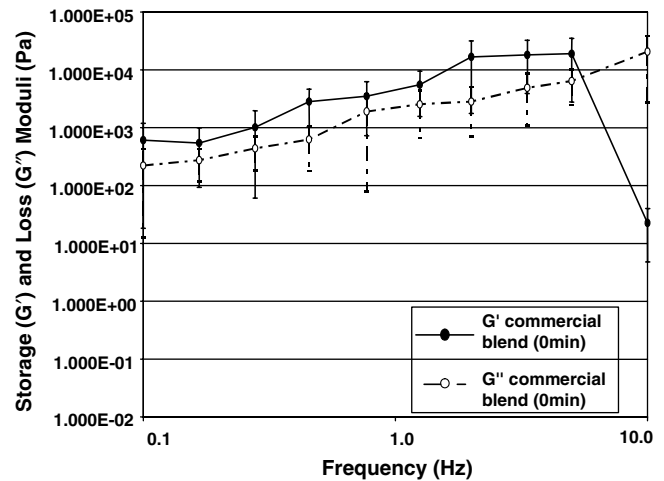


Fig. 4. Frequency sweep curve, showing rheology of partially crystallised commercial shortening at 0 min of stirring at 31 °C.

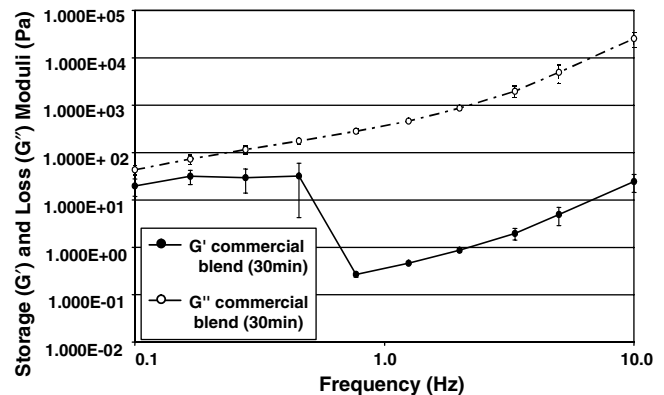


Fig. 5. Frequency sweep curve, showing rheology of partially crystallised commercial shortening at 30 min of stirring at 31 °C.

dominating the physical behaviour. The growth of such structures in mixed lipid systems has previously been reported by Narine and Marangoni (1999), who suggested that the textural properties resulted from a combination of “strong” and “weak” regions. Shi, Liang, and Hartel (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.

Studies on the “low-*trans*” blend indicated a dramatic change in the physical characteristics of the samples between 0 and 15 min at 31 °C (Figs. 6 and 7). The rheology, initially, was similar to that of the commercial shortening, with weak liquid-like behaviour. However, the change to a very weak viscoelastic “gel”, with reduced frequency dependence, occurred within 15 min of stirring. (The change in commercial shortening occurred after 30 min of stirring.)

For the “high-*trans*” blend, crystallisation of the fats and the associated changes in their physical characteristics had already occurred, even before the fat had reached the

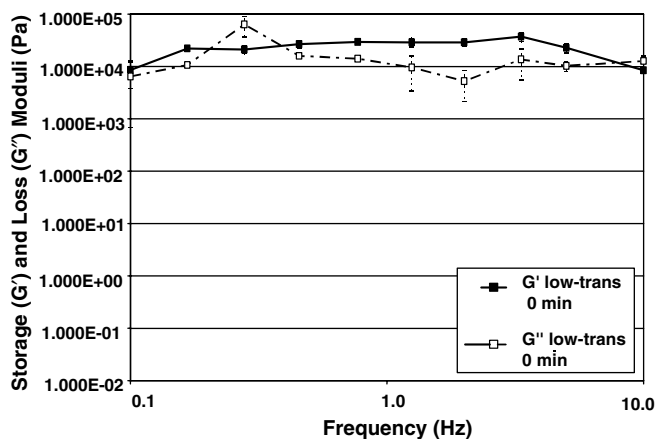


Fig. 6. Frequency sweep curve, showing rheology of partially crystallised low-*trans* blend at 0 min of stirring at 31 °C.

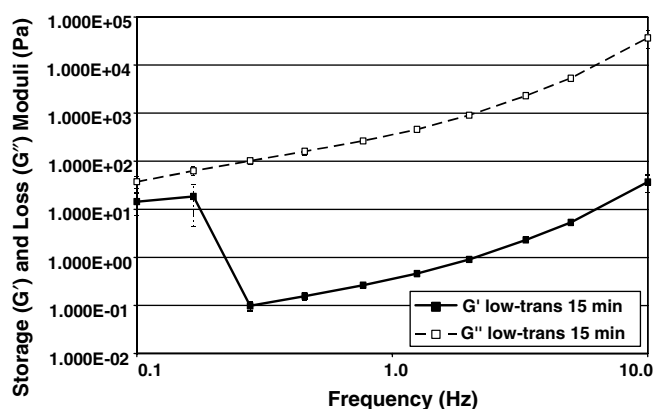


Fig. 7. Frequency sweep curve, showing rheology of partially crystallised low-*trans* blend at 15 min of stirring at 31 °C.

31 °C test temperature. The rheological profile at 0 min of stirring (Fig. 8) was similar to that of the “low-*trans*” blend after 60 min of stirring. The frequency required for loss of structure decreased with increasing stirring time, but the basic structure remained unchanged (Fig. 9).

In general, the sequence of changes in the physical state of all the fats tested was similar, with the composition determining the rate of structure development in each sample group. The authors accept that the differences in structure development may affect the linear viscoelastic region of each system, but the effect of this was minimised by using a controlled stress instrument, which reduces the overall strain at higher frequencies. Breakage in the structure, therefore, is much more likely to be due to a change in the degree of interactions present between the crystals than to damage induced during measurement. In fact it seems likely that these rheological changes are related to the size and number of spherulites that determine the space occupied in the matrix by the crystals.

In conclusion, the rheology would suggest that the lipids present in the melt, crystallise from the less structured liquid phase into specific fat crystal polymorphs that then

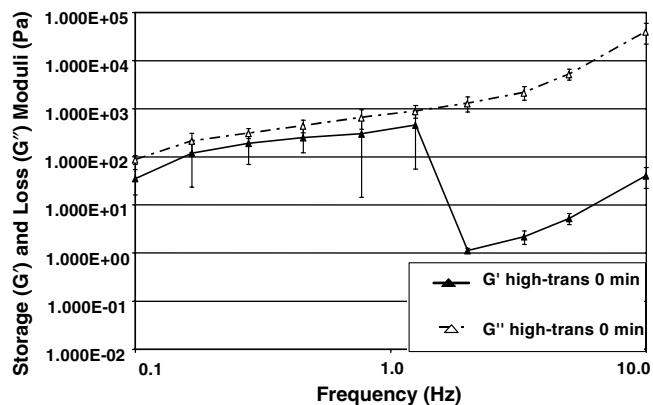


Fig. 8. Frequency sweep curve, showing rheology of partially crystallised high-*trans* blend at 0 min of stirring at 31 °C.

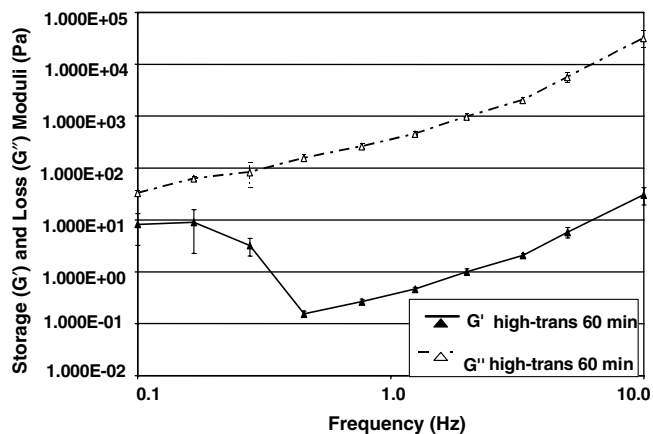


Fig. 9. Frequency sweep curve showing storage (G') and loss (G'') moduli of partially crystallised high-*trans* blend at 60 min of stirring at 31 °C.

grow into larger crystalline structures. These then form networks by aggregation or weak networks via “cross-linking material” in the liquid phase. However, the extent of such “structuring” seems heavily dependent, not only on the dynamic shearing conditions during crystallisation, but also on the triacylglycerol composition. Overall, while it is known that a higher solid fat content leads to higher values of elastic moduli (G') in any given mixture, the nature of the liquid phase, as well as the crystal size, packing density, polymorphic form and crystal shape may all play a part (Marangoni & Hartel, 1998).

3.3. Melting behaviour of solidified fats

For the commercial shortening solidified after 0 min of stirring at 31 °C, the melting profile after solidification showed a single, broad melting peak (Fig. 10). After 60 min of stirring at 31 °C, the DSC melting profile of the solidified fat showed two broad peaks. The second of these completed melting at higher temperature than did the previous single, broad peak. This would suggest that a higher melting polymorph or mixed crystal is forming

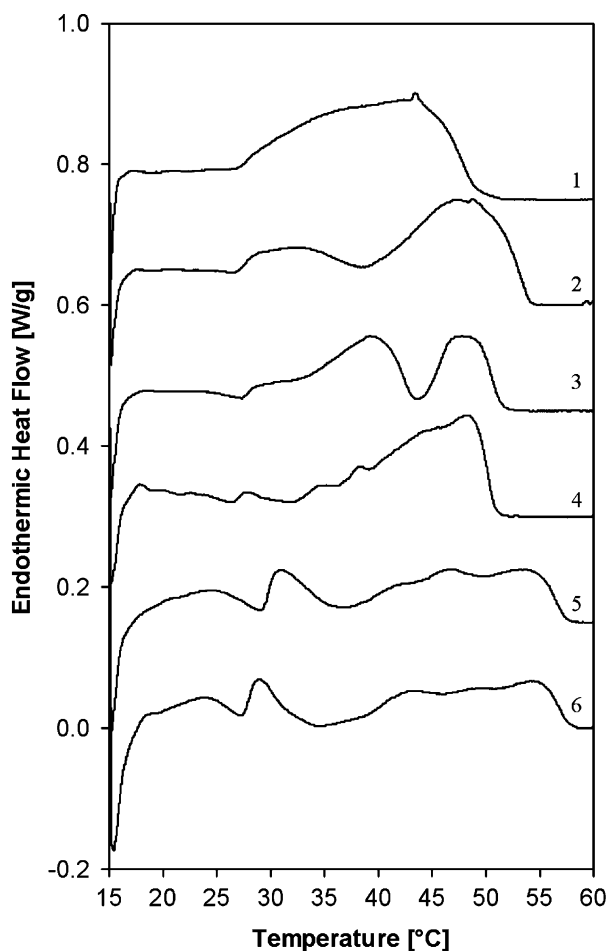


Fig. 10. DSC melting curves of commercial shortening, high *trans* and low *trans* fats solidified at $-20\text{ }^{\circ}\text{C}$ after 0 and 60 min of stirring at $31\text{ }^{\circ}\text{C}$, measured at $15\text{--}60\text{ }^{\circ}\text{C}$ with melting rate of $5\text{ }^{\circ}\text{C}/\text{min}$.

during the crystallisation at $31\text{ }^{\circ}\text{C}$ than is formed during the rapid cooling of the uncrystallised sample at 0 min. Commercial shortenings normally crystallise as β' fat crystals (Narine & Humphrey, 2004).

For the low-*trans* fat, two peaks are seen initially, indicating that crystallisation of the molten oil during freezing occurred in two main fractions. During 60 min of crystallisation at $31\text{ }^{\circ}\text{C}$, the lower melting of these fractions diminishes, being incorporated into the second peak. However, the final melting point of the peak is not altered. This suggests that a different polymorphic form or mixed crystal is forming at $31\text{ }^{\circ}\text{C}$ (Fig. 10). The sample consisted of palm fractions dispersed in a liquid oil, and consequently the polymorphs melting in the range observed are likely to be β'_1 , melting above $15\text{ }^{\circ}\text{C}$, and β_1 , melting above $30\text{ }^{\circ}\text{C}$, based on the literature reports of the melting behaviour of palm oil (Che Man & Swe, 1995). β' and β crystals were also confirmed to be present in canola-palm oil mixtures (D'Souza, de Man, & de Man, 1992).

For the high-*trans* fat, a relatively small change is observed between the melting profile of the fats solidified

after 0 and 60 of min stirring. This is likely to be due to the occurrence of crystallisation prior to reaching $31\text{ }^{\circ}\text{C}$, as noted earlier. However, the proportion of the higher melting peaks does increase after 60 min (Fig. 10). It is clear that the crystallisation of triacylglycerols during stirring was changing the melting profile for all three fat blends by causing an increase in the amounts of higher melting triacylglycerols.

4. Conclusions

During crystallisation, the rheology of the fats changed from a weak viscoelastic solid system to a weak viscoelastic liquid. It appears that, initially, the rheology was dominated by the few large crystals present but, after longer stirring, weak viscoelastic liquid behaviour, characteristic of liquid slip planes between solid crystals, dominated the behaviour. The rate of change was fastest for the high-*trans* blend, with the low-*trans* blend being intermediate, and the commercial shortening being the slowest to undergo this change at $31\text{ }^{\circ}\text{C}$. The rheological changes were primarily dependent on the composition of the fat, which determined the rate of solid fat development and the size and number of spherulites formed, which in turn determined the rheology. The solidification rate of shortenings can be of significance in bakery products, such as savoury pastries, where the fat must solidify in the product as it cools to avoid fat loss, which gives an oily paste (Podmore, 2002). Small β' crystals are preferred in fats for cakes since they give increased firmness and air incorporation in the batter at a given solid fat content. Compounded shortenings containing a mixture of larger β and β' crystals, perform well in short pastry recipes. Consequently, differences in bakery product quality may occur due to differences in the crystallisation behaviour of the fats.

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