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SEMI-SOLID PROCESSING OF CHOCOLATE AND COCOA BUTTER
The Experimental Correlation of Process Rheology with Microstructure

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This paper reports experimental observations on changes in process rheology caused by successive processing of chocolate and cocoa butter in a semi-solid state. Experiments were carried out using a multi-pass rheometer where successive extrusion passes were used with different time delays between each pass. The results show that both chocolate and cocoa butter are sensitive to process history. Additional microstructural data was obtained by using an *in situ* X-ray facility coupled to the multi-pass rheometer and results obtained using this technique indicate that the process rheology changes are coupled with matching changes in the amount of crystal phase present.

Keywords: chocolate; cocoa butter; extrusion; microstructure; X-ray diffraction; rheology; process history.

INTRODUCTION

Chocolate products are usually given their final shape by pouring molten chocolate into a mould or onto a sweet centre at temperatures around 30°C, where the chocolate behaves as a viscous fluid, with both a yield stress and mild shear-thinning characteristics (Chevalley, 1999). The chocolate product is then cooled before demoulding and packaging, in order to allow solidification of the main lipid components (cocoa butter and, if present, milk fat) of the chocolate to occur (see e.g., Beckett, 1999, 2000). More recently, it has been shown that certain types of chocolate products can be formed by 'cold' extrusion of the chocolate through a convergent die at temperatures between 5 and 25°C (Beckett *et al.*, 1994; Ovaici *et al.*, 1998). The extruded product is both shape retaining and has temporary flexibility. When the material leaves the die it maintains the precise sectional profile of the die, however if the extrudate is a filament of sufficiently small diameter, say 3 mm, the material is also flexible and in some cases the filament can even be tied in knots. An initially surprising feature of the process was that the extrusion is essentially isothermal and no detectable temperature change occurred between the initial solid chocolate pieces that were introduced into the extruder and the flexible extrudates produced by the process.

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Previous ram extrusion experiments on this 'cold extrusion' of chocolate have shown that as a piston advances within a barrel of an extruder the barrel pressure rises sharply and often shows a sharp peak as illustrated in Figure 1, associated with yield and the commencement of flow (Crook, 1997; Mulji, 2000; Ovaici *et al.*, 1998; Ovaici, 1999). Subsequently the extrusion pressure reaches a constant value, which is essentially independent of the extruder piston speed but is a strong function of extrusion temperature. When the piston stops, a certain component of the extrusion pressure decreases within a time scale of a few seconds, leaving a residual barrel pressure that decays on a much longer time scale. The results are consistent with modelling the material as a near perfect plastic material (Mulji and Mackley, 2003, 2004) with a temperature-dependent yield stress for the constant-pressure part of the extrusion curve. The yield pressure is also strongly temperature dependent (Crook, 1997; Mulji, 2000; Ovaici *et al.*, 1998: Ovaici, 1999).

The microstructure of chocolate is complex as a commercial chocolate contains cocoa butter/milk fat, sucrose, cocoa particles, milk particles, surface active ingredients (e.g., lecithin) and flavours (e.g., vanillin). In relation to this paper, components of interest are the solid sugar crystals, which are assumed to remain unchanged during cold extrusion processing, and of greater relevance, the semi-crystalline fat matrix, consisting mostly of triglyceride molecules (originating from the cocoa butter and, when present, milk fat). It is the semi-crystalline component that is of greatest interest in relation to cold

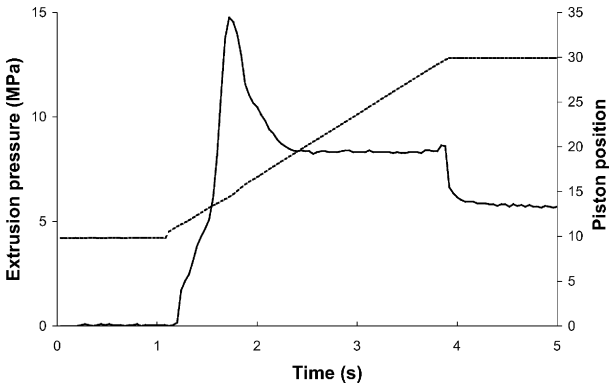

Figure 1. Example of the development of barrel pressure during a ram extrusion of chocolate, measured in the MultiPass Rheometer just upstream of extrusion die. Solid line: barrel pressure. Broken line: piston position.

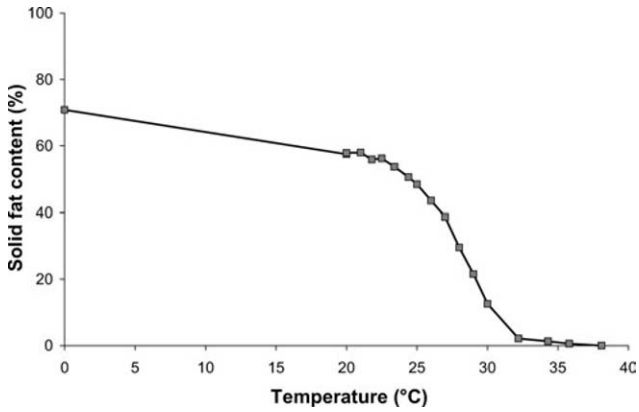

Figure 2. Melting curve of the milk chocolate used in our experiments, as obtained by p-NMR. Samples were held for at least 60 min at each temperature before taking the NMR measurement.

extrusion as this component provides the plastic flow characteristics of the material (Deman and Beers, 1987; Narine and Marangoni, 1999a, b).

In the original paper on cold extrusion of chocolate (Beckett *et al.*, 1994) it was conjectured that the work dissipated during cold extrusion went into converting a certain fraction of crystal phase triglycerides to the liquid state and that it was this additional amount of liquid phase that gave the material its unusual flow and subsequent flexible response. Subsequently work by Mulji *et al.* (2003) using NMR techniques showed that the liquid fraction of cocoa butter decreased after extrusion, indicating that it had increased during extrusion. They also measured a small temperature increase of the extrudate after extrusion and this indicated the occurrence of recrystallization during the recovery period. All these results are consistent with extrusion causing an increase in liquid phase content and post-extrusion recovery relating to a return to the original crystal fraction.

In this paper we use a double-piston multi-pass rheometer (Mackley *et al.*, 1995) to subject chocolate or cocoa butter to successive multiple extrusions and therebye establish how the material responds to different process histories. In addition we use X-ray diffraction to probe the crystal fraction of the fat matrix present at any time from which the liquid fraction can be obtained. The coupled data gives insight into the way processing influences both the rheology and microstructure of the materials.

MATERIALS AND EXPERIMENTAL TECHNIQUES

Materials

Chocolate

Milk chocolate in the form of solid granules ($x < 5$ mm) was provided by Nestlé Product Technology Centre York (York, UK) and analytical data describing the composition of the material are given in Table 1.

Table 1. Composition of the milk chocolate used in our experiments.

Sugar content	48% of total mass
Milk particles	16% of total mass
Cocoa particles	5% of total mass
Total fat content	29.4% of total mass
Milk fat content	5.4% of total mass
Moisture content	1.25% of total mass

The melting characteristics of the same milk chocolate, as measured by pulsed nuclear magnetic resonance (p-NMR), which quantifies the different amounts of solid and liquid triglycerides via the different proton spin relaxation times of their hydrogen atoms when exposed to a pulsed magnetic field, are given in Figure 2.

Cocoa butter

The fatty acid composition of the cocoa butter used is given in Table 2.

The melting characteristics, as measured by p-NMR are given in Figure 3.

The Multi-Pass Rheometer

The 'Cambridge MultiPass Rheometer' (MPR), shown schematically in Figure 4, is a double-piston capillary rheometer that allows repeated processing of samples at a controlled temperature and mean hydrostatic pressure. As the sample is completely enclosed within the rheometer, evaporation, drying or other artefacts caused by free surfaces are avoided (Wee and Mackley, 1998). The device enables a single sample to be processed many times in a systematic and controlled way. After the material under test has been loaded into the MPR, the mean hydrostatic pressure within the test section can be fixed by moving the pistons towards each other. Subsequently the two

Table 2. Fatty acid composition of the cocoa butter used in our experiments.

Chain length : unsaturated bonds	Fraction (% per weight)
14 : 0	1.2
16 : 0	24.3
18 : 0	37.3
18 : 1	32.4
18 : 2	3.0
18 : 3	0.1
20 : 0	0.2
22 : 0	0.2

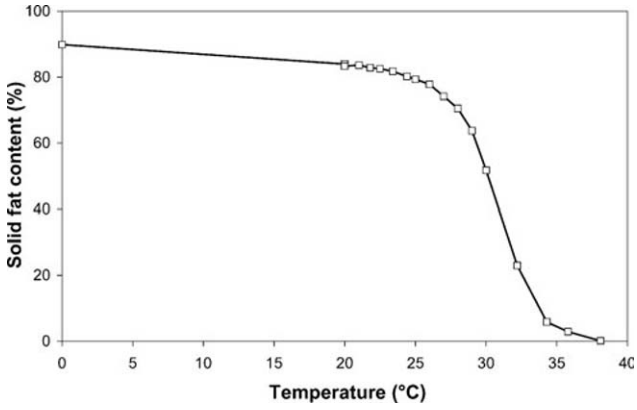

Figure 3. Melting curve of the cocoa butter used in our experiments, as obtained by p-NMR. Samples were held for at least 60 min at each temperature before taking the NMR measurement.

pistons are moved together in the same direction in a synchronized fashion to conduct the tests. In the tests reported in this paper the pistons move together at a constant speed and for a set time. There is then a rest time before the piston motion is reversed and the process repeated, which could vary between a fraction of a second or hours. In this way, the test material can be subjected to successive processing through a capillary section under very controlled conditions. Two pressure transducers are positioned above and below the test section capillary and this enables time-dependent measurements of differential pressure between these two locations to be made (Mackley and Spitteler, 1996; Ranganathan *et al*., 1999). The 'MPR Mark3', or MPR3, was used for the experiments described in this paper. This instrument has barrel diameters of 15 mm and the capillaries used had an internal diameter of 4 mm, 10 mm length and an entry angle of 45°.

In addition to these process rheology measurements, it is possible to use the MPR3 together with an X-ray scattering facility (Mackley *et al.*, 2000) and Figure 5 is a schematic representation of the MPR and X-ray configuration. In this case a beryllium capillary (to allow sufficient transmission of X-rays) is used in the test section and *in situ* X-ray data can be obtained during MPR processing, which enables simultaneous measurements of microstructure and process rheology. The X-ray system used for the *in situ* diffraction measurements consisted of a Siemens Kristalloflex 760 generator (sealed tube type; maximum power 2.2 kW), graphite monochromator (Huber), beam collimator and a two-dimensional detector (Siemens HI-STAR). The whole system was mounted inside a metallic cabinet built on a moveable trolley and could be set up around the MPR. The X-ray detector could be positioned at different angles in order to study different parts of the diffraction spectrum.

Extrusion Loading and Operation Protocol

The chocolate and cocoa butter were in granular/powder form at the temperature of interest, and therefore a special sample loading procedure for the MPR was developed. To maintain the particular polymorphic form of the crystalline triglyceride molecules, melting the chocolate and solidifying it in the instrument was not considered a viable option, as this would have required a well-controlled 'tempering' inside the instrument. Instead, chocolate granules were

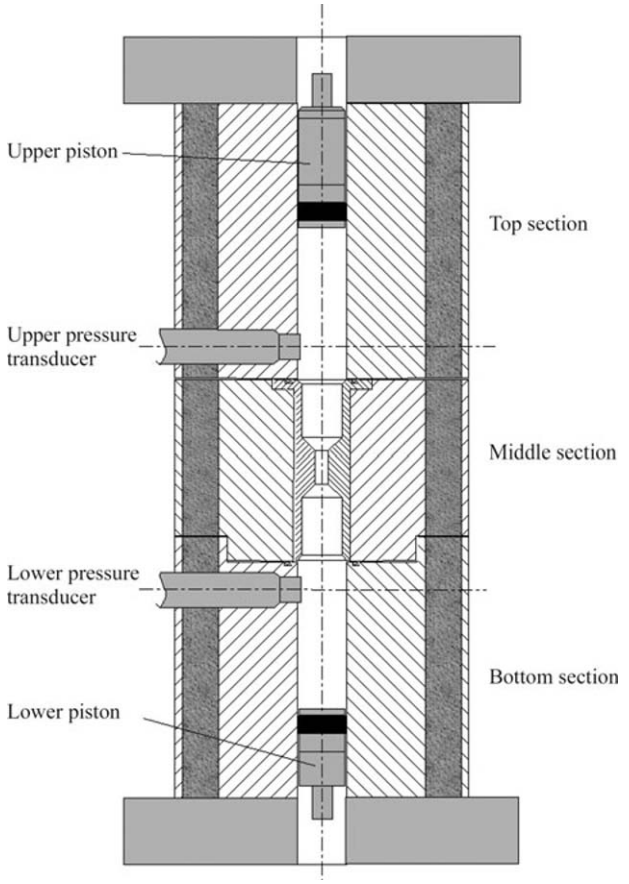

Figure 4. Schematic diagram of the the MultiPass Rheometer, showing the top, bottom and middle sections.

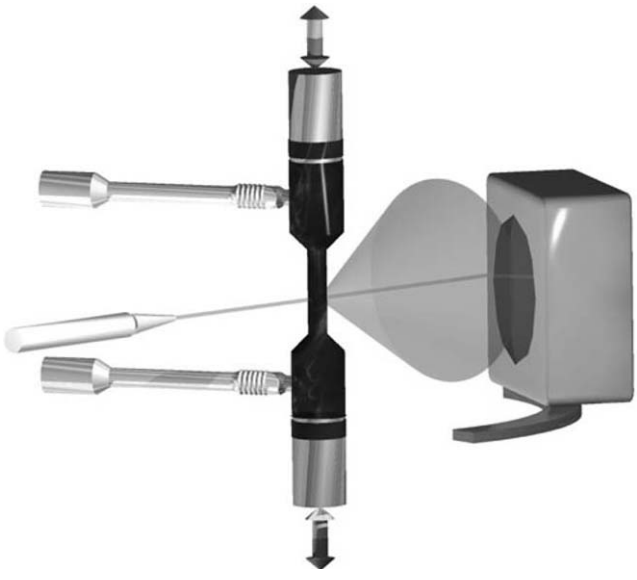

Figure 5. Schematic diagram of the MultiPass Rheometer, showing positions of the pressure transducers, X-ray beam, diffracted radiation cone and moveable two-dimensional X-ray detector.

compacted in a medical syringe made of plastic (from which the front part had been sawn off) and then fed from this syringe into the bottom and top sections of the MPR and into the wide parts of the capillary section. The pistons were then moved towards the sample in small steps in order to compact the material without extruding it yet. The end of the compaction phase was arbitrarily chosen when moving the pistons towards each other by 1 mm increased the static pressure of the samples permanently by more than 0.1 MPa. Extrusion sequences were then conducted by moving both pistons synchronously. The temperature of the barrel system was kept constant at $20 \pm 1^{\circ}$C during the extrusion sequences.

RESULTS AND DISCUSSION

This section describes the experimental observation of four interrelated effects that occur during the extrusion of semi-solid chocolate and cocoa butter: mechanical softening and re-hardening, as well as melting of triglycerides and their re-crystallization. We first studied rheological changes by differential pressure measurements in single and multi-pass extrusion experiments, then changes in structure by using *in situ* X-ray diffraction during such experiments, finally their relation to each other.

Extrusion Softening

When the MPR was used to extrude semi-solid chocolate in a 'single-pass' mode, as shown in Figure 6, the transient extrusion pressure showed the same characteristics that had been previously observed for chocolate extrusion in simple ram piston extruders. The pressure trace shows a pressure overshoot followed by a region where the extrusion pressure P_{flow} is constant. On the cessation of piston movement the pressure starts to decay. The extrusion pressure in these single-pass experiments was found to depend only very weakly on piston velocity, or flow rate: for example in the case of milk chocolate extruded at 20°C, a 10-fold increase in piston velocity increased the extrusion pressure by only a factor of 1.5.

When the MPR was used in 'multi-pass' mode to conduct sequences of extrusion, additional information was obtained concerning the effect of the past mechanical work on the material properties. A set of typical pressure profiles obtained during an extrusion sequence is shown in Figure 7. In this case a zero time delay was chosen between the 'up' and 'down' motion of the pistons. The initial extrusion shows the highest extrusion pressure and subsequent extrusion strokes show a progressive decay. After approximately 20 extrusions, no substantial further change of the extrusion pressure profile occurred. The initially unexpected increase of the extrusion pressure at the end of each extrusion pass was presumably caused by the fact that material entering the extrusion die at the end of each pass had not completely passed through the die during the previous extrusion passes and thus had been subjected to a smaller amount of work. This material had therefore experienced less processing than the material passing the die during the middle of each extrusion pass and therefore required a larger driving pressure.

The successive effect of work softening can be seen in Figure 8 where the extrusion pressure minimum at each mid-stroke is plotted against the number of the extrusion passes, for a milk chocolate and for a cocoa butter. The behaviour of cocoa butter is very similar to that of chocolate and both show a progressive decay in extrusion pressure with increasing number of passes and a final plateau where the extrusion pressure is essentially independent on the amount of further processing cycles. The results show that the softening is a consequence of changes in

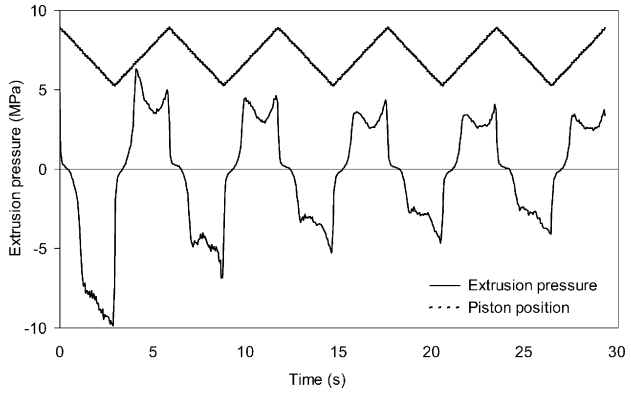

Figure 7. Piston movement and associated extrusion pressure in a sequence of extrusions without delay time ('multipass experiment'). $T = 20^{\circ}$C.

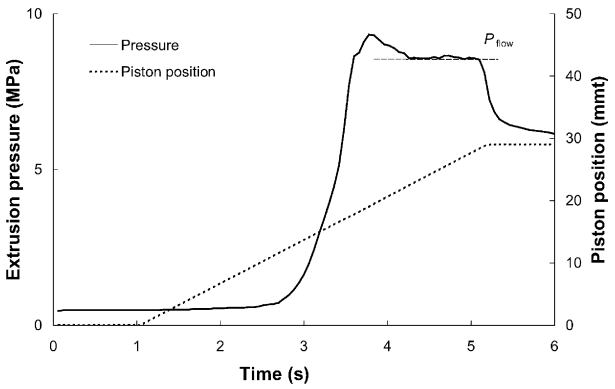

Figure 6. Evolution of differential pressure for a single extrusion pass ($T = 20^{\circ}$C).

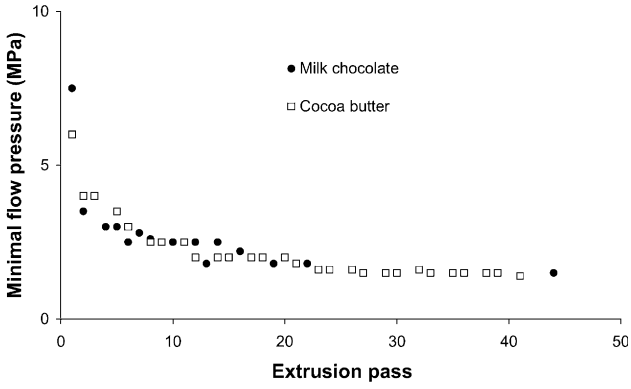

Figure 8. Evolution of differential pressures for milk chocolate and cocoa butter in a multi-pass experiment. Each point corresponds to the minimum extrusion pressure during one extrusion pass.

the triglyceride matrix of chocolate and does not involve the presence of other particles, such as the sugar, cocoa and milk particles present in chocolate.

Re-hardening

Generally, work softening of a material can be fully or partially reversible (thixotropic materials) or irreversible, depending on whether the material can return to an equilibrium state within the time scale of the observation (Barnes, 1997; Tanner, 2000). Earlier experiments on the hardening effect of cold extruded chocolate indicated that after single pass extrusion the extruded material recovers nearly all its original properties (Ovaici, 1999). In order to study any effect that re-hardening may have on processibility, a series of experiments was carried out where the time delay between each successive pass was varied. If the work softening were an irreversible effect then it would be expected that the delay time would have no influence on the observed extrusion pressure evolution.

Figure 9 shows the effect of the delay time between successive extrusions of a milk chocolate on the extrusion peak and flow pressure (taken as the minimum pressure during each pass, as seen in Figure 7) attained after two extrusions. In addition, for reference, the peak and flow pressures for a single, and the flow pressure for 10 multipass extrusions without delay time are included. Figure 10 shows a similar experiment for cocoa butter. The data shows for both chocolate and cocoa butter that if the delay time is short, the extrusion pressure does not recover, however if the delay time is of order 40 min, near complete recovery of the extrusion pressure is reached. For the case of chocolate (Figure 9) 're-hardened' chocolate with delay times $t_{\text{delay}} > 2$ min required an even higher peak pressure to initiate flow than for unprocessed chocolate, presumably due to the compaction of the chocolate during extrusion.

Both the multi-pass experiments with no time delay and the experiments with finite time delay show that the process behaviour of the semi-solid chocolate and cocoa butter is sensitive to the amount of work that has been applied and to the time between application of this work and further processing.

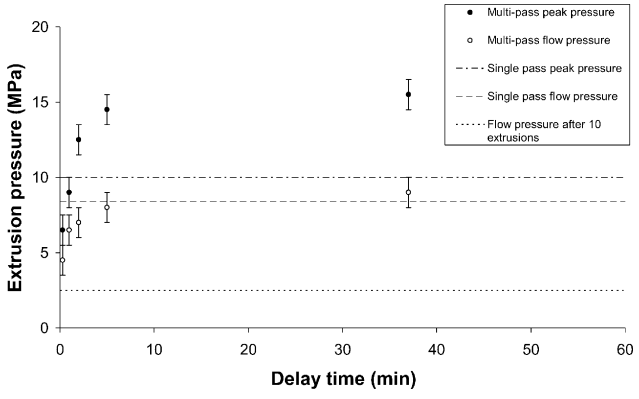

Figure 9. Magnitude of extrusion pressure (peak and flow) as a function of the delay time between extrusion passes for milk chocolate at $T = 20^{\circ}$C. Single-pass peak and flow pressures as well as multi-pass flow pressure after 10 passes also shown for reference. Piston velocity $U = 5$ mm s^{-1}, duration of piston movement $t \approx 2$ s.

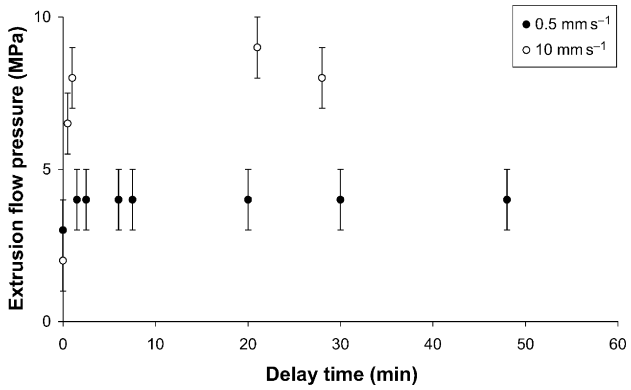

Figure 10. Magnitude of flow pressure after two extrusion passes as a function of the delay time between extrusion passes for cocoa butter at 20°C for two different piston velocities. Duration of piston movement $t = 1.5$ s ($U = 0.5$ mm s^{-1}) respectively $t = 30$ s ($U = 10$ mm s^{-1}).

Microstructure Changes: Melting and Re-crystallization

A difficulty in applying X-ray diffraction to study triglyceride crystallization in chocolate is the presence of sugar crystals as their strong diffraction peaks mask some of the characteristic diffraction peaks of the triglyceride crystals (Beckett, 2000). However, by focussing on the 'long spacings' of triglyceride crystals, where sugar crystals do not contribute to the diffraction pattern, allowed us to observe the change of triglyceride crystal content during extrusion processing and subsequent recovery period. The observed small-angle diffraction pattern shown in Figure 11 with the two strong peaks corresponding to spacings of 63, respectively 32 Å is characteristic for a crystal structure with triple-chain length stacking, such as β_2-3 or β_1-3 (also called 'Form V' respectively 'FormVI'; see Wille and Lutton, 1966; Van Malssen *et al.*, 1999). No other long spacings were observed in our experiments, indicating that no significant crystallization other triglyceride polymorphs occurred. Furthermore, in all our experiments the changes of these two peaks were proportional to each other, indicating that they corresponded to the same crystal form.

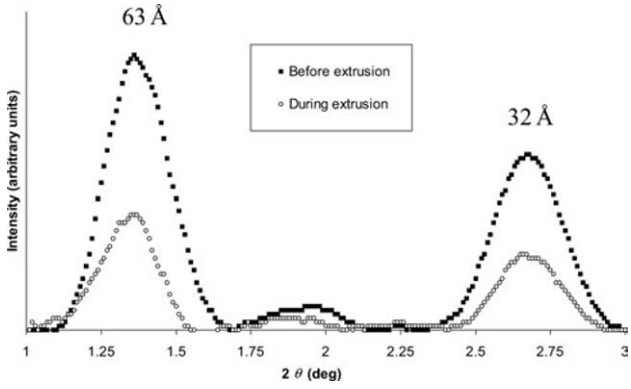

Figure 11. Small-angle X-ray diffraction from milk chocolate sample before and during a multi-pass extrusion experiment with a barrel temperature held at $T = 20^{\circ}$C. Extrusions carried out with no delay time and a piston velocity of $U = 5$ mm s^{-1}.

Figure 11 shows the diffraction profile during extrusion processing where it is seen that the intensity is diminished by approximately 50%. If we assume that the diffraction peaks correspond to a single crystal form (which is supported by the fact that their areas are proportional at any degree of intensity decrease), the integrated intensity, i.e., the area under all the peaks, should be proportional to the crystal content.

By examining the relative decrease of integrated intensity at different processing flow rates (Figure 12), it can be seen that the amount of processing-induced melting depends only weakly on the rate of processing and this result is consistent with the assumption that the amount of the processing-induced melting is a function of the work dissipated during extrusion. This in turn is proportional to the upstream extrusion pressure, which depends only weakly on the rate of extrusion.

In order to show that there is a recovery in the crystal fraction of the triglycerides after extrusion a series of X-ray data was obtained at different times after the extrusion had stopped. This data is shown in Figure 13, where the total integrated intensity of diffracted radiation recovers over a period of 40 min and correlates with the re-hardening kinetics shown in Figure 9. Matching recovery experiments were carried out with cocoa butter alone and similar, but faster, recovery kinetics were observed, where recovery took place within a period of approximately 10 min.

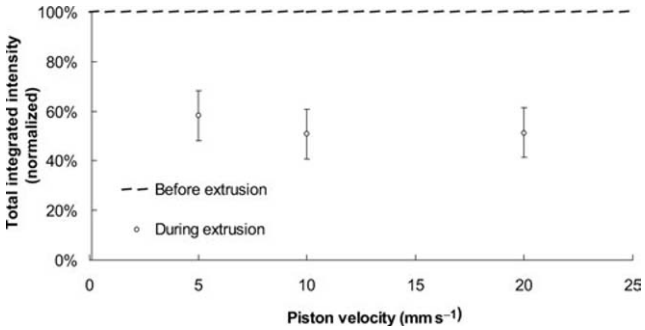

Figure 12. Total integrated intensity of diffracted X-ray radiation before and during multi-pass extrusion of milk chocolate without delay time and for different piston velocities. Barrel temperature held at $T = 20^{\circ}$C.

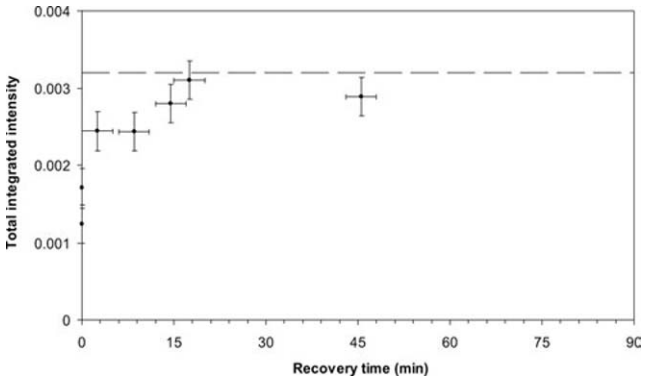

Figure 13. Integrated intensity of diffracted X-ray radiation at different times after a multi-pass extrusion experiment for milk chocolate with a barrel temperature of $T = 20^{\circ}$C. Extrusions carried out with no delay time and a piston velocity of $U = 5$ mm s^{-1}.

The X-ray results show that the crystal triglyceride fraction decreases during processing and recovers with certain kinetics after extrusion. The fact that the magnitude of the extrusion speed does not appear to affect the amount of crystal fraction lost is consistent with the concept that the increase in liquid phase depends on the amount of work done.

CONCLUSIONS

Systematic extrusion sequences using a multi-pass rheometer have shown that milk chocolate at ambient temperature is softened considerably by extrusion processing, leading to a strong decrease of the pressure required to extrude it repeatedly at the same flow rate. A few extrusion passes are sufficient to reduce the extrusion pressure (at the same flow rate and temperature) by up to an order of magnitude, depending on temperature and flow rate.

If a rest time is introduced between the extrusions, the decrease of extrusion pressure is less pronounced, suggesting that a re-hardening takes place, an observation that is consistent with earlier studies that showed re-hardening of single pass extrudates. The recovery of the original extrusion pressure with delay time indicates that microstructural reorganisation of the material occurs typically over a period of 1 h.

In situ X-ray characterization of the triglyceride matrix in milk chocolate during and after extrusion showed a processing-induced melting of triglyceride crystals which re-crystallized during the 'rest period' after an extrusion. The kinetics of the re-crystallization were similar to those of the re-hardening and therefore there is strong evidence that the melting and recrystallization of the triglycerides are responsible for the softening and re-hardening behaviour.

Finally, we have shown that cocoa butter, which consists almost entirely of triglyceride molecules shows qualitatively the same softening and re-hardening behaviour as chocolate, providing further backing for the hypothesis that the triglyceride molecules are responsible for these phenomena.

Our observations show that characterization of the cold extrusion of chocolate using a perfect plastic model with a constant plastic yield stress is insufficient to completely describe the processing behaviour. An extended model that includes the effect of work-induced phase changes and their effect on the rheological properties of chocolate and which is able to predict the local solid and liquid phase contents of the triglycerides will be presented in a separate paper.

NOMENCLATURE

P	extrusion pressure
Q	volumetric flow rate
t	time
T	temperature
U	piston velocity
x	largest dimension of chocolate granules

Greek symbols

α	die entry angle
θ	diffraction angle

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