

LITERATURE REVIEW

Crystallisation of Cocoa Butter

Dimick and Manning [1] conducted studies to determine the thermal properties and glyceride composition of cocoa butter crystals formed under static conditions. Prior to this investigation, it was reported that cocoa butter contained between four and six polymorphic states of crystallisation. The various nomenclature assigned to these states emphasises the lack of consistency between data. This research deals with the crystals formed under static conditions at temperatures near practical tempering conditions. Its major objective was to shed new understanding on the morphological, thermal and compositional characteristics of pure Ivory Coast cocoa butter crystals.

Differential scanning calorimetry (DSC) and high performance liquid chromatography (HPLC) were used to determine the thermal properties and glyceride composition. In addition visual characterisation of the crystallites was obtained with polarized light microscopy (PLM). Crystals were formed under controlled static or motionless conditions at formation temperatures of 26, 28, 30, 32 and 33°C. Preparatory techniques were developed using laminated polyethylene with plastic hoops in order to grow the crystals for isolation and visual identification by PLM prior to DSC assay. Cocoa butter was also crystallised from liquid oil directly in the DSC pans prior to thermal assay.

Thermal and morphological differences observed indicated numerous crystalline forms present at 26, 28, 30, 32 and 33°C. The three crystals formed at 26°C were designated 'temper', 'individual' and 'feather' crystal. During static crystallisation a trend grew which showed an increase in melting point as the incubation temperature was increased from 26-33°C. Apart from the 33°C incubation, in all other cases, the large feather formation was accompanied by much smaller yet distinct solitary 'spiny' crystals.

The composition of each crystal was defined to determine the role each triglyceride assumes in the crystal formation process. At each crystal formation temperature, various crystallite types grew, each with varying triglyceride composition (PLiP, POO, PLi, POP, SOO, SLiS, POS, SOS, SOA). Thermal analyses in these studies illustrated that as the formation temperature increased the melting point of crystals increased. In the higher melting crystals compositional data exhibited significant increases of SOS. It therefore generalised that the various cocoa butter triglycerides act in a manner characteristic of fractional crystallisation. The incompatibility of POP, containing four less carbons, compared to the compatibility illustrated by SOS and POS, emphasised that structurally symmetrical triglycerides like SOS will be more suited to solidify with those triglycerides that possess similar chain lengths and symmetry. It was also found that the remaining triglycerides of lesser concentration were not as compatible due to larger differences in chain length symmetry and degree of unsaturation.

Effects of Tempering and Temperature in Chocolate Manufacture

Cebula, Dilley and Smith [2] using pilot scale tempering apparatus conducted a study of the complex process of tempering in both batch and continuous systems. The main area of interest was to understand the effects major triglycerides and minor components have on the continuous tempering of chocolate. Ranges of model chocolates were achieved by controlled addition of specific glyceride components to each fat phase. Each was tested and their effects on the tempering process determined using a 3-stage tempering unit (3STU). This unit consists of a worm screw feeder and three heat exchangers each set to a different temperature. The first removes the sensible heat from the chocolate reducing the temperature from 40 to 27°C, the second a continuous cooling process allowing nucleation to continue. The final chamber is set to 29°C to melt any lower polymorphic crystals which may have formed and allow the chocolate to become a pumpable liquid. Upon exit from the final stage the tested chocolate was passed through a heat exchanger set to 45°C which melted out all crystals, thus de-seeding the chocolate ready for the next experiment. Tempering temperatures, heat exchanger characteristics and flow rates were all tested using the 3STU. The tolerance of the fat system was also examined using the final heat exchanger; by setting the temperature

either too high or too low the chocolate can be under or over tempered respectively. All samples were tested using the Greer assessment and the solid content was measured by Nuclear Magnetic Resonance (NMR). The rheology of the produced chocolates was also determined.

Results obtained for chocolates based on a range of fat systems showed that there was not a unique set of processing conditions to produce tempered chocolate. Instead a rather complex, but evidently general, relationship existed between the various temperatures and flow rates.

Three main fat types found in chocolate were investigated: POP (1, 3 di-palmitoyl 2-oleoyl glycerol), Diglycerides and Trisaturated triglycerides. As the POP level was increased there was a need to reduce the temperatures throughout the system. Tempering times were also found to increase suggesting a harsher cooling system was required. The presence of diglycerides halved the required tempering times for the batch processes, however, similar results were not found for the continuous process. The trisaturated triglycerides had little effect on the fats ability to form the correct crystal type for nucleation, although they did dramatically affect the viscosity of the material. A significant reduction in viscosity was observed with the addition of a small amount of trisaturated triglyceride.

Stapley and Fryer [3] further studied the effects of shear rate, tempering time and re-warm temperatures with pre-tempered chocolate using equipment designed to maximise uniformity of shear rate. The chocolate was melted to 50°C and held at that temperature for 5 minutes. The temperature was then lowered to 22°C at a rate of 1°C/min (i.e. a 28 minute cooling period). Once this temperature was reached the chocolate was left for a set tempering time varying from 100 to 600 seconds. The chocolate was then re-heated to a specified temperature (29-34°C) and held for a further 5 minutes. A small quantity was then removed and transferred to a Differential Scanning Calorimeter (DSC) for subsequent cooling, monitoring how the sample crystallised and concluding the type of polymorphic crystal formed.

The experiments showed two distinct groups forming corresponding to Form V crystals and a lower polymorph. Form V crystals presented a definite melting range of 28-30°C with a slightly wider range of cooling points, 16-23°C. The lower polymorph showed a melting range of 16-19°C and a cooling range of 12-13°C. The results also showed a definite transition point between tempered (mpt. 28-30°C) and untempered chocolate (mpt 16-19°C) as each of the tested parameters were varied. In the case of tempering time, it appeared that a critical period must be exceeded if tempering is to be achieved. This was found to lie between 200 and 300 seconds on average when tempering to 22°C and re-warming to 30-32°C. Experiments varying the shear rate showed a transition from tempered to untempered occurring between 26 and 35 s⁻¹. This indicated there is a critical shear rate that must be exceeded for seed crystals to be produced, thus demonstrating the importance of shear on the tempering process. The re-warming process was simply conducted to melt all lower polymorphic forms leaving only Form V, thus subsequent cooling will result in the production of Form V chocolate. Obviously if the re-warming temperature is too high Form V crystals may also be melted, this was found to occur between 33 and 33.5°C. It was also found that re-warming to a temperature just below 33°C reduced subsequent crystallisation, due to a small number of small Form V crystals remaining.

Loisel, Keller, Lecq, Launay and Ollivon [4] conducted studies detailing the crystallisation of dark chocolate during different tempering processes in a lab scale Scraped Surface Heat Exchanger. The aim of this research was to study the nucleation of cocoa butter during the course of chocolate tempering. This was achieved by directly monitoring, in a heat exchanger, the equivalent viscosity of chocolate during its tempering process at a laboratory scale. The linear relationship between torque and viscosity made possible the control of chocolate crystallisation during tempering by following torque variations versus time and converting to equivalent viscosity values. These variations of equivalent viscosity of chocolate observed during tempering were correlated with temper-meter measurements which had been related to the content of cocoa butter seeding crystals and thus determining the amount of nuclei formed.

A temperature cycle enabled preparation of a well-tempered chocolate stable for ≥ 30 minutes at that temperature. The perfect temperature control of the jacket ($\pm 0.5^\circ\text{C}$) yielded reproducible measurements of torque which were very sensitive to nuclei. The seed growth of cocoa butter of chocolate was quantified as a function of time and temperature from 26.1°C to 32.9°C. This well-tempered chocolate was

characterized by a seed crystals content of $\approx 1.15 \pm 0.1\%$ of cocoa butter, crystallisation of $23.9 \pm 0.2^\circ\text{C}$ in the temper meter and an equivalent viscosity of 3.0 ± 0.4 Pas. It was discovered that the lower the temperature, the faster the crystal growth. A null growth was observed at 32.9°C while above this temperature, the slow viscosity decrease indicated a progressive melting of seeds. It was also found that although very high viscosities could be measured, when chocolate was over-tempered (many seed crystals) the equivalent viscosity of a well tempered chocolate was close to that of an under cooled sample. In general, the optimization of the classical tempering process, using a temper-meter, has shown that it is essential to associate the slope and temperature measured at the inflection on a cooling curve to fully characterize chocolate seeding.

Moulding of Chocolate

The moulding of chocolate is technically challenging as it is difficult to achieve the required Form V crystals by simple cooling of chocolate. If the cooling rate is excessive other polymorphs can nucleate and grow during moulding. Tewkesbury, Stapley and Fryer [5], developed a computational model to predict the temperature in the mould as a function of space and time. The aim of developing this mathematical model was to make the process of chocolate manufacture less empirical. The model uses enthalpy-temperature data obtained over a range of cooling rates. This study was further validated using thermocouple data taken from a model mould during air cooling over commercially relevant conditions ©2000 Published by Elsevier Science Ltd.

Experimental work was carried out to obtain temperature data to validate the mathematical model. Temperature control is crucial to the moulding process and this work was intended to study the spatial and temporal variation of temperature in chocolate moulds. The experiments used tempered, untempered chocolate and paraffin wax. Paraffin wax, which does not exhibit a phase change, was used both as an initial validation of the model and to identify appropriate surface heat transfer coefficients.

It was discovered that crystallisation caused a significant reduction in the cooling rate resulting in the evolution of latent heat. However, the major problem in modelling the cooling in crystallising systems occurs in predicting this latent heat production. The study confirmed previous work that the effective specific heat of chocolate is a strong function of cooling rate and process history. This was achieved using both tempered and untempered chocolate, where different cooling behaviour was observed.

Simulations which used a specific heat data set for a single cooling rate alone failed to predict the temperature at which crystallisation occurred. However, alteration of the program (allowing specific heat data for chocolate to be calculated as a function of both temperature and cooling rate) fitted experimentally measured mould temperatures well within a cooling rate range of $0.5\text{-}2^\circ\text{C}/\text{min}$. It was concluded that overall this study showed that it is possible to develop a mathematical model that can accurately represent the behaviour of chocolate and fillings in commercial manufacture. In the absence of kinetic description of the crystallisation process, this assumption that the thermal effects can be predicted using effective specific heat capacity data as a function of temperature and cooling rate is an acceptable engineering approximation over the range of cooling rates of commercial concern.

The Effect of Milk Fat in Chocolate Manufacture

The rheological behaviour of plastic fats is governed by interactions between fat crystals in an aggregated three dimensional solid liquid matrix. The liquid portion of the fat, interspersed throughout the aggregated fat network, serves as a continuous phase and, in conjunction with the solid fraction, is responsible for viscoelastic behaviour. The primary factor of importance concerning rheological behaviour is the amount of crystalline fat and the type of crystals present in the fat crystal network. Rheological measurements of fats can be performed at low temperatures or high deformation. In the latter, the fat crystal undergoes irreversible deformation, whereas in the former, viscoelasticity is measured below the yield point and any permanent strain remains upon complete release of stress. Materials can be linear elastic, elastoplastic, or nonlinear elastic. Linear elastic materials show a straight line through the origin of a stress versus strain curve. Elastoplastic materials show straight lines until the yield point is reached, and then permanent

deformation occurs with higher stress. Nonlinear elastic materials do not show linear behaviour in any range of stress.

Herrera and Hartel [6] studied the effect of processing conditions on the rheological behaviour of three blends of 30, 40 and 50% of high-melting fraction in low-melting fraction of milk fat. These different blends were examined by dynamic mechanical analysis (DMA) after crystallising at different temperatures, different agitation and cooling rates, as well as studying the effects of storage time on the rheological properties. Compression tests were performed on samples using frequency values within the linear viscoelastic range (1-10 Hz). It was discovered that, on average, loss modulus was 10 times lower than elastic modulus and generally was unaffected by processing conditions. The samples, however, showed a more solid-like behaviour, better described by storage modulus. For all processing conditions used in the study, it was discovered that storage modulus varied at every variable. Different rheological properties were found, even for the same solid fat content. Even though solid fat contents of samples remained the same when measured after 24 hr at 10°C, storage and complex modulus increased with temperature of crystallisation (25°C to 30°C). For samples crystallised at slower cooling rates, moduli were higher, agitation rate decreased and were found to be lower for the 30-70% blend at all processing conditions used. It was also observed that storage moduli increased with storage time. The shear storage modulus calculated using the DMA experimental data in this study, agreed with the values found in literature for butter systems. The reported softening effect for working of butter was also in agreement with the fractional dimensions calculated for these systems, showing a significant decrease as agitation rate increased.

In general, milk fats delay the onset of crystallisation and lower the melting point of the polymorphic forms of cocoa butter. Chocolates containing higher concentrations of milk fat require lower temperatures and longer times during tempering. As well as being less costly than cocoa butter it has also been reported that the incorporation of the high melting fraction of milk fat into chocolate reduces fat bloom. Experimental work by Barna et al observed distinct differences in the tempering profiles for chocolates containing different levels of solvent-fractionated milk fat. It was also reported that chocolates containing high melting fractions (HMF) at 20% and middle melting fractions (MMF) and low melting fractions (LMF) at 30% replacement levels of cocoa butter were untemperable.

Similar studies were also carried out by Reddy, Full, Dimick and Ziegler [7] to determine the tempering procedures for milk chocolate formulated with anhydrous milk fat (AMF) and its fractions as replacements of cocoa butter at different concentrations. Chocolates containing AMF or its fractions of up to 20% (total fat basis) were tempered after a conventional thermocycling tempering process (50°C/30min, 27.7°C/4min, 31°C/2min) to obtain good products with good contraction and mould release properties. For formulations that did not temper by conventional methods resulting in poor contraction and mould release, a new tempering profile was developed. Lower crystallisation temperatures and/or longer holding times were required at concentrations of AMF, MMF, LMF above 20%. Chocolate which contained HMF required slightly higher crystallisation temperatures due to high viscosity. Those chocolates which contained up to 35% HMF and up to 40% of the total weight of fat in the chocolate of AMF, MMF and LMF were successfully tempered by adjusting crystallisation time and temperature. These results confirmed that milk fat delays the onset of crystallisation, lowers the melting point of cocoa butter and that chocolate containing milk fat requires lower temperatures and longer times for tempering.

Metin and Hartel [8] further studied the effect of milk fat on chocolate manufacture by evaluation of isothermal crystallisation kinetics of binary fat blends of cocoa butter with milk fat and milk fat fractions by applying the Avrami equation. Isothermal Avrami kinetics is concerned with the overall crystallisation process, including nucleation and growth. The equation is as follows, where X is the fraction of crystal transformed at time t during crystallisation, k is the crystallisation rate constant, which depends on crystallisation temperature, and n, the Avrami exponent, is a constant relating to the dimensionality of the transformation.

$$(1 - X) = e^{-kt^n}$$

It has been shown that heat is released or absorbed during crystallisation transformation, therefore a DSC was used to monitor transformation and the Avrami equation applied. Three classes of milk fat fractions were tested, classified by their melting points (very high, high and low). The following temperature protocol was used: hold at 80°C for 5 minutes, cool to 50°C at a rate of 100°C/min, hold for 3 minutes, cool at 100°C/min to crystallisation temperature of 15, 20 and 25°C and hold for 3 hours. After 3 hours the samples were then re-heated to 80°C at a rate of 20°C/min and the melting points recorded. The recorded isothermal DSC data was used to calculate the Avrami constants. Crystal fractions as a function of time were calculated by integration of the DSC crystallisation curves and an average X found for each tested condition. The crystalline structure and thus polymorphic form of each sample was determined using an X-ray diffractometer (XRD) after 3 hours of solidification.

Results showed a good fit to the Avrami equation, and plots versus time proved both n and k values. n values of 4 would suggest spherical crystal development with a constant nucleation rate independent of time. The original milk fat produced an n of 3, suggesting spherulitic growth, but from instantaneous nuclei. Tests involving very high melting point milk fractions produced an n value of 2 possibly indicating plate-like growth, with an initially rapid growth, which depletes with time. These suggested that differences in chemical composition of fats may lead to different crystallisation mechanisms. It was also found that the melting points corresponded to the suggested n values, in general the melting point increased as the n value decreased.

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