The Effects of Shear and Temperature History on the Crystallization of Chocolate

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ABSTRACT: Experiments have been carried out on the tempering of chocolate using a temperature-controlled shearing rig with a concentric cylinder geometry. This design maximizes uniformity of shear rate during tempering in contrast to most tempering devices where shear is often concentrated in a small part of the chocolate mass. Samples were subsequently cooled in a differential scanning calorimeter (DSC) to monitor how the sample crystallized, and then reheated to gain further information on the melting points of the polymorphs formed. The results can be interpreted using established theories on the crystallization mechanism. It was found that at least two polymorphic forms could be generated. The higher melting form predominated provided the shear rate was high enough, the temper time long enough, the rewarm temperature low enough, and the DSC scan rate slow enough. For parameters affecting the nucleation stage (temper time and shear rate), it was found that the transition was a sharp one, reflecting the notion that seed crystals need to grow past a threshold point in order to be stably formed. Raising the rewarm temperature had the effect of destroying seed nuclei, but this was a more gradual process. The bimodal nature observed of the melting points compared to the more spread-out behavior of crystallization temperatures reflects the kinetic constraints found in crystallization which are not found on melting.

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In many processed foods the product food structure depends not only on the ingredient formulation but also on the processing history of the material. This is particularly true for chocolate molding during which the fat component (cocoa butter for dark chocolate and cocoa butter and milk fat for milk chocolate) solidifies. The cocoa butter forms crystals but these can be in a number of different "polymorphic" forms (1). At least five (and possibly six) independent polymorphic forms are known to exist. Those with the lower melting points are formed most readily but are thermodynamically the least stable (2). The polymorph known as Form V has long been accepted as the optimal form for commercial chocolate manufacture, in that its melting range (which for milk chocolate lies between 20 and 30°C) is high enough for chocolate to be hard at room temperature, but also low enough that the product can melt in the mouth. The form also exhibits good demolding properties (3).

Unfortunately, Form V does not form in bulk by simple cooling of chocolate. A small quantity of seed crystals of the polymorph form needs to be present so the remaining fats can solidify around it. This can be achieved by adding pre-made seed crystals to the mixture, but most current large-scale chocolate production involves subjecting the chocolate to tempering. During tempering the chocolate is subject to a well-controlled temperature program under the action of shear. Proper tempering is a vital part of successful chocolate manufacture as it determines the quantity and size distribution of seed crystals of each polymorphic form—the initial conditions for the crystallization that occurs in the molding step (1).

A number of industrial chocolate tempering processes have been recently reviewed by Nelson (4) and Jovanovic *et al.* (5) who also summarized much of the background science behind tempering.

The essential features of the tempering cycle are as follows: (i) Melted chocolate arrives from the conching stage at about 40–50°C. At this point there is very little (possibly no) crystalline material in the chocolate; (ii) the chocolate is cooled to a holding temperature where it is held for about a minute. During this stage some crystallization occurs; (iii) the chocolate is warmed and this melts out some of the more unstable forms, leaving predominantly Form V; (iv) the chocolate is then ready to be deposited in molds where it is cooled.

A number of tempering studies have recently been published. Cebula *et al.* (6) used a commercial three-stage temperer to assess the impact of different triglyceride and diglyceride compositions on tempering. Increasing the concentration of POP (1,3-dipalmitoyl-2-oleo glycerol) requires either lower temperatures or longer temper times to maintain the same level of temper, and the presence of diglycerides retards the formation of stable nuclei. Yella Reddy *et al.* (7) used a tempering kettle to examine the effects of adding milk fat fractions. These are found to lower the temper temperature and/or increase the temper time required for tempering. Loisel *et al.* (8) used a scraped surface heat exchanger (SSHE) to temper chocolate. Using torque readings from the

SSHE, an "equivalent viscosity value" was estimated using a calibration from a Newtonian liquid (silicone oil). The equivalent viscosity value was used to monitor the tempering process in real time; it was found that an induction period occurred before viscosity dramatically increased as a result of the creation of seed crystals. Using this method and a Grant temper meter, the optimal process was proposed involving holding at 26°C, before heating to 30.5 and then 33.3°C. Bolliger *et al.* (9) compared the tempering performance of a conventional temperer (Aasted temper AMT 250) and a high-shear crystallizer. It was found that tempering could be achieved using a much shorter residence time with the high shear crystallizer.

Control of temperature and the thermal history is a vital component to tempering, but it is also apparent that shear is an important factor in the tempering process. It is not clear why shear is so important. A number of possible reasons can be hypothesized: (i) Shear breaks up crystallites, which creates a greater number of seed crystals (lengthscale of microns). This is a form of secondary nucleation (2); (ii) shear aligns triglyceride molecules parallel to each other in the shear field, and then moves them past each other. This would make nucleation events more likely; and (iii) better overall mixing.

Although the shear environments in the above papers are reproducible, the shear fields are not uniform and shear rates cannot be accurately quantified. We have thus designed a small tempering device of a similar construction to a concentric cylinder viscometer to enable better control of shear within the chocolate. Temperature control is achieved using a water jacket around the outer cup attached to a programmable water bath. The shear rate is varied by a variable power supply to the motor.

It is important to understand and describe (i) the state of the chocolate after the tempering stage and how tempering conditions affect this, and then (ii) how this state affects the molding process when chocolate is cooled in the mold and crystallization occurs. The chocolate solidification stage can be probed by differential scanning calorimetry (DSC). This monitors the heat required to heat or cool the sample at a specified rate relative to a reference pan, and can be used to measure specific heat capacities and information on enthalpic events such as crystallization and melting. In this work DSC was used to probe the thermal events occurring as chocolate is cooled from 30 to −10°C and then rewarmed by scanning back up to 50°C. Effective specific heat capacity curves can be obtained (see Materials and Methods section) which include a latent heat component if a phase change is taking place. Crystallization is a kinetic process which is governed by crystal nucleation and growth. A sizable temperature driving force for crystallization is required, and thus crystallization occurs a few degrees below the melting point of the sample. For properly tempered chocolate, growth occurs around the Form V seed crystals. For untempered chocolate lower polymorphs nucleate instead and grow. Melting is less kinetically constrained and so the reheating scan gives better information about the melting point profile of the solidified sample, assuming no interpolymorphic transitions occur during reheating (10).

In a different series of experiments, a "model" tempering regime was chosen and a number of samples were run through DSC at various scan rates. These were compared to the results of similar scans performed on (i) untempered chocolate and (ii) chocolate tempered in a pilot plant scale temperer. The aim is to assess how tempering parameters affect the crystallization process as measured by DSC, and then to interpret this by considering the underlying science of the crystallization mechanism.

MATERIALS AND METHODS

Tempering apparatus. A schematic of the apparatus is shown in Figure 1. The basic geometry is similar to a concentric cylinder viscometer. The inner bob (diameter 54 mm) is of aluminum construction and is hollow to minimize the thermal mass and thermal lag of the system. The inner bob is connected by a shaft and gearbox to a DC motor. The inner bob rotates about a locating pin centered at the bottom of the outer cup (i.d. 60 mm, height 100 mm) which is made of stainless steel and incorporates a water jacket. The gap width is thus 3
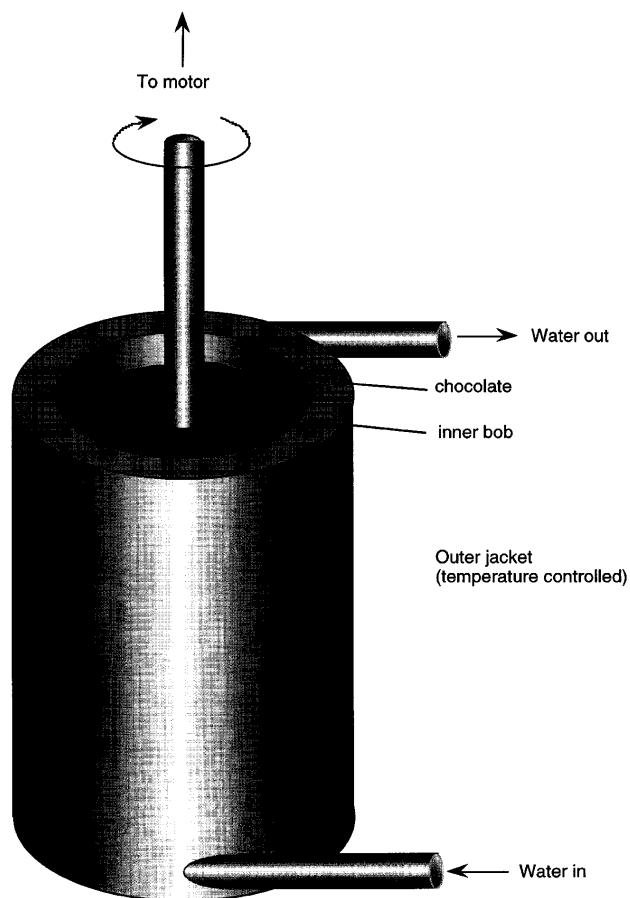

FIG. 1. Diagram of the concentric cylinder shearing apparatus used to temper chocolate.

mm. Water is supplied along lagged plastic tubing (length 1m) from a Haake DC5 water bath with a Haake K20 cooling unit. The temperature in the water bath was controlled using Haake Thermpro software *via* a PC. The time constant for the thermal response of chocolate in the annulus of the rig to changes in water bath temperature was of the order of 1 min. For all experiments an average shear rate for the chocolate was calculated by dividing the velocity of the outside of the bob by the gap width. In practice, there will be a slight variation in local shear rate across the annulus due to geometry (10% for a Newtonian fluid), and (more importantly) the non-Newtonian nature of the chocolate may lead to different zones of flow. From visual observations this appears to only become significant after solidification has begun to occur, and thus is not critical to the initiation of the nucleation process.

Tempering method. Approximately 70 g of a Cadbury Dairy Milk chocolate bar, were melted in the empty cup at 50°C, and the inner bob was gradually lowered. Once the chocolate had fully melted and the inner bob been correctly positioned, the motor was switched on, and the motor speed adjusted to the prescribed rotational speed. The shaft speed was calculated by measuring the time taken to achieve a prescribed number of revolutions (over a period of roughly 1 min). The motor power was left untouched over the duration of the shearing regime. The temperature program was then initiated, following the pattern shown in Figure 2(a), i.e.: (i) hold at 50°C for 5 minutes; (ii) cool at 1°C/min to the temper temperature (22°C in all cases), this was found to give tempering over a reasonable time-scale; (iii) hold at that temperature for a particular temper time; (iv) reheat to a rewarm temperature at 4°C/min; (v) hold at the rewarm temperature for 5 minutes; transfer to the DSC (over the course of 5 minutes, having weighed the DSC sample).

The tempering conditions were varied by individually altering the tempering time, the final melt temperature and the shear rate. Experiments were conducted in an air-conditioned environment. Towards the end of the shearing program the air temperature of the lab was raised to between 27 and 29°C, to minimize crystallization in the sample that occurred while transferring to the DSC.

DSC scanning procedure. At the end of the tempering regime, the inner bob was raised out of the rig. A small quantity of chocolate was removed from halfway up the side of the bob using a metal microspatula. The chocolate was then weighed into 50 µL aluminum pans and then sealed. The capsules were inserted into a PC-driven Perkin-Elmer DSC-7 differential scanning calorimeter, with an empty pan serving as the reference. For all scans, ~ 3 min was allowed between insertion of the sample and the start of the scan, for thermal equilibrium to be established at the start temperature. This procedure was found to maximize scan reproducibility. The samples then followed the program shown in Figure 2(b), which involves a cooling (crystallization) step followed by a rewarming (melting) step. The steps were separated by a one min isothermal period, which enables the isothermal heat flows to be assessed, and provide a baseline for the data. The only DSC parameter that was
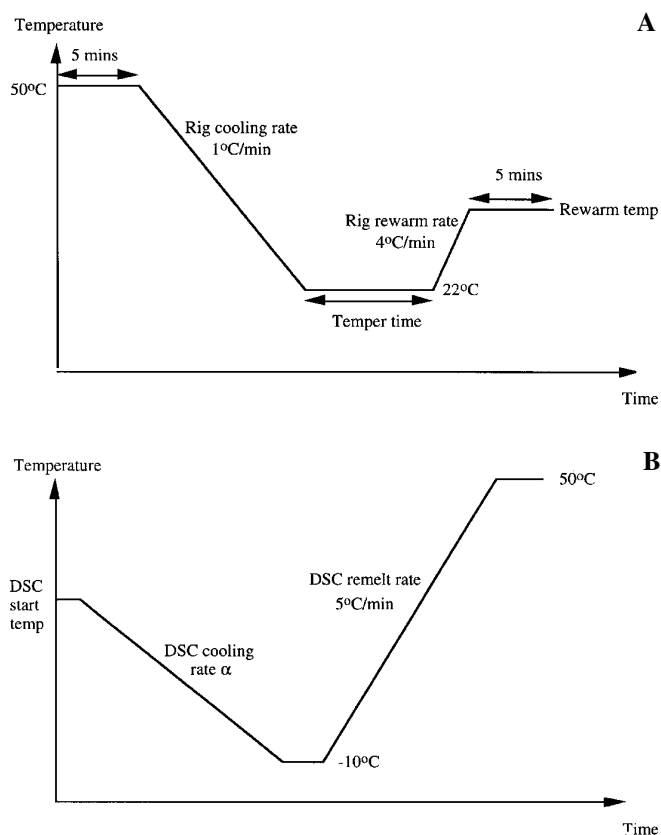

FIG. 2. (A) Temperature history used in the shearing apparatus to temper chocolate; (B) temperature history used in the differential scanning calorimeter (DSC).

varied in the experiments was the cooling rate, but unless otherwise specified this was kept to 2°C/min. All remelt experiments were conducted at a scan rate of 5°C/min; the legend on the remelt plots refers to the prior cooling rate. The resulting traces (differential power vs. program temperature) for both cooling and melting steps were recorded to disc. Data were analyzed using the "Kaleidagraph" computer software package, on data downloaded in text format from the Perkin-Elmer software package. All data are presented as the effective specific heat capacity of the material calculated using Equation 1. This takes explicit account of the differences in scanning rate and sample mass to produce normalized results (11);

$$c_p = \frac{W}{\alpha \cdot m} \qquad [1]$$

where c_p = effective specific heat capacity (J/g·K), W = power supplied to sample relative to reference pan (W), α = scanning rate (K/s), m = sample mass (g).

Calibration of the DSC data. The DSC was calibrated for temperature and power readings on a 2-mon basis, by scanning aluminum pans containing indium and then zinc. A scan using a fresh sample of *p*-nitrotoluene (mp 51.3°C) was also performed as a daily check.

Experiments performed. Experiments were performed as above using a base case of an average shear rate of 53 s^{-1},

temper time of 400 or 600 s, DSC scan rate of 2°C/min, and a rewarm temperature of 30 or 32°C. The following parameters were varied (holding all others constant) to assess their effect on the resulting DSC curves: varying rewarm temperature (temper time 600 s) from 29.5 to 34.0°C; varying temper time (rewarm at 30 and 32°C) from 0 to 600 s; varying shear rate (temper time 400 s) from 0 to 53 s^{-1}; varying scan rate (temper time 400 s) from 0.2 to 3°C/min.

For comparison, scans were also made (at various scanning rates) of untempered chocolate (0.1 to 10°C/min) and chocolate that had been tempered in a pilot scale tempering plant (0.1 to 10°C/min).

RESULTS

Untempered chocolate. DSC scans for crystallizing untempered chocolate (melted at 50°C) are shown for various scan rates in Figure 3A. In all cases a single peak predominates, the temperature of which varies slightly with scan rate—from 15.4°C for 0.1°C/min to 11.6°C for 10°C/min. Three other peaks are also discernible but are very minor: (i) at about 20–22°C; (ii) a shoulder to the main peak and in some instances a slight peak at 15°C, and (iii) at just below 0°C.

The subsequent melting profiles are shown on Figure 3B. The peak temperatures are higher than for crystallization by 5–6°C. This is to be expected as melting will take place near the thermodynamic melting point(s), whereas crystallization requires some degree of supercooling. Scans from samples cooled at higher cooling rates show multiple subpeaks which suggest that the resultant crystals have a variety of sizes, compositions, and/or polymorphic forms. Peak temperatures of samples cooled at 0.1 and 0.2°C/min are noticeably higher from samples cooled at higher rates. The melting range of the sample cooled at 0.1°C/min is also the narrowest. These observations all support the idea that crystallization is more uniform at lower cooling rates, reflecting the fact that conditions are closest to equilibrium.

Pilot plant tempered chocolate. Pilot plant tempered chocolate is designed to yield higher melting polymorphs than untempered chocolate when cooled. This is reflected in the cooling curves for pilot plant tempered chocolate (Fig. 4A). It is immediately apparent that peak temperatures are higher than for the untempered samples (from 24.7°C for samples previously cooled at 0.1°C/min to 11.3°C at 10°C/min). Pilot plant tempered chocolate also showed a greater variation of cooling peak temperature with scan rate. This suggests that crystal growth is a slower process for tempered chocolate than untempered, as processes that take time to occur will be more affected by changes in cooling rate. At the highest cooling rates the peak for tempered chocolate is very similar to that of the untempered material. Thus at higher cooling rates, the more unstable polymorphic forms are seen to form. What is observed is a result of a competition between the slow growth of high stability polymorphs and the rapid nucleation and growth of lower stability polymorphs (2). The higher stability polymorph can form at a higher temperature
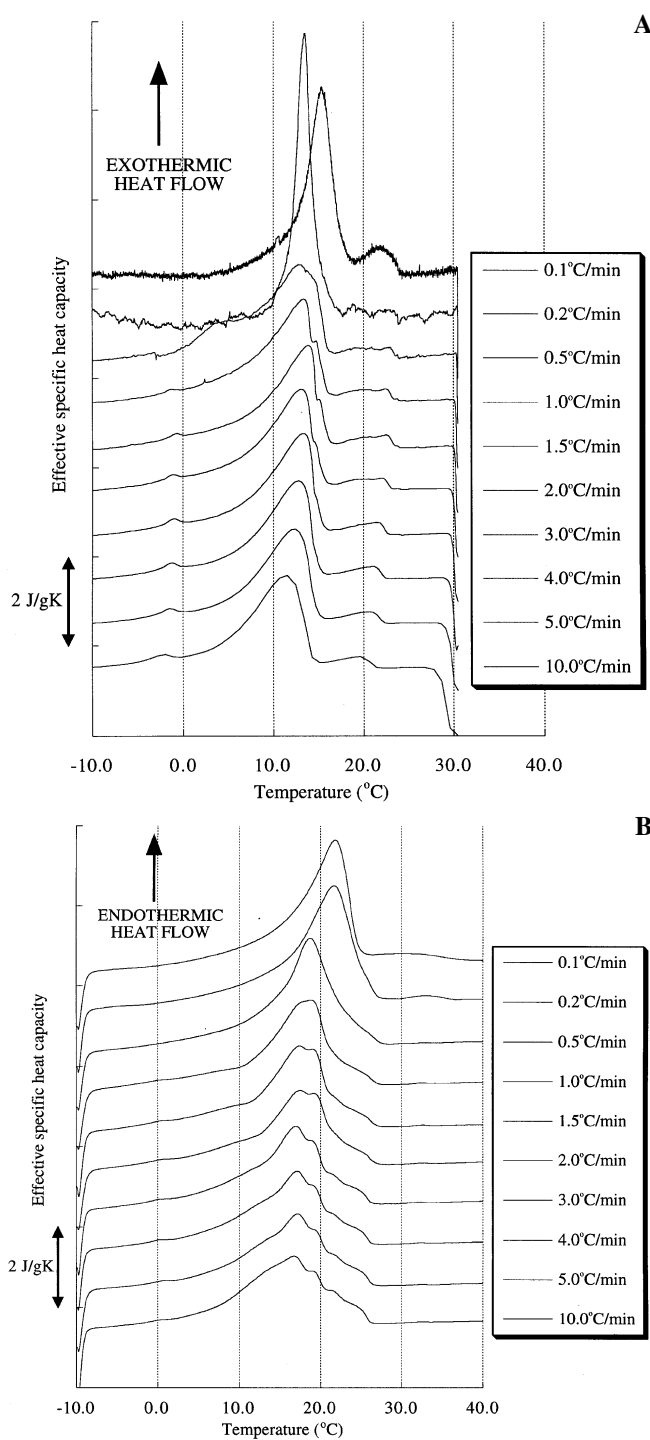

FIG. 3. (A) DSC cooling curves of untempered chocolate (melted at 50°C) at a variety of scan rates. (B) Subsequent DSC remelting curves (at 5°C/min) of untempered chocolate. The legend refers to the DSC cooling rate prior to remelting. For abbreviation see Figure 2.

than the lower stability polymorph as it possesses a higher melting point, and seed crystals are already present. However, the kinetics of formation of the lower polymorph are much faster once it has reached sufficient supercooling for nucleation to occur. This is evidenced by the greater variation of peak temperature with scan rate for tempered compared to un-
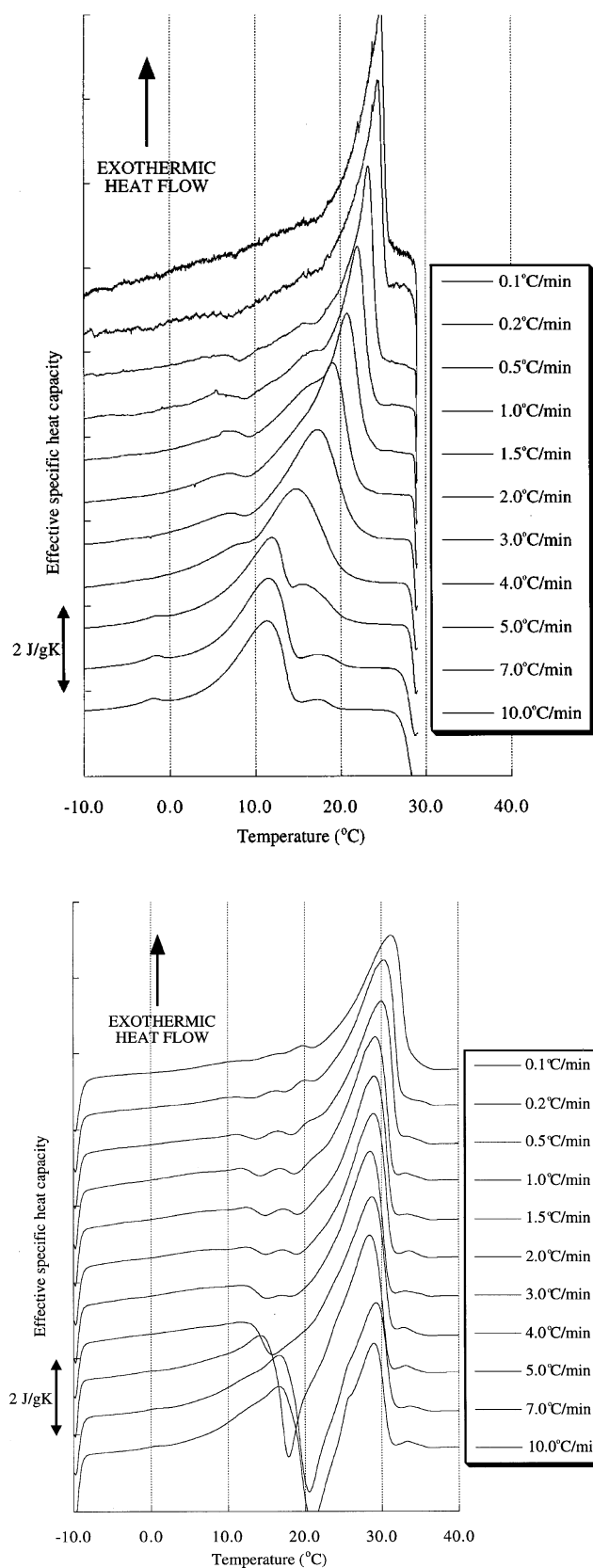
A

B

FIG. 4. (A) DSC cooling curves of pilot plant tempered chocolate at a variety of scan rates. (B) Subsequent DSC remelting curves (at 5°C/min) of pilot plant tempered chocolate. The legend refers to the DSC cooling rate prior to remelting. For abbreviation see Figure 2.

tempered chocolate. Hence at low cooling rates there is more time to crystallize material into the higher polymorph and thus the lower polymorph does not start to nucleate and grow. Scans at a slower cooling rate were also observed to be narrower and sharper, and at a much higher temperature, as time has been allowed for more uniform crystal growth. The melt curves (Fig. 4B) show little dependence of peak temperature with the cooling scan rate (29–31°C), reflecting the more thermodynamically controlled nature of the melting process. For samples that had been previously cooled above 4°C/min in the DSC, however, the melting curves show an trough at *circa* 18–20°C. Some points even show the DSC is recording a negative apparent specific heat capacity, i.e., heat evolution. This is most likely due to a lower polymorph melting and then recrystallizing into a more stable, higher form.

Effect of process variables: rewarm temperature. The peak temperatures for crystallization curves for chocolate are highly sensitive to the rewarm temperature. Figure 5A shows the main peak temperature gradually varying from 13°C at 34°C rewarm to 23°C for a 30°C rewarm. The majority of scans show evidence of at least one subpeak in addition to the main peak. The melt profiles (Fig. 5B) show two distinct melting peaks—29°C for rewarms up to 33°C and 16.5°C for the others, although 33.5°C showed a small peak at 29°C too. At lower rewarm temperatures a further peak is apparent at 33°C which will correspond to either Form V or VI.

The effect of rewarm temperature is to melt away some of the crystals formed during crystallization (at the tempering temperature). The rewarm temperature will affect the number and possibly also the size of seed crystals remaining at the end of temper. This is critical to the subsequent molding stage as it both affects the viscosity of the chocolate when depositing, and determines the number density of crystals in the final product. The fewer seed crystals there are, the slower crystallization will be, and this is evidenced by the lower crystallization temperatures found at higher rewarm temperatures (Fig. 5A). By a rewarm temperature of 34°C all of the seed crystals appear to have been destroyed, rendering the sample effectively untempered. The peak temperatures on the crystallization and remelt curves are similar to the untempered material in Figures 3A and 3B. Rewarming at 29.5°C appears to promote the formation of the higher melting forms. Any Form VI created would be undesirable as it has an unsatisfactory mouthfeel.

Effect of process variables: temper time. A first set of experiments were carried out at a rewarm temperature of 30°C, for which temper times were varied between 0 and 600 s. Different crystallization behavior was observed depending on the temper time used. Temper times up to 200 s resulted in crystallization peak temperatures of 13°C, whereas during times above 300 s, peak temperatures of 21–23°C were recorded (Fig. 6A). This was reflected in the melting curves, Figure 6B, which showed peak temperatures of 18°C for temper times up to 200 s and 29°C for temper times above 300 s, although holding at 200 s also caused a significant peak at 29°C.
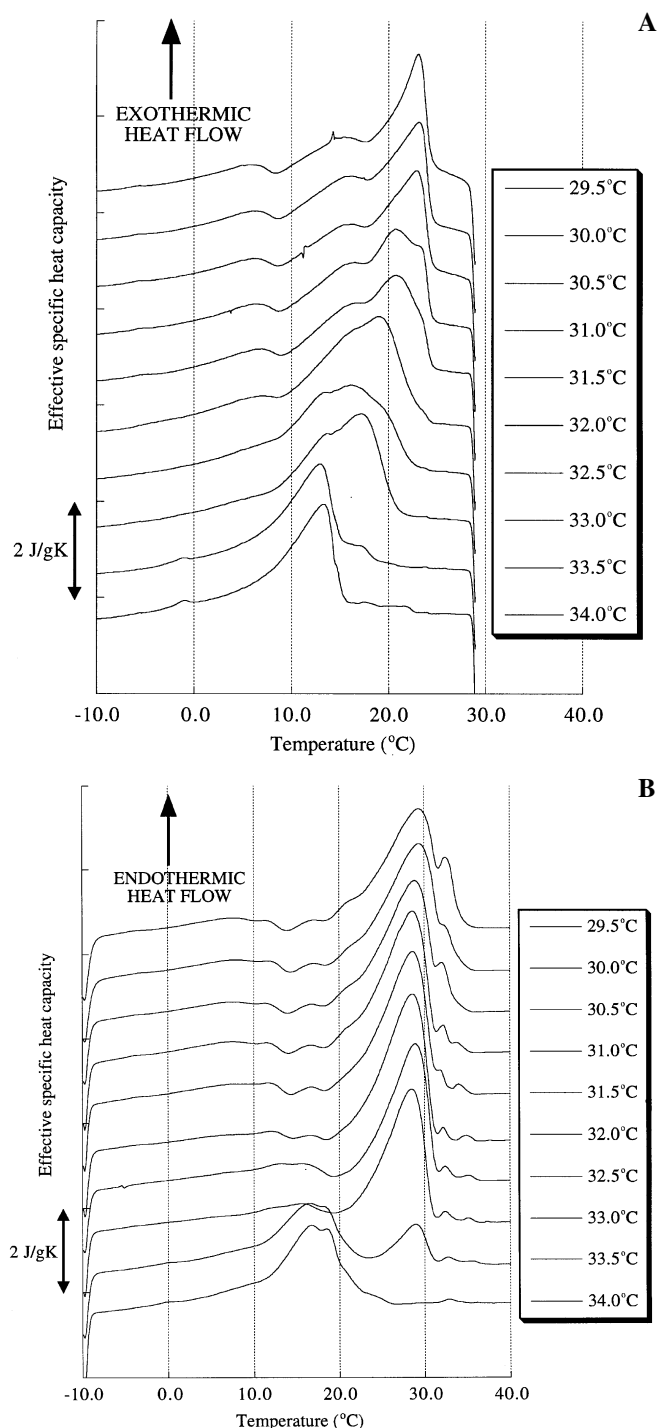
FIG. 5. (A) DSC cooling curves (at 2°C/min) of chocolate after processing at an average shear rate of 53 s^{-1}, holding at 22°C for 600 s, and then warming to a variety of final hold temperatures. (B) Subsequent DSC remelting curves (at 5°C/min). The legend refers to the final hold temperatures of the tempering process. For abbreviation see Figure 2.

Similar behavior was observed when a rewarm temperature of 32°C was used (Fig. 7A,B). The only major difference was that a temper time of 200 s gave no peak at 29°C on the remelt. Thus it is apparent that under the shear rate (53 s^{-1}) and temperature (22°C) used, a period of between 200 and 300 s must pass before seed crystals are stably formed. Below
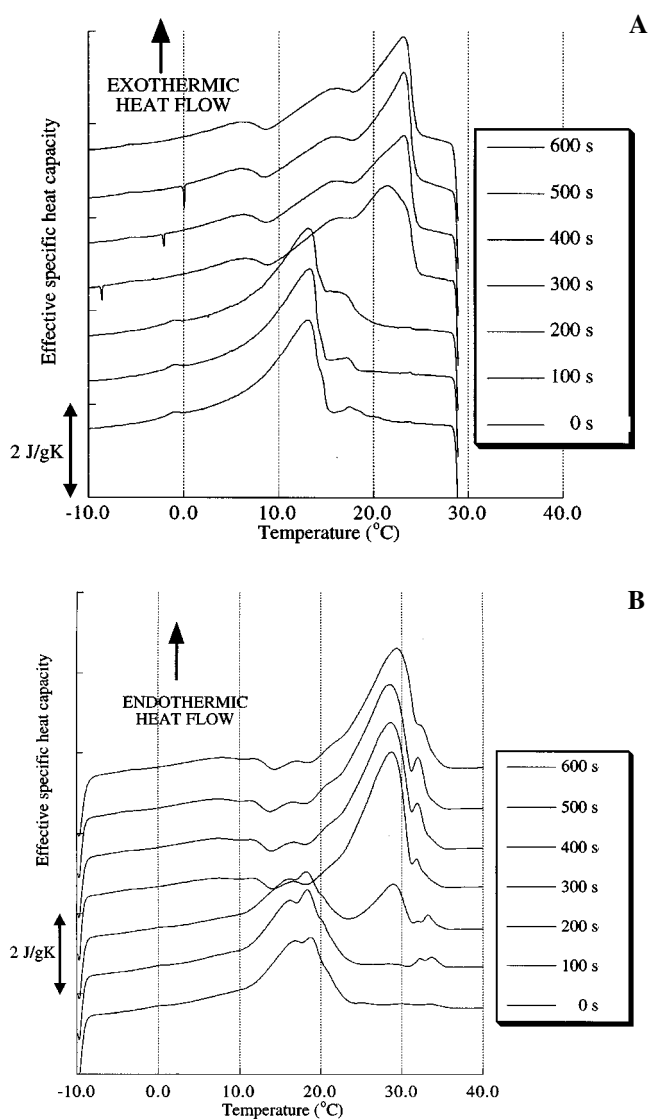

FIG. 6. (A) DSC cooling curves (at 2°C/min) of chocolate after processing at an average shear rate of 53 s^{-1}, holding at 22°C for a range of times, and warming to 30°C. (B) Subsequent DSC remelting curves (at 5°C/min). The legend refers to the holding time at 22°C. For abbreviation see Figure 2.

this time, low temperature peaks are seen characteristic of those from untempered chocolate shown in Figures 3A and B. Unlike changing the rewarm temperature, which has a gradual effect on the DSC cooling curves by gradually destroying seed crystal, changing the temper time has a more sudden effect. This fits with what is commonly observed in crystallizing systems—that the observed nucleation of stable seeds only occurs after a well-defined induction time has passed (2,12). The evidence also suggests that it is not necessary to continue tempering beyond this point, as it will not have a significant effect.

Effect of process variables: shear. The previous sections have demonstrated the effect of temperature and time on the tempering process. It is known that shear is important, but previous work has been unable to study it quantitatively. Figure 8A
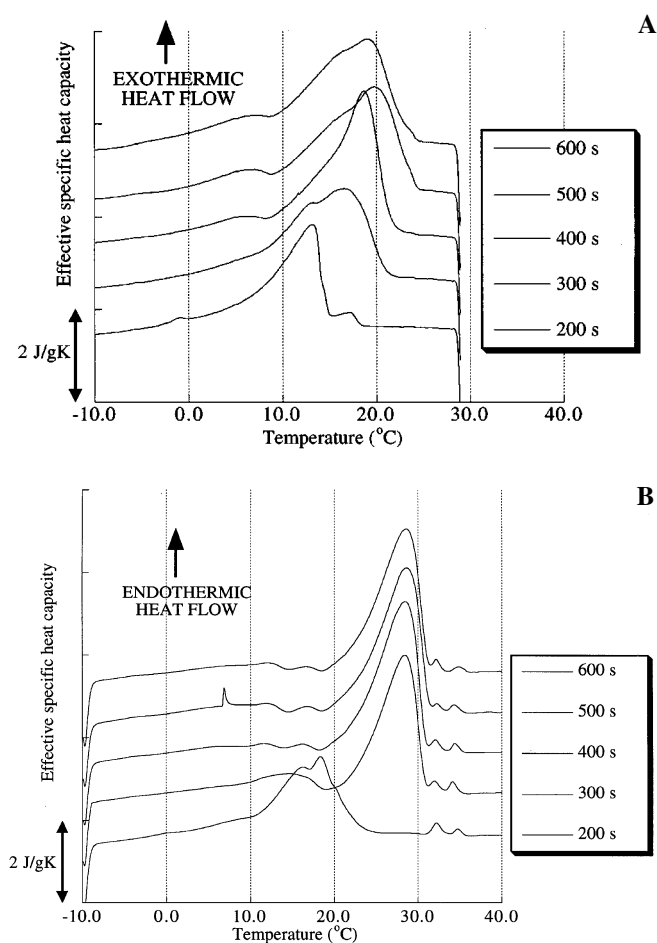
FIG. 7. (A) DSC cooling curves (at 2°C/min) of chocolate after processing at an average shear rate of 53 s^{-1}, holding at 22°C for a range of times and warming to 32°C. (B) Subsequent DSC remelting curves (at 5°C/min). The legend refers to the holding time at 22°C. For abbreviation see Figure 2.

FIG. 8. (A) DSC cooling curves (at 2°C/min) of chocolate after processing at a range of shear rates, holding at 22°C for 400 s, and warming to 32°C. (B) Subsequent DSC remelting curves (at 5°C/min). The legend refers to the average shear rate. For abbreviation see Figure 2.

shows the effect of varying the average shear rate (with a temper time of 400 s) on crystallization. Again two types of peak are observed. At low shear rates (up to 27 s^{-1}) the peak crystallization temperature of 13°C is recorded, characteristic of untempered chocolate. At shear rates above 35 s^{-1} the peak temperature rises to 18–19°C. The melt curve (Fig. 8B) peaks at approximately 18°C up to shear rates of 27 s^{-1}, and 29°C above 35 s^{-1}, but the 27 s^{-1} run also shows a small peak at 29°C. Thus for a set temper time there is a critical shear rate that must be exceeded in order for seed crystals to be produced. This will presumably vary with temper time which was not tested here. As with changing the temper time, the transition is sharp rather than gradual. The shear rates used in these experiments are much lower than those encountered in commercial tempering devices where it is reported that shear rates of typically 500–12,000 s^{-1} can be generated (4). These high shear rates, however, are localized within a small fraction of the chocolate volume (for example, close to the rotating blade tips), whereas in our experiments the shear is more uniformly distributed. Complete uniformity of shear is difficult to achieve, especially in the latter stages of tempering
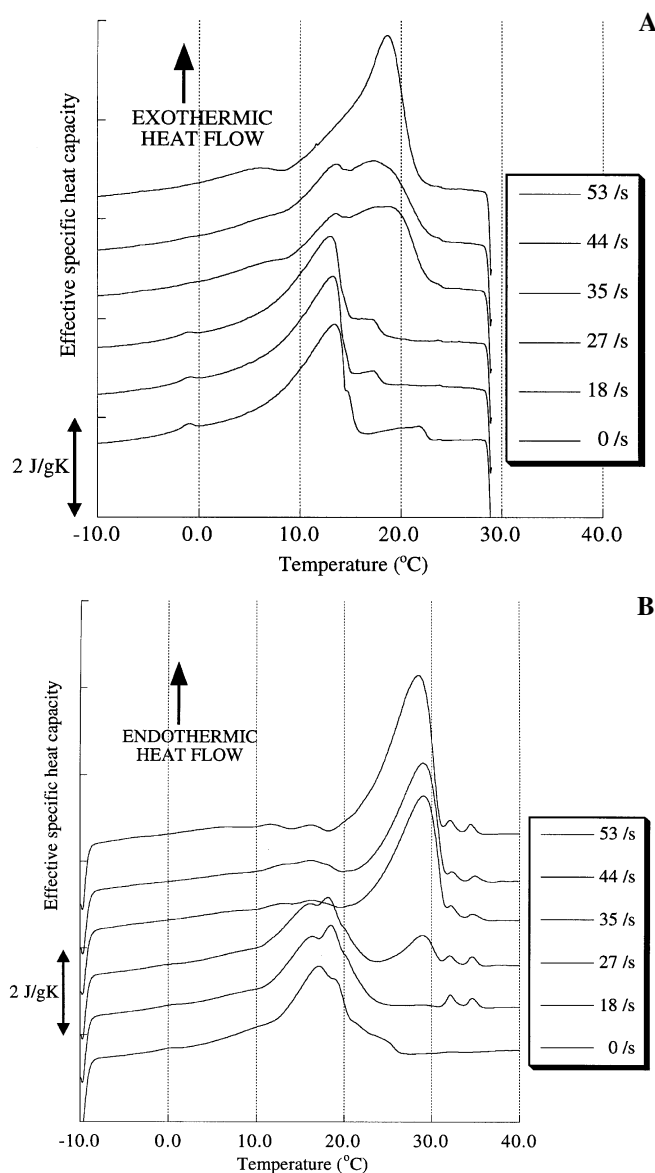
where the rheology is likely to be more non-Newtonian. It was suspected from visual observations that toward the end of the isothermal tempering period most shear occurred in a relatively small zone midway between the two cylinders. This would presumably be a result of the production of seed crystals making the chocolate rheology more viscous and non-Newtonian.

Effect of DSC scanning rate. Conditions were chosen for tempering in the shearing rig that were adjudged to most closely match the chocolate produced using the pilot plant tempering unit. These were a temper time of 400 s, a shear rate of 53 s^{-1}, and a rewarm temperature of 32.0°C. DSC scans were taken at a number of scan rates so that a detailed comparison between the two tempering regimes could be made. Cooling peak temperatures for the shearing rig tem-
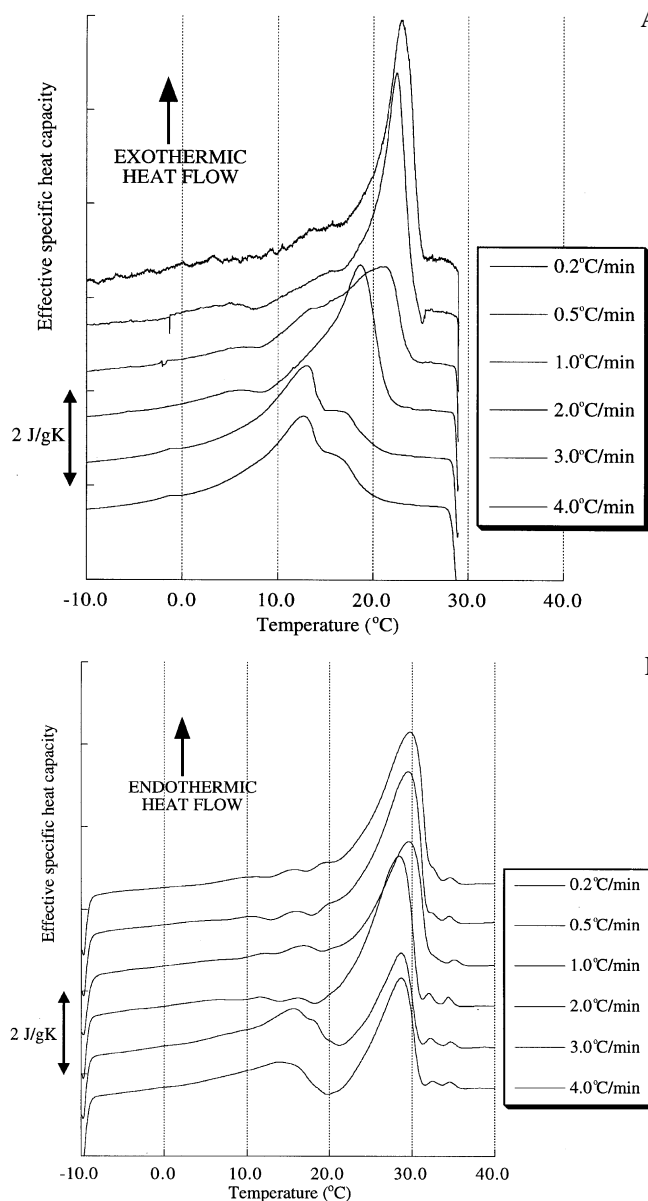
FIG. 9. (A) DSC cooling curves at a variety of scan rates of chocolate after processing at an average shear rate of 53 s⁻¹, holding at 22°C for 400 s, and warming to 32°C. (B) Subsequent DSC remelting curves (at 5°C/min). The legend refers to the DSC cooling rate prior to remelting. For abbreviation see Figure 2.

pered chocolate (Fig. 9A) were similar to those observed for pilot plant tempered chocolate (Fig. 4A), ranging from 13°C at a 4°C/min scan rate to 23°C for a 0.2°C/min scan rate. The scan for 1°C/min, however, was not as smooth as with the pilot plant tempered chocolate, and crystallization temperatures were also about 1°C lower. All melting curves showed a peak temperature of 29°C although the 3 and 4°C/min curves also showed a peak at 17°C. The 4°C/min curve shows some evidence for the exothermic peak seen on the remelts of pilot plant tempered chocolate at high cooling rates, however, no results were taken for higher cooling rates. Nevertheless, these curves are very similar to those found for the pilot plant tempered chocolate, demonstrating that the shearing rig can

be used to reproduce pilot plant tempering. The advantage with the concentric cylinder geometry is that the shear rate is more uniform and can be quantified more accurately. The shearing rig is also more portable, and experiments can be performed more easily and cheaply.

Peak enthalpy data. Enthalpy data were obtained from each sample by subtracting a baseline calculated from the high end of the melting curve (40–50°C) and then integrating the areas under the curves from –7.5 to 28°C for crystallization curves and up to 40°C for melt curves. There was some scatter in the data but there were clearly greater enthalpies for tempered than for untempered samples (tempered being defined as those samples having a peak temperature of greater than 28°C). The average crystallization enthalpies for untempered and tempered samples were 19.7 ± 2.9 J/g and 28.2 ± 5.7 J/g, respectively, and those for melting were 24.5 ± 2.3 J/g and 29.5 ± 2.8 J/g, respectively. Melting enthalpies were thus on average greater than crystallization enthalpies. The discrepancy can be attributed to the presence of seed crystals in the tempered chocolate before cooling in the DSC. Thus, the chocolate is already slightly solidified so that the total crystallization enthalpy is not measured by the DSC during cooling. The crystallization enthalpy of these seed crystals needs to be included for a direct comparison to be made between crystallization and melting enthalpies as measured by the DSC. The values found are lower than those reported by Chevalley *et al.* (13) (44 J/g). This may be due to differences in the cocoa butter content of the chocolate, and also larger enthalpies would be expected for chocolate that has been stored for some time as a greater proportion of the fats would have solidified.

DISCUSSION

A series of experiments has been carried out to quantify the effect of processing on the thermal behavior of chocolate during solidification and subsequent remelting. It is clear that the shear and thermal history of the material have a very strong effect on the structure of the final chocolate. The results can be interpreted in light of the polymorphism of the system. The polymorphism is most clearly evident from the remelt curves where two distinct types of melting profiles are observed: a higher melting range (peak temperature 29–30°C), and a lower melting range (peak temperature 16–18°C). Few results show peaks at intermediate temperatures. The higher melting points represent the higher polymorph associated with tempered chocolate and the lower representing untempered chocolate. The relative proportions of the two can be used as a measure of the degree of temper. It has been shown to be possible to vary the extent of temper by changing the following parameters: temper time, shear rate, and final melt temperature. Usually the transition occurs in a narrow interval. Proper tempering is encouraged by: (i) long hold times at 22°C (here more than 300 s); (ii) high shear rates (here above 35 s⁻¹), and (iii) a rewarm temperature below 33°C. The DSC cooling rate is also crucial. Too high a cooling rate results in untempered material forming, which converts into the higher polymorph on reheating.

The polymorphic forms are less easily distinguished on the crystallization curves as kinetic factors also govern the timing and temperature at which crystallization events occur. Examination of the figures in this paper shows a greater spread of crystallization peak temperatures compared to the bimodal distribution of melting temperatures. The same factors (temper time, shear rate, final melt temperature, and DSC scan rate) affect the position of the peak temperature on the cooling curves as on the remelt. For parameters affecting the nucleation stage of the tempering process (temper time and shear rate), the transition occurs over a narrow interval, corresponding to whether seed nuclei have reached a threshold of stability. There is thus a well defined "induction time," which was also observed by Loisel *et al.* (8), and is commonly found in crystallizing systems (12). The results of Bolliger *et al.* (9) suggest that the induction time is lowered if higher shear rates are used. It appears that shear has a direct effect on the kinetics of nucleation. Raising the final melt temperature gradually destroys seed crystals and this effect occurs over a range. Changing the DSC cooling rate also has a gradual effect on the position of the peak temperature, reflecting the kinetic constraints of crystal growth.

The amounts of higher and lower polymorphs occurring on the remelt, however, do not always match the proportions that would be predicted from the cooling curves. It appears that only a slight amount of crystallization of the higher polymorph is required in order for large amounts of the higher polymorph to be observed on the remelt, and that melting peaks of 28–29°C can be produced from systems where the cooling peak is as low as 12°C. This may be due to the higher polymorph crystallizing at these lower temperatures, or, more likely, that the lower polymorph is formed initially but subsequently converts to the higher polymorph, a phenomenon that was directly observed when pilot plant chocolate was rewarmed after quench cooling.

Overall, the results demonstrate that a difficult processing problem can be approached using this simple experimental system. The concentric cylinder geometry enables quantified shear-temperature-time profiles to be applied which allows the underlying reasons for the thermal behavior of the system to be more apparent.

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