Characterization of Chocolate Using Power Compensated DSC

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Introduction

Cocoa butter, one of the main ingredients used to produce chocolate, can exist in multiple and unstable crystalline forms, known as polymorphs. The given processing or thermal history of the cocoa butter and chocolate can generate different polymorphic forms which will affect the final properties (melting characteristics, appearance and physical handling) of the chocolate. The melting properties of cocoa butter and chocolate are very important, as the melting is what delivers the 'feel' and taste of the chocolate to the mouth. It becomes important to characterize and understand the melting properties of the chocolate as it is related to essential consumer aspects. One of the best analytical techniques for this purpose is differential scanning calorimetry (DSC).

DSC

Differential Scanning Calorimetry measures the heat flow into or from a sample under heating, cooling or isothermal conditions. With DSC, a complex program with multiple heating, cooling and iso steps can be easily constructed and utilized to simulate real-life processing conditions.

For the characterization of the metastability or polymorphism of cocoa and/or chocolate, the best DSC for this purpose is the power compensated DSC approach. The PerkinElmer Pyris 1 DSC system uses this power compensated means. With the power compensated DSC, both the sample side and reference side have their own independently controlled furnaces, which provides a direct calorimetric measure of the true heat flow. In contrast, the heat flux DSC uses a single furnace for both the sample and reference and measures a temperature differential, which is then converted to a heat flow.

The power compensated DSC gives a number of advantages in chocolate analysis over the heat flux DSC device in a number of important areas. First, the design of the sample and reference low mass furnaces yields very close control over the sample environment. This allows the DSC to produce specific and accurate thermal treatments for reliable material comparison or to investigate the effects of changes in processing conditions. Second, the sensitivity of this type of DSC to small changes makes it an ideal tool to identify sample characteristics or processing changes.

In addition, mold cooling rates can be better simulated on a Pyris 1 DSC due to the low mass micro-furnace design. Each of the two furnaces weighs only about 1 gram, compared with heat flux DSC designs, which are typically more than 150 grams. Actual cooling rates of up to 500^{O}C/min are reproducible and accurately achievable with the power compensated DSC. The ability to perform very rapid cooling permits studies of polymorphism and crystal growth in chocolate under conditions close to those realized during actual processing. Controlled cooling is easily attained, and to achieve these high cooling rates, the Pyris 1 DSC can use a number of different cooling systems to suit different purposes. The Pyris 1 DSC system uses a platinum resistance thermometer (PRT) to measure sample temperatures. This provides for the highest possible accuracy and precision, especially in comparison to the lesser performing thermocouples used with heat flux DSC devices.

Samples

The four samples analyzed were in the form of packaged chocolate bars, and were labelled as follows:

Sample 1 – "Grey" sample
Sample 2 – Crystallized afterwards
Sample 3 – Batch 3
Sample 4 – Batch 4

Experimental

The samples were analyzed using the PerkinElmer Pyris 1 DSC equipped with an Intracooler 2P cooling accessory which allowed the system to attain a starting analysis temperature of -60^{O}C although the

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Figure 1. DSC comparison of samples 1 and 2 with equivalent thermal histories.

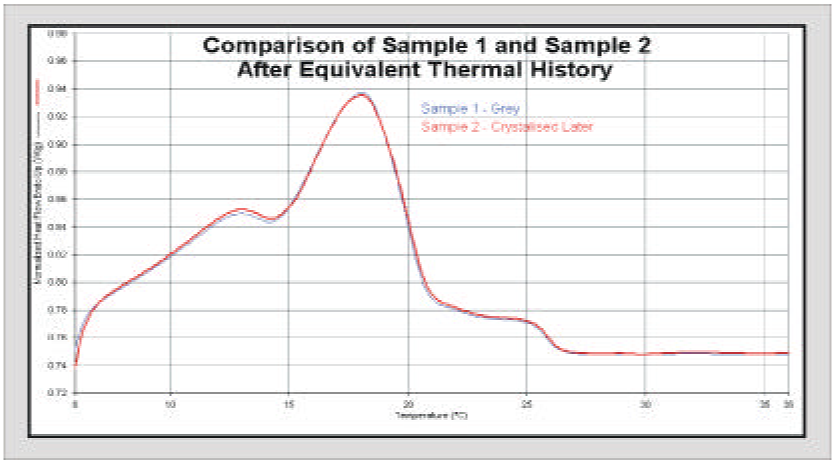
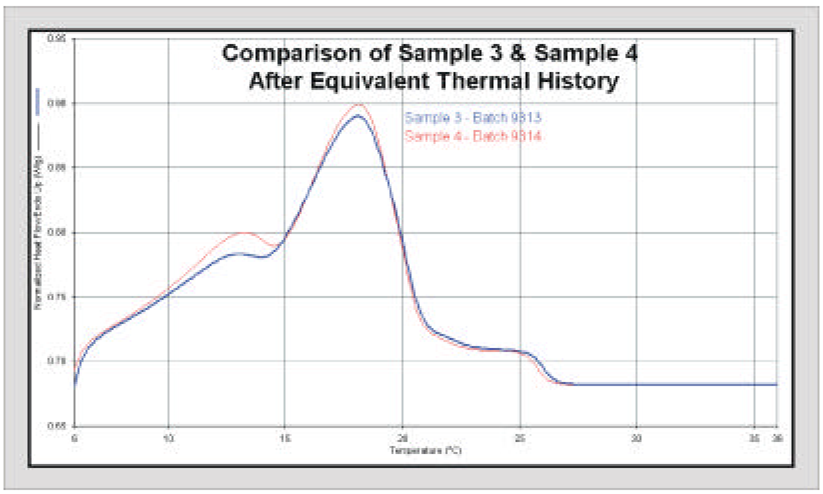


Figure 2. DSC comparison of samples 3 and 4 with equivalent thermal histories.



program requested started at 5°C. The additional cooling allows for much faster controlled (programmed) cooling rates to be used if required. The DSC was purged using an inert nitrogen atmosphere at 30 cc/min to prevent any possibility of oxidation of the sample at elevated temperatures.

Temperature and energy calibrations were performed on the Pyris 1 DSC using indium and zinc calibration reference materials as supplied with the DSC. These certificated materials allow temperature calibration for the full range of the DSC using a two-point calibration. A one-point energy calibration is provided by measuring the melting peak area of the indium sample since with a power compensation DSC, the energy calibration is linear over the whole temperature range, giving a direct readout of the transition energy.

Each sample was cut from the top edge of the blocks of chocolate using a scalpel, and then carefully weighed into a 50µL aluminum DSC sample pan. Once weighed, the sample was then crimped using a 30µL sample pan as a cover to ensure good thermal contact and to prevent sample movement during the analysis.

Several different test programs were conducted, and the following is an example of one such program. This example was used to prove that the data was identical when the sample was given an identical thermal treatment. [The data from such an experiment is seen in Figure 5]. This complex program, conducted over a narrow temperature interval and at fast heating and cooling rates, demonstrates the need for a DSC instrument capable of maintaining tight temperature control. The ability to maintain precise control is why the power compensated DSC is the instrument of choice of the analyses of chocolate and cocoa butters.

Load sample at 20°C.
Cool sample at 5°C/min and hold for 5 minutes
Heat from 5°C at 5°C/min to 40°C and hold for 1 minute
Cool from 40°C at 5°C/min to 5°C and hold for 10 minutes
Heat from 5°C at 5°C/min to 40°C and hold for 1 minute
Cool from 40°C at 5°C/min to 5°C and hold for 10 minutes

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Heat from 5°C at 5°C/min to 40°C
and hold for 1 minute

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Figure 3. DSC comparison of initial heats for samples 1 and 2.

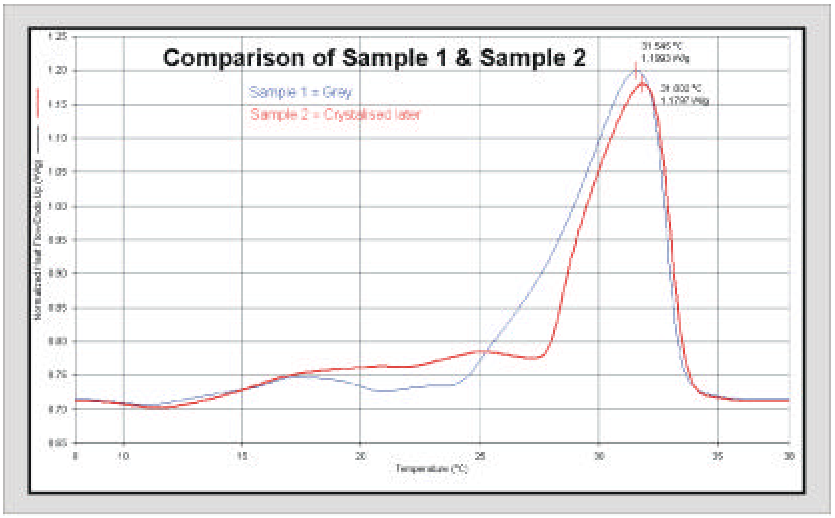
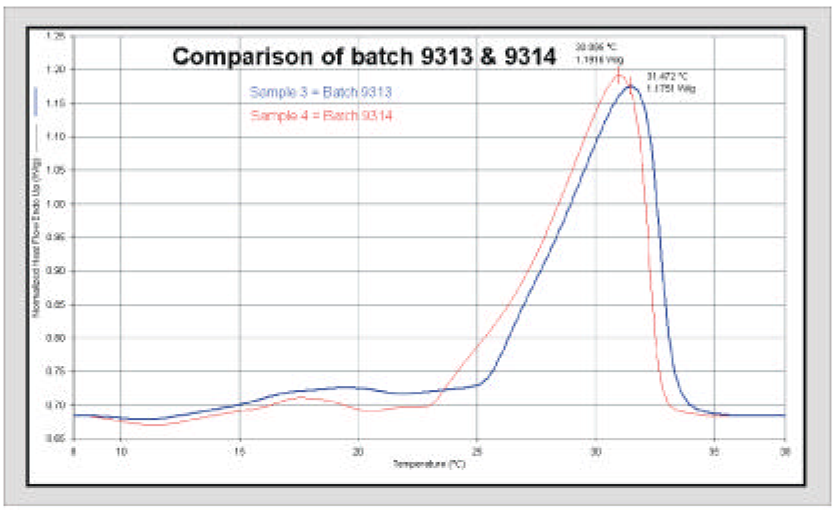


Figure 4. DSC results on as-received chocolate samples 3 and 4.



Cool from 40°C at 5°C/min to 5°C and hold for 10 minutes
Heat from 5°C at 5°C/min to 40°C and finish

The explanation of why this particular thermal program was selected is given later in the discussion section.

Results and Discussion

Shown in Figure 1 is data from a heating cycle of sample 1 compared with that of chocolate (i.e., tempering). The profiles are almost identical with the polymorphs in the same ratio and temperatures.

The results presented in Figure 2 shows data for sample 3 and sample 4 after each specimen was subjected to a known thermal history. In fact, this treatment was the same thermal treatment as seen in the data shown in Figure 1. It may be seen that the polymorphic peaks at 13°C and 18°C are not equivalent in magnitude for each of the two samples. Sample 4 yields the greater peak intensities, which is indicative of a significantly greater crystalline content in the polymorphs. The power compensated Pyris 1 DSC has the necessary high resolution to make the clear distinction between the melting differences between samples 3 and 4.

Figure 3 presents the initial heating of samples 1 and 2, and it is clear that the curves are significantly different. Based on the data produced for the "crystallized later" sample, it suggests that the sample was held at around 27°C to produce the observed peak shape. The calculation to determine the peak maximum shows that the "grey" sample 1 has a peak maximum which is about 0.3°C lower than the "crystallized later " sample 2.

Figure 4 shows and compares the initial heating (as-received) for sample 3 (batch 9313) and sample 4 (batch 9314), and it will be seen that the polymorph combination is very similar. This indicates that the manufacturing process has been reasonably successful in producing an equivalent texture for that batch of cocoa butter, even though the peak maximum is higher by 0.5°C for sample 3 than for sample 4.

The results shown in Figure 5 demonstrate that the Pyris 1 DSC is capable of reproducing **exactly** the

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Figure 5. Comparison of DSC Data for Sample 4 after Repeatable Temperature Cycling.

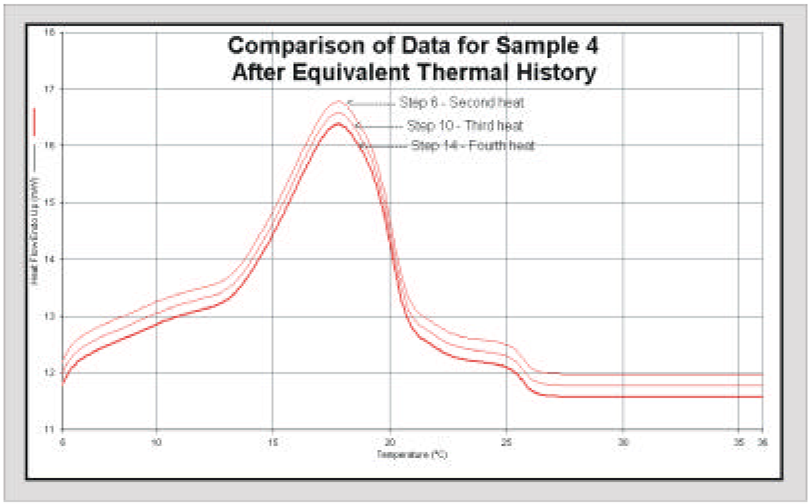
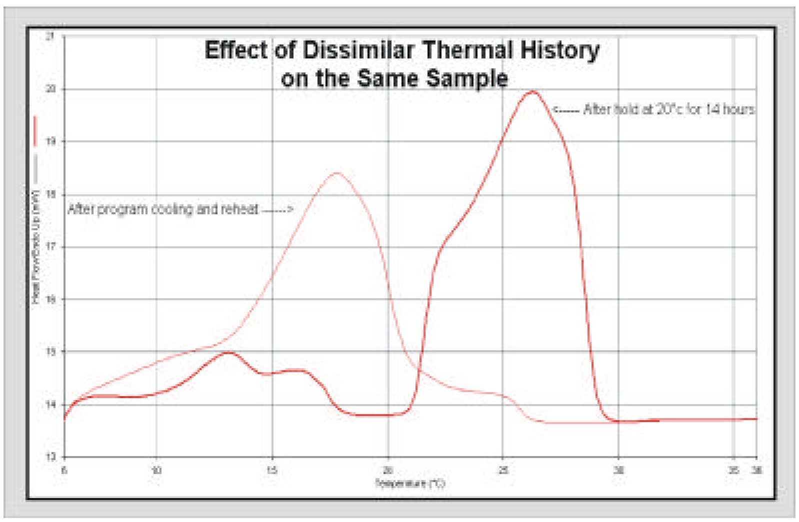


Figure 6. DSC results showing effect of dissimilar thermal history on Sample 4.



thermal conditions from run to run, since it is vital that instrument differences do not interfere with the sample examination. [Note that the data has been offset, via the software, after the run was completed. Otherwise, it was impossible to see the differences since each individual curve overlaid exactly with the others. This demonstrates the very high reproducibility of the power compensated Pyris 1 DSC].

The initial heating results of sample 4 (after it had been treated at 20°C for 14 hours in the DSC) are presented in Figure 6. This tempering thermal history treatment has produced a main peak that starts melting immediately above 20°C. Two other peaks are observed at about 13°c and 16°c on this curve. The other curve shown on this plot is the same sample but with a different cooling cycle, or thermal history (which is identical to that presented in Figure 5).

Discussion

Cocoa butter and chocolate are both highly susceptible to the manner in which they are thermally treated during processing. There are six polymorphic 'forms', or crystalline states, that can be produced in the temperature range from 10°C to 38°C. The presence (or absence) of a particular combination of these polymorphic forms are what produces the texture in a particular brand of chocolate. During processing, the fats are tempered to produce the desired form, and various different tempering steps may be necessary, depending on the batch/source of the cocoa butter used. DSC can provide valuable information as to a chocolate's given thermal history. This yields insight if processing upsets occurs and can provide information on causes and solutions.

The data in displayed in Figure 1 shows that it is possible to say that the differences between the data observed on the initial heat in Figure 3 can be eliminated by correct thermal treatment. In addition, that the chocolates are identical apart from the processing or storage of the finished product. Greater familiarity with a

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particular process/factory may well give the experience to show at a glance, the cause or effect of different treatments.

With the data from Figures 2 and 4, it appears that the batches of chocolate are different, but have been treated in such a way that the texture is likely to be equivalent for both samples. This can be shown by examining the initial heating data in Figure 4, which is very similar (given that the chocolate is from different batches) in relation to the data in Figure 2

The DSC data in Figure 5 is included to demonstrate that, when the sample environment is controlled as tightly as it is in a power compensation DSC, it is possible to produce data that is indistinguishable from each other. In other words, the power compensated DSC gives exactly the same treatment each time on chocolate samples, which are highly susceptible to subtle changes in thermal histories. Further evidence is seen Figure 6 which demonstrates that even the length of time that a sample is "held" under a specific temperature environment is critical in the processing of chocolate.

It should be noted that the DSC is capable of providing clues as to incorrect storage temperature conditions for chocolate that has been returned as being of "faulty manufacture".

Summary

The high performance of the PerkinElmer Pyris 1 DSC for chocolates has been demonstrated by its ability to provide highly reproducible thermal histories in samples which will readily show significant differences if the treatments are not identical. The high resolution of the Pyris 1 DSC instrument provides the ability to observe the different polymorphic crystalline forms associated with the fats in chocolate. The melting characteristics of these polymorphic forms are directly related to the textural properties of the chocolate when eaten. The Pyris 1 DSC offers fast sample turnaround that can be helpful in problem solving in production environments where speed of resolving a problem can be critical.

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