EFFECT OF SHEAR ON THE CRYSTALLIZIATION OF CHOCOLATE

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Abstract

The objective of this research was to determine the effect of shearing on the crystal structure of chocolate. The crystal structure was examined with various techniques including x-ray diffraction, differential scanning calorimetry, thermal analysis and optical microscopy. This report found that shearing during tempering increases crystallinity in chocolate.

Chapter 1: Introduction

Chocolate is formed through the processing of the cocoa bean. The cocoa bean is fermented and roasted to form chocolate liquor. The chocolate liquor is further processed to separate the cocoa powder and cocoa butter. Cocoa powder and cocoa butter are used in addition to sugar and/or milk to make sweet or milk chocolate.

Cocoa butter has six possible crystal structures. Structure V is the ideal structure as it forms a chocolate that is glossy, firm, and melts near body temperature. This structure is not formed easily, thus a process of tempering and seeding is used to aid the formation of structure V. Wiley [1] describes tempering as heating the chocolate to 50˚C to melt all six forms of the cocoa butter crystals. The chocolate is then cooled to approximately 27˚C to allow Structure IV and V crystals to form. The chocolate is then agitated through stirring or mechanical means to form crystals throughout the chocolate. The chocolate is then heated again to around 31˚C to eliminate most of the Structure IV crystals. The chocolate is then allowed to cool naturally after the last heating.

The stirring of the chocolate through mechanical means induces a shear rate to liquid chocolate. This shear rate may effect the crystallization of the chocolate. Various studies have been done on the effects of shear rate with chocolate. This report seeks to determine the effect of shear rates on dark chocolate through the investigation of DSC, X-Ray Diffraction, and Optical Microscope, as the earlier studies have been focused on cocoa butter or milk chocolate rather than pure chocolate liquor. The X-Ray Diffraction also aids in determining the chemical makes up of the chocolate to determine the ingredients that affect the chocolate the most.

Chapter 2: Review of Literature

2.0 Ingredients in Chocolate

2.0.1 Cocoa Bean

The cocoa bean is the raw ingredient that all cocoa products contain. The cocoa beans are produced in thirty different locations around the world, mainly confined to 20˚ south or north of the equator. The cocoa trees need the hot climate of this area to thrive, but must have production from shade of larger trees in the area.[1]

The cocoa pods are harvested from the trees and the beans are removed from the pods. The cocoa beans are fermented for a number of days, depending on the manufacturer. The fermentation process begins to develop of the chocolate flavor. Once fermentation is complete, the cocoa beans are dried either by natural sunlight or through mechanical means. The drying process removes most of the moisture from the bean and takes up to a week to complete the process. The beans are then cleaned before roasting. Once roasting is completed, the bean shells are removed, leaving the "nib." The "nibs" are milled and form chocolate liquor.[2] Figure 1 presents this process in detail.

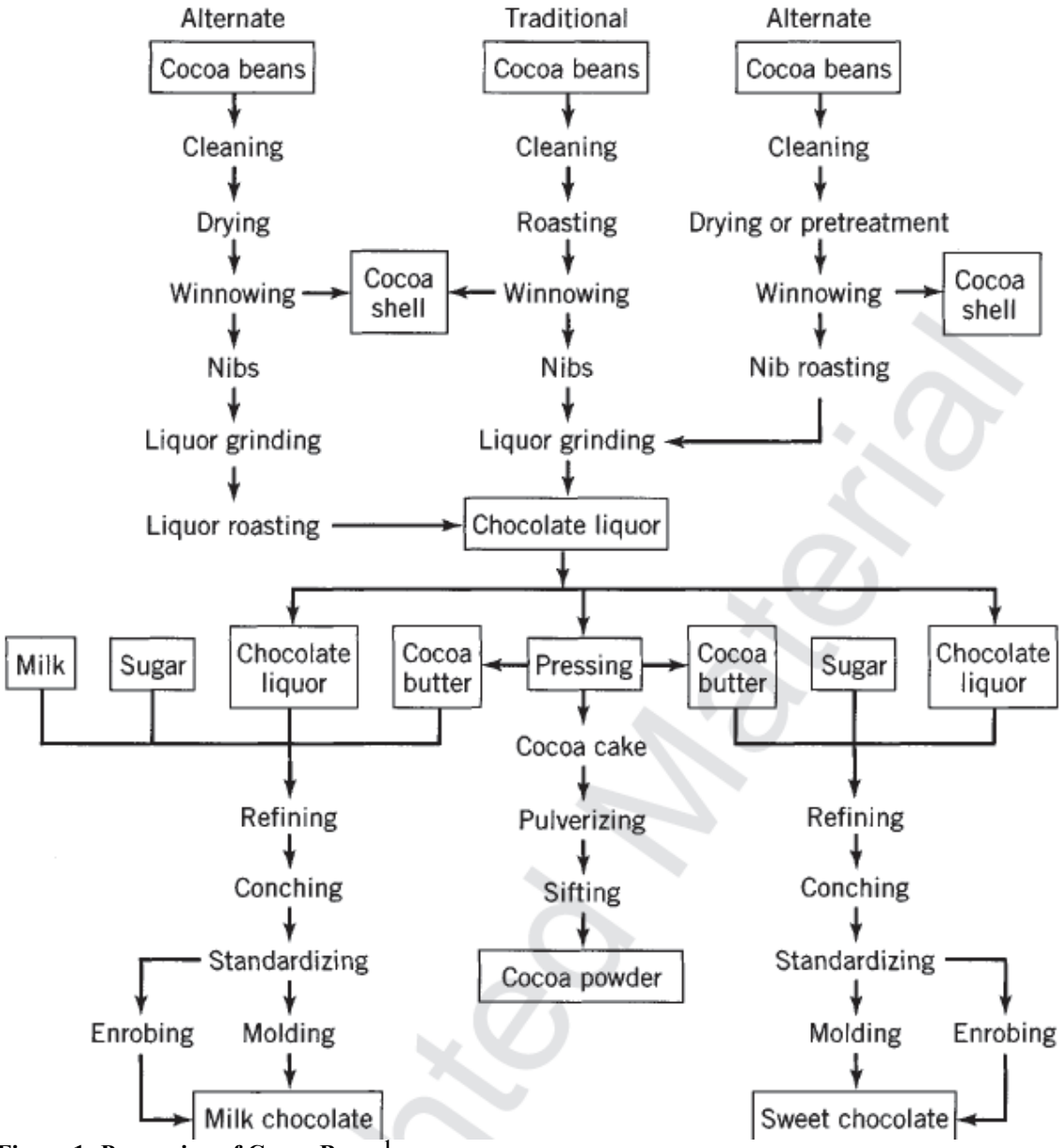

Figure 1: Processing of Cocoa Beans[1]

2.0.2 Cocoa Butter

Through the processing of the chocolate liquor, cocoa butter can be extracted. Wiley[1] describes cocoa butter as "the main carrier and suspending medium for cocoa particles in chocolate liquor and for sugar and other ingredients in sweet and milk chocolate." Cocoa butter is composed of mainly three fatty acids: stearic, palmitic, and oleic. These make up the three dominating saturated triacylglycerols (TAGs) in cocoa

butter. Below the structure of the saturated triacylglycerols is shown in Figure 2, where p, q, and r are the different lengths of the fatty acid residues. The combination of different lengths of fatty acid residues is what makes each TAG unique.

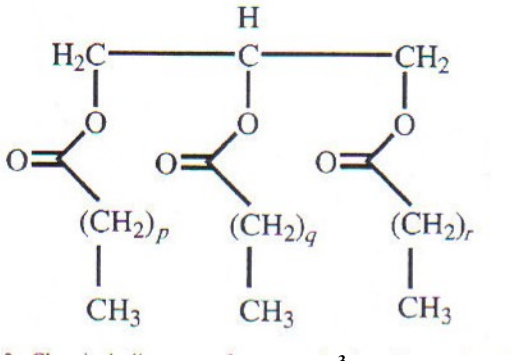

Figure 2: Triacylglycerol Structure[3]

Cocoa butter is the preferred fat for chocolate products due to its low melting temperature. Cocoa butter is solid at room temperature and begins to soften at 30˚C. At 37˚C, cocoa butter is completely melted through. Due to its structure, cocoa butter is also one of the most stable fats known with a shelf life of up to 5 years. This makes cocoa butter highly desirable in food production, pharmaceuticals, and ointments.

2.0.3 Cocoa Powder

Cocoa powder is the solid that remains after the cocoa butter is removed from the chocolate liquor. There are two types of cocoa powder: Dutch processed and natural. Dutch processed cocoa powder is a red-brown shade and has a mild cocoa flavor. This is what is used in retail cocoa powder and beverages. Natural cocoa powder is a yellow-orange color that produces a light brown product. It is mainly used in candy, syrups, and toppings.[4]

2.0.4 Cocoa Composition

Chocolate and cocoa products contain alkaloids. Theobromine is the main alkaloid present in cocoa products, with small amounts of caffeine. Other components present in chocolate include oleic acid, stearic acid, palmatic acid, epicatechin, gallic acid, tryptophan, and phenethylamine. [5]

2.1 Types of Chocolate

2.1.1 Milk and Sweet Chocolate

The majority of chocolate consumed in the United States is in the form of milk chocolate or sweet chocolate. Milk chocolate is a blend of sugar, cocoa butter, chocolate liquor, milk or milk solids, and vanilla. In the production of milk chocolate, the water must be removed from the milk before it is added to the mixture. According to the FDA standards for milk chocolate, it cannot contain less than 3.66% milk fat and 12% milk solids. It should also contain 10% chocolate liquor.

Sweet (dark) chocolate is a blend of sugar, cocoa butter, and chocolate liquor. Generally, sweet chocolate should not contain milk products, but is allowed to contain up to 3.6% milk fat.[1]

2.1.2 White Chocolate

White chocolate is a blend of sugar, cocoa butter, milk, and vanilla. In the United States, there is no standard for the identification for white chocolate; however, the European Economic Community Directive 75/155/EEC is considered the standard for white chocolate. It describes that in order to be considered white chocolate, the product must be free of coloring products and consisting of cocoa butter in excess of 20%, sugar less then 55% and milk products or cream in excess of 14%.[1]

2.3 Crystallization of Chocolate

2.3.1 Types of Chocolate Crystals

The cocoa butter in chocolate products crystallizes in six different structures. Table 1 gives basic information and melting temperatures for the six structures of cocoa butter.

Table 1: Types of Chocolate Crystals[6]

Crystal	Melting Temp.	Notes
I	17 °C (63 °F)	Soft, crumbly, melts too easily.
II	21 °C (70 °F)	Soft, crumbly, melts too easily.
III	26 °C (78 °F)	Firm, poor snap, melts too easily.
IV	28 °C (82 °F)	Firm, good snap, melts too easily.
V	34 °C (94 °F)	Glossy, firm, best snap, melts near body temperature (37 °C).
VI	36 °C (97 °F)	Hard, takes weeks to form.

2.3.2 Ideal Crystallization

High-quality chocolate contains mostly type V crystals as it has the best appearance, texture, and stability after processing. The difference between the crystal packing of different crystal forms can be seen below in Figures 4 and 5 where β refers to forms V and VI and β' corresponds to form IV. The β structure is more tightly packed than the β', meaning that forms V and VI will give a harder chocolate that will hold its shape better than form IV. Form V is the most desired out of the two closed packed structures because it is a hard chocolate, but not too hard, as is the case for form VI.

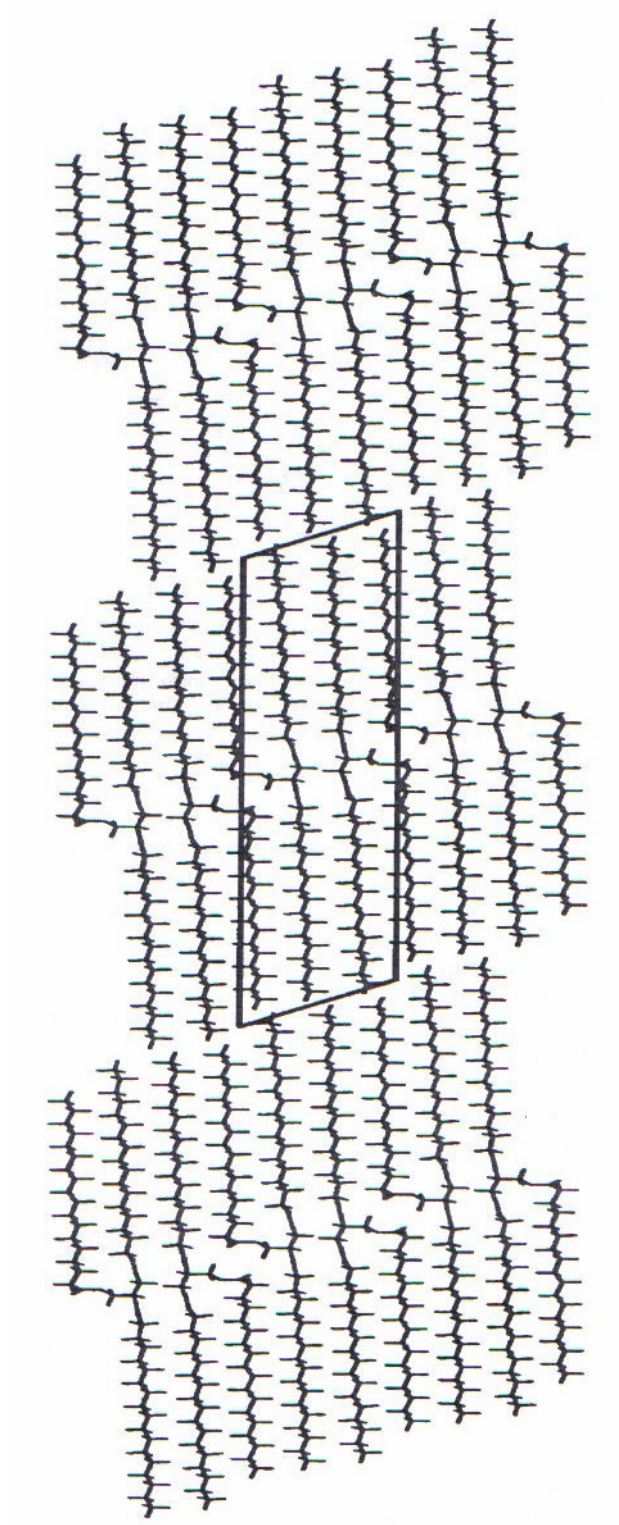

Figure 3: Crystal packing of β structure with *c*-axis perpendicular to the plane of the paper[8]

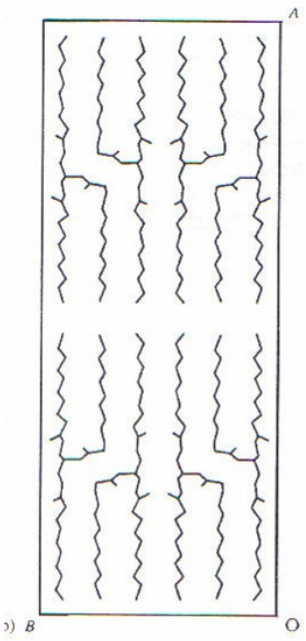

Figure 4: Crystal Packing for β' structure perpendicular to ab-plane[8]

A process called tempering aids in ensuring the cocoa butter is mostly type V crystals. Tempering is a series of heating and cooling steps performed to initiate and nurture the formation of type V crystals. Later in the chapter, tempering is more thoroughly discussed.

2.3.3 Issues of Crystallization

Fat blooms are a formation of fat crystals on the chocolate surface. They are noticeable due to their white appearance on the surface of the chocolate, as shown in Figure 5. Typically, the presence of fat blooms correlates to the transformation of the chocolate from Structure V to structure VI.

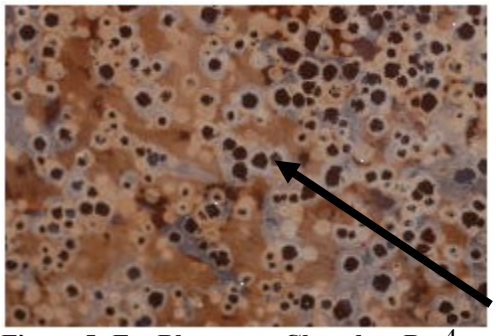

Figure 5: Fat Blooms on Chocolate Bar[4]

Loisel et al [7], presented F*at Bloom and Chocolate Structure Studied by Mercury Porosimetry*. This study analyzed the structure of dark chocolate in order to determine if fat blooms formed in correlation to the amount of pores in the chocolate through mercury porosimetry. The study determined that the pores located on the chocolate surface had contained liquid cocoa butter. The decreasing of these pores occurred when the chocolate was well tempered. As the amount of pores in chocolate increases, the chance of fat bloom formation on the chocolate surface also increases.[7]

Other issues in crystallization present themselves in the formation of the crystals. Structure V and VI are the hardest crystal structure to form in comparison to Structure IV because the crystals are packed more closely. This is shown in Figures 3 and 4.[8] The crystallization of Structures V and VI is dependent on the crystal history of the cocoa butter. This is why the tempering process is essential in the production of chocolate.

2.3.4 Use of X-Ray Diffraction

Understanding the crystallization process is critical to producing good chocolate. Poor crystallization will cause the texture and taste to suffer, along with a lower resistance to fat bloom. X-Ray powder diffraction (XRPD) is used to study the different

crystal structures and phases transformations in chocolate. An example of this is displayed in Figure 6.[8]

X-Ray diffraction is able to detail the internal structure of matters 10^{-7} mm in size. As the voltage in the x-ray tube is moved about a critical value, dependant on the target material, intensity maxima appear at certain wavelengths. The placement of these intensities provides data regarding the composition of the material being tested.[9]

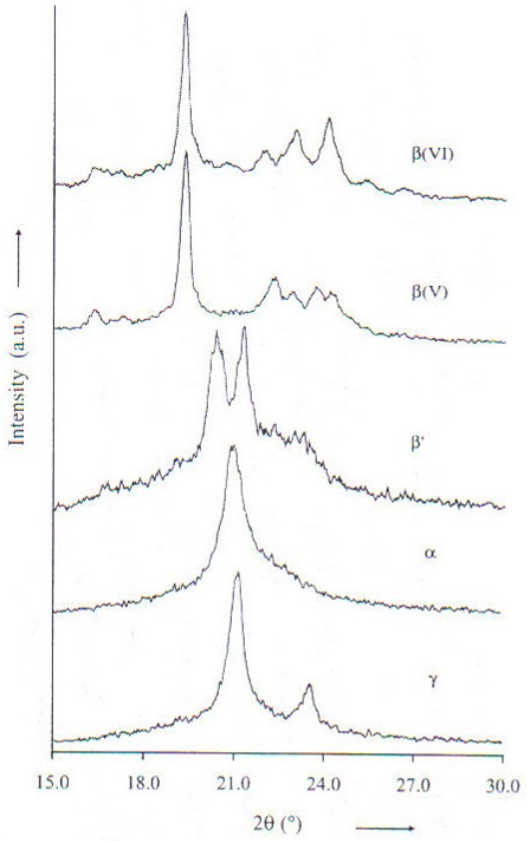

Figure 6: XRPD Diffraction Example of Cocoa Butter[8]
(Form V and Form VI correspond to two different β phases, Form IV and Form III correspond to β', Form II to α, and Form I to γ)

2.3.5 Use of Differential Scanning Calorimetry

Differential Scanning Calorimetry (DSC) heats a sample to a specified temperature at a specified rate and compares the heat flow to a standard. This is useful in understanding the crystallization of chocolate because each crystal will emit an endothermic change in heat flow when melted. An example is shown below in Figure 7.

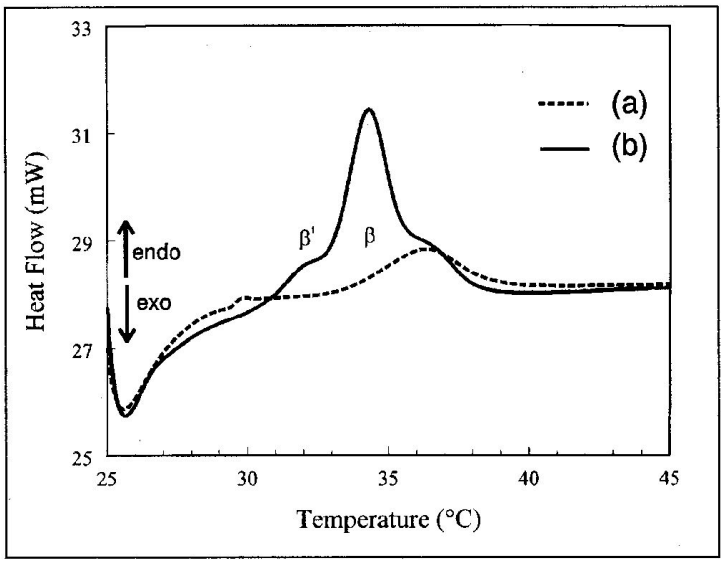

Figure 7: DSC Recording of Dark Chocolate during a) first and b) second steps of the crystallization process[15]

The graph shown in Figure 7 was obtained from a sample weight of 30mg, which was a mixture of low-fat dark chocolate and pure cocoa butter with a fat content of 32.4%. The sample was prepared in a Scraped Surface Heat Exchanger (SSHE) at 20 RPM, where the chocolate was heated to 45°C and rapidly cooled to 31°C. DSC analysis reheated the chocolate to 45°C at a heating rate of 10°C/min[15]. The difference between the two profiles can be seen clearly, as (a) has a lower peak occurring at a higher temperature than (b). This corresponds to different crystals, (a) can be classified as β

crystals and (b) as β' crystals, which emphasizes the importance of the crystallization process and the use of DSC to understand this process.

2.4 Tempering of Chocolate

2.4.1 Introduction to Tempering

Tempering chocolate aids in the formation of the required form of cocoa butter crystals. As previously discussed, cocoa butter of good chocolate should be Structure V. This structure produces the best appearance, texture, and taste.

The crystallization of Structure V and VI are affected by the crystal history of the cocoa butter. If the cocoa butter is half melted and then cooled, the cocoa butter retains the previous crystal history and will re-crystallize into its previous forms. As the following tempering process describe, the insurance of Structure V can be done through seeding or specified temperature ranges for heating and cooling.

2.4.2 Tempering Process

Many different variations of tempering exist that are dependant on the manufacturer. Wiley [1] describes tempering as heating the chocolate to 50˚C to melt all six forms of the cocoa butter crystals. The chocolate is then cooled to approximately 27˚C to allow Structure IV and V crystals to form. The chocolate is then agitated through stirring or mechanical means to form crystals throughout the chocolate. The chocolate is then heated again to approximately 31˚C to eliminate the majority of Structure IV crystals. The chocolate is then allowed to cool naturally after the last heating.[1] Basic Tempering curves are shown in Figure 8, but will vary depending on the specific tempering process.

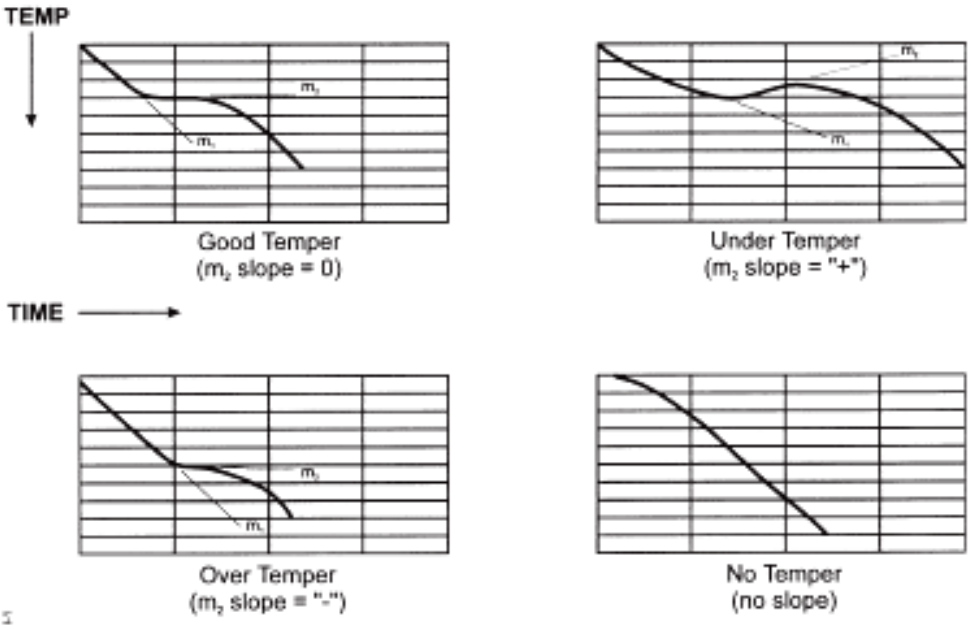

Figure 8: Typical Chocolate Tempering Curves[9]

The graphs in Figure 8 show that a good temper for chocolate is when the slope of the second region of the curve (m_2) is equal to zero. If m_2 is either positive or negative, you will have under and over tempering of the chocolate. If there is no change in slope, then no tempering has occurred. This means that a desirable temper occurs when the temperature of the chocolate is decreased, held at a constant temperature, and then cooled.

2.4.3 Studies in Tempering

Loisel et al [11], studied the use of a scraped surface heat exchange in the tempering of chocolate. Loisel[11] experimentally determined the optimal procedure for tempering chocolate using the scraped surface heat exchanger. Loisel[11] melted the chocolate at 45ºC for several hours, cooled to 38.5 ºC and then cooled to 26.1ºC ± 0.1º C to allow for crystallization. After the crystallization began, the chocolate was then heated

to different temperatures between 30.4ºC and 38.2ºC. Overall, this study determined that a temperature for the final stage of 35 – 35.5ºC produced well-tempered chocolate.

2.5 Shearing of Chocolate

2.5.1 Effects of Shearing on Tempering

Part of the tempering process is transporting liquid chocolate to molds. Transportation to molds can occur via tubes or direct pouring from the container that the chocolate was tempered in. When the liquid chocolate is transported, shear is induced, and its effect on the crystal structure of chocolate must be taken into consideration. The shear may change the crystal structure from the desired form V to other structure types. The task is to determine whether inducing shear during the tempering process will encourage or inhibit the desired crystal formation.

Okechukwu[12] studied how shearing affected tempering of milk chocolate using a rheometer. The rheometer induced a shear rate of 30 s^{-1} for 300 s after the chocolate was heated to 50 ºC. Shear rates of 15 s^{-1} and 30s^{-1} were used when the chocolate was cooled to 24 ºC and then held for 0, 400, 600 and 800 seconds for each shear rate. The chocolate was then heated to 30ºC and sheared for 90s before steady shear flow analysis was performed. The steady-shear flow analysis increased the shear rate linearly from 0 to 100 s^{-1}. These studies showed that during the cooling process, the viscosity followed the equation:

$$\eta = A\exp(Ea/RT) \qquad (1)^{12}$$

Where η = apparent viscosity (Pa*s), A – Arrhenius constant (Pa*s), Ea – activation energy (cal/g*mol), R = ideal gas constant (1.987 cal/g*mol*K), T = temperature (K).

The effect of the two different shear rates is shown in Figure 9. The effect of the holding time can be seen in Figure 10.

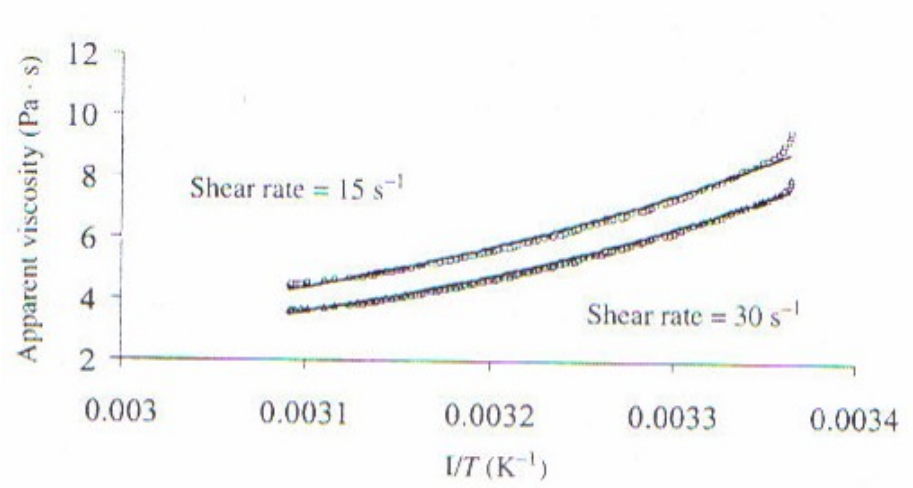

Figure 9: Shear Thinning of Chocolate at Shear Rates of $15s^{-1}$and $30s^{-1}$

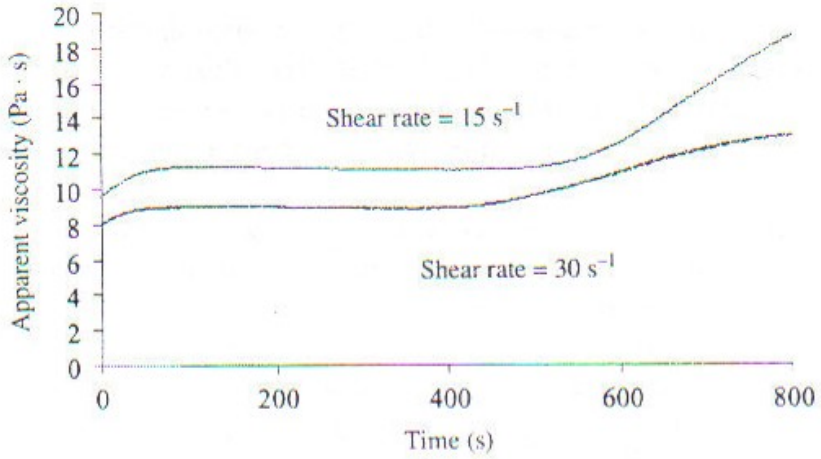

Figure 10: Apparent Viscosity of Chocolate at Shear Rates of $15s^{-1}$ and $30s^{-1}$

A longer induction time was observed for the slower shear rate, showing that the crystal formation was slower than the induction time under a higher shear rate. Studying the effects on chocolate by the re-warming process, it was found that lower shear rates produce large, unstable crystalline particles. In addition, samples held for 0s – 200s had no crystal formation, while samples held over 400s had the greatest crystal formation. The steady-shear flow analysis used the following equations,

$$\sigma^{0.5} = K_1 (\gamma)^{0.5} + \sigma_o^{0.5} \text{ (Casson Model)} \quad (2)[12]$$

$$\eta = K (\gamma)^{n-1} + (\sigma_o/\gamma) \text{ (Herschel-Bulkley Model)} \quad (3)[12]$$

where σ = shear stress (Pa), K_1 = Casson viscosity [$(Pa*s)^{0.5}$], γ = shear rate (s^{-1}), σ_o = yield stress (Pa), K = the consistency coefficient ($Pa*s^n$), n = flow behavior index (dimensionless), and η = apparent viscosity. It is shown in Tables 2 and 3 that a longer holding time results in a higher flow behavior index, as well as yield stress. The consistency coefficient decreased with a longer holding time.

Table 2: Rheological Parameters of Casson Model (T = 30°C)[12]

Time (s)	$\dot{\gamma}$ (s^{-1})	σ_o (Pa)	K_1 [$(Pa \cdot s)^{0.5}$]
None	30	13.1	3.8
400	30	15.1	4.4
600	30	13.5	5.1
800	30	14.1	5.2
400	15	13.8	4.3
800	15	15.4	5.3

Table 3: Rheological Parameters of Hershel-Bulkley Model (T = 30°C)[12]

Time (s)	$\dot{\gamma}$ (s^{-1})	σ_o (Pa)	K ($Pa \cdot s^n$)	n (–)
None	30	10.6	14.2	0.77
400	30	19.4	13.8	0.81
600	30	31.7	11.0	0.89
800	30	32.8	11.3	0.89
400	15	20.3	12.4	0.83
800	15	127.0	13.7	0.85

The Casson Model was used in another study with the temperature kept at 40°C. Figure 11 displays these findings. As shown, the plastic viscosity (internal resistance to fluid flow) and yield stress varies depending on the ingredients of the chocolate.

Brand Name	Temp. (°C)	Shear Rate (s^{-1})	Plastic Viscosity, η_∞ (Pa s)	Yield Stress (Pa)
AmiCoop	40	5–60	2.5	10.9
		60–5	2.5	9.1
Cailler (Nestle)		5–60	3.7	16.5
Cadbury Dairy		5–60	4.4	33.7
Milk GB		60–5	4.8	20.5
Galaxy GB		5–60	4.7	78.0
		60–5	4.9	49.2
Lindt F		5–60	1.8	10.3
		60–5	1.9	8.9
Nestle F		5–60	2.6	19.8
		60–5	2.6	15.9
Poulain F		5–60	2.7	19.4
Suchard Milka		5–60	1.9	12.2
		60–5	1.9	9.4
Yorkie GB Dark chocolate		5–60	4.2	10.0
Bournville		5–60	3.9	42.9
Black Magic		5–60	2.4	10.1
Cote d'Or F		5–60	4.0	23.8
Cremant		5–60	2.70	25.8
Terry Plain GB		5–60	1.90	20.4
		60–5	1.90	19.0
Nestle White		5–60	4.70	14.2
Rowntree White		5–60	6.20	9.6
Suchard White		5–60	2.40	38.5

Note: The rheological method is Haake RV20.

Figure 11: Casson Model Parameters of Commercial Chocolate Samples (1991)[12]

Bolliger[13] also studied cocoa butter and chocolate using a shear crystallizer. The liquid was preheated to 50°C and pumped through to the stirring vessel, which had a gap width of 6 mm between the cylinder and rotor shaft. Rotor speed range was 300 – 1300 rpm. For cocoa butter, the mass flow rate was 20 kg/h and the exit temperature was 25°C. For chocolate, the mass flow rate was 27 kg/h and the exit temperature was 28.7°C. Using differential scanning calorimetry (DSC), a sample size of approximately 20mg was measured. The insert temperature was 24°C, with a starting temperature of 25°C and a heating rate of 4°C/min, ending at 40°C. Viscosity was measured in a viscometer and temper curves with a Tempermeter. Near-Infrared Spectroscopy was

used to calculate viscosity, crystal content, slope, and solidification time. Solidification time and slope decreased with and increasing rotor speeds, where as viscosity and melting enthalpy increased. With an increase of crystal content %, there was an increase in viscosity, showing that higher rotor speeds produce greater crystal content.

Figures 12 and 13 display these results.

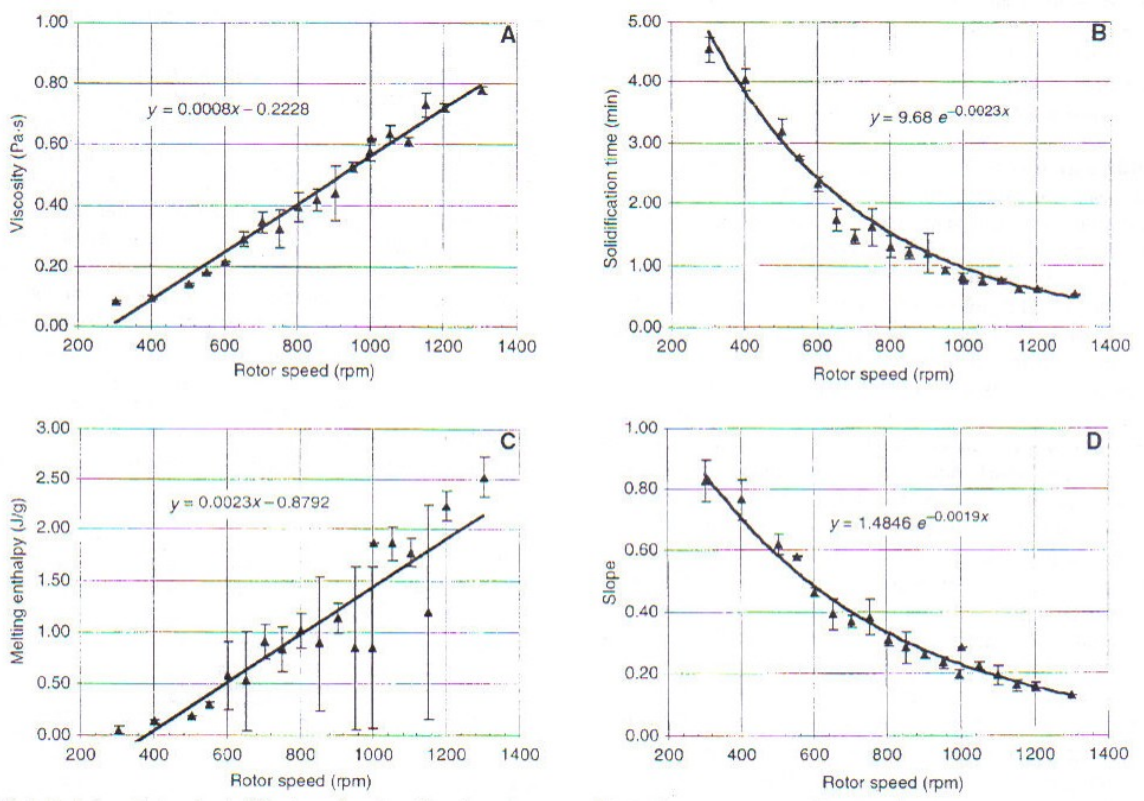

Figure 12: Effects of Rotor Speed on Various Elements
(A: Viscosity at shear rate = 28.4 s^{-1}, t = 21.7s; B: Solidification time t, t = time reading at viscosity of 1 Pa.s ; C: Melting enthalpy, heating rate of 4°C/min from 25°C to 40°C; D: Slope values, slope = tangent in second point of inflection of cooling curve)

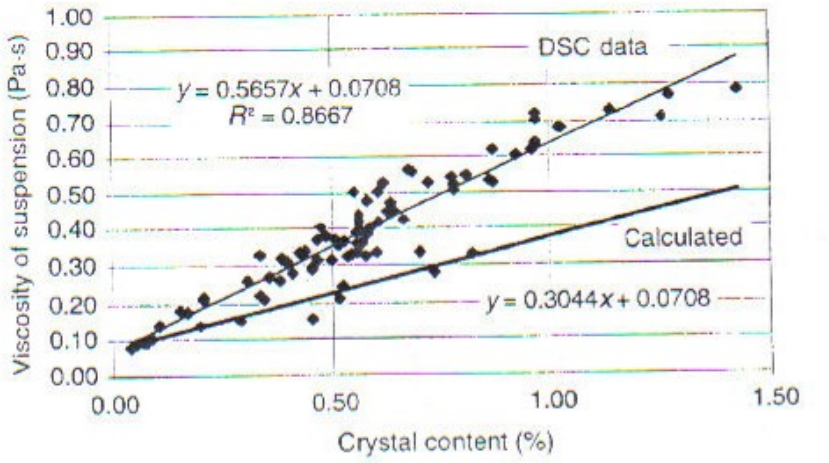

Figure 13: Viscosity as a function of crystal content %

In chocolate, the crystallization of cocoa butter is used to create certain characteristics. In order to produce desired characteristics, the size, shape, and polymorphic state of crystals must be controlled. In addition, the development of the crystals and the rheology must also be controlled. Toro-Vazquez[14] studied these rheological measurements using a helical ribbon impeller, and isothermal crystallization thermograms were done using DSC. For DSC a sample approximately 8 mg was held at 80°C for 20 min, and cooled to 53°C at 20°C/min. It was held for 2 minutes at 53°C, and cooled at 1°C/min to the T_{Cr}. The T_{Cr} chosen were 18, 18.5, 19, 20, 22, and 26.5°C. The peak melting temperature of the cocoa butter vs. crystallization temperature can be seen in Figure 13. The different stirring rates studied were static, 1 RPM, 120 RPM, and 400 RPM. Figure 14 shows that around a crystallization temperature of 22°C, the peak melting temperature is very similar for each stirring condition. However, if that crystallization temperature is exceeded, then the cocoa butter subjected to the stirring rate of 1 RPM has the highest peak melting temperature. A higher peak melting temperature is desired, because more energy is required to heat the butter, meaning there is greater crystal formation. As 22°C is approximately room temperature, it would be desirable to

have the crystallization temperature of the chocolate be close or above this temperature. If this is the case, then chocolate manufactures can allow the chocolate to cool to the temperature of the room as opposed to using more energy to cool the chocolate further than room temperature. Another benefit for having the crystallization temperature the same or above room temperature is that the temperature is going to be the ideal storage temperature for the chocolate. If the crystallization temperature is below room temperature, then changes may occur when the chocolate is allowed to reheat to room temperature.

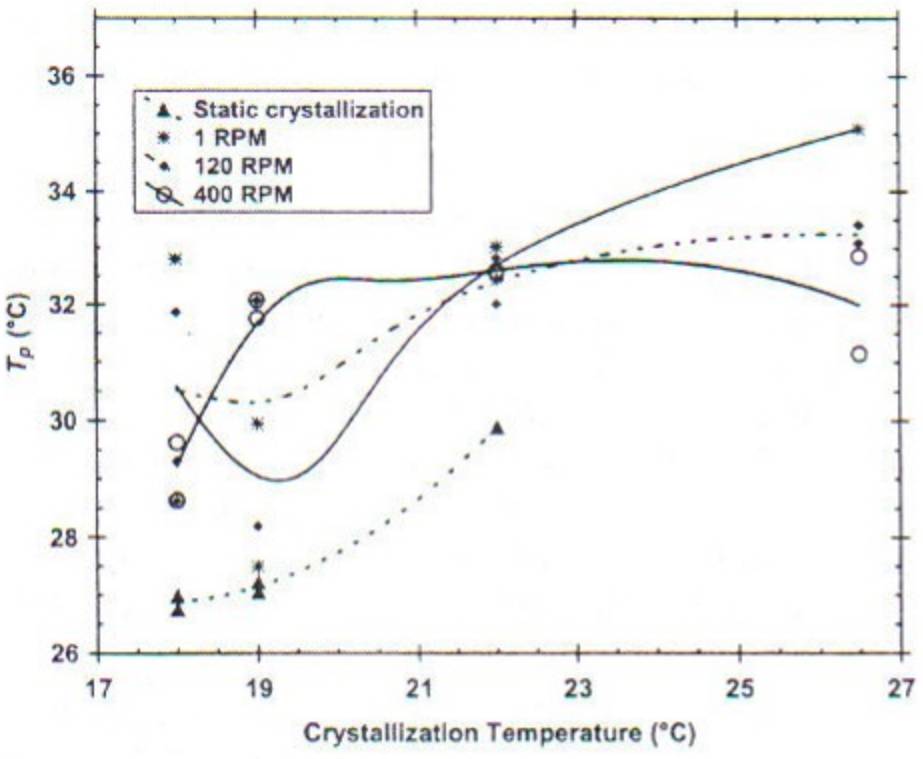

Figure 14: Peak Melting Temperature (Tp) for Cocoa Butter crystals vs. Crystallization Temperatures (°C)

2.6 Additional Concerns

Many of the studies explored the shearing of milk chocolate or cocoa butter, leaving gaps in research with chocolate liquor. An investigation in the microstructure and effects of shearing on chocolate liquor is needed to understand the varying nature of chocolate. Chocolate liquor is used as a base in many different chocolate applications.

Chapter 3: Objectives

1. Develop an understanding of the microstructure of chocolate.
2. Develop a method to shear dark chocolate at various rates.
3. Investigate the effect of shear rate on chocolate's microstructure.

Chapter 4: Design of Experiments

Equipment List:

- 100% Cocoa Chocolate
- Wax Paper
- Ziploc Bags
- Perkin-Elmer DSC 7
- DSC Aluminum Cups
- Brookfield Programmable Rheometer Model DV-III+
- X-ray diffraction
- Denver Instrument Company (A-250) scale
- Thermocouple wire
- Copper capsule with cork top
- Hot plate
- LabView 7
- Thermometer – Type T
- Slides
- Superglue
- Razor Blade

The type of chocolate selected for the experiment was 100% Cacao dark chocolate made by Ghirardelli. This type of chocolate was chosen for the absence of milk products, which would add additional interference to experiments. The Ghirardelli brand was used because it was readily available. Once the type of chocolate was determined and obtained, the method to apply various shear rates to the melted chocolate and tests to quantify the results were chosen.

In order for the shear rates to be applied, the chocolate must first be re-melted. When chocolate is re-melted, there remains a crystal history based on previous tempering. However, if the chocolate is held at a high temperature for an extended amount of time, the crystal history is erased. The temperature chosen for this experiment was 50°C, with the chocolate held at this temperature for 20 minutes. This will be

sufficient to erase the crystal history of the chocolate from the tempering process performed by Ghirardelli.

The shear rates initially chosen for the experimentation were $10s^{-1}$, $20s^{-1}$, $30s^{-1}$, $40s^{-1}$, and $50s^{-1}$ based on similar investigations on chocolate liquor and cocoa butter.[13] One study used $15s^{-1}$ and $30s^{-1}$[12], another 28.4^{s-1}[13], and finally shear rates ranging from $5\text{-}60^{s-1}$ as shown in Figure 11[12] were tested in another study. The overall range of these numbers is $5 - 60s^{-1}$, with an average around $30s^{-1}$. Therefore, $30s^{-1}$ was chosen, then shear rates that were lesser and greater. The shear rate $10s^{-1}$ was chosen as the least shear rate because the study that tested $15s^{-1}$ already determined that lower shear rates produced unstable crystalline particles, however that was milk chocolate rather than dark chocolate. These shear rates typically correspond to the shear rates where the chocolate viscosity decreased appreciably from the zero shear viscosity. Milk chocolate has more ingredients, such as sugar and milk, which increases the interference with crystallization. The fact that chocolate shows shear thinning behavior[12] based on Figure 8 must be taken into consideration. This behavior is documented using the following equation.

$$\eta = K(\dot{\gamma})^{n-1} \qquad (4)$$

Where η is viscosity, K and n are constants, and $\dot{\gamma}$ is shear rate.

To melt the chocolate for shearing, it was determined the best method was to heat the chocolate in the cup for the rheometer while attached to the machine. This would prevent the chocolate from cooling if transferred from one container to another and would keep the chocolate melted throughout shearing. A beaker filled with water was placed around the cup and heated with a hot plate, using a thermometer to monitor the

temperature. The crystal history of the chocolate was erased, and then sheared while maintaining a temperature of 50°C to keep the chocolate melted.

Once the chocolate was sheared, the samples were viewed with an optical microscope. The highest magnification possible without the chocolate touching the lens of the microscope was 20x. The samples were attached to a slide using superglue. Some were sheared with a razor blade to expose an even surface of chocolate. To obtain a higher magnification image of the chocolate samples, pictures were taken with a Scanning Electron Microscope (SEM).

Differential Scanning Calorimetry (DSC) was used to monitor the reheating and cooling of the chocolate. The chocolate was heated from room temperature to 50°C to ensure the chocolate was fully melted, as the highest melting temperature for any crystal form is 36°C. The heating rate was chosen to be 5°C/min based on previous DSC experiments on chocolate.

Another method to observe the heating and cooling of chocolate was the use of a thermocouple and the program LabView 7 to record the temperature changes. This allowed the temperature peaks during heating and cooling of chocolate that relate to crystallization to be seen at their respective temperatures. A container was made out of ¾" copper tubing to contain the chocolate. The dimensions were chosen based on the surface area (SA) to volume (V) ratio of the cup used for the rheometer. The basic dimensions for the rheometer cup and copper capsule are shown in Figure 15.

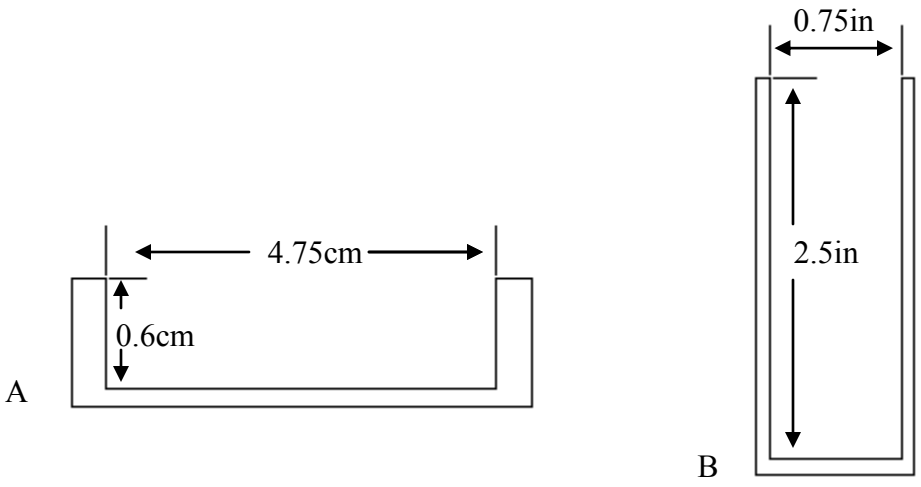

Figure 15: Drawing and dimensions of A) Rheometer cup and B) Copper Capsule

The cup for the rheometer has a SA/V ratio of 2.42cm^{-1}. Copper tubing with a diameter of ¾" tubing was available, so the length was chosen to be 2.5in to give a SA/V ratio of 5.75in^{-1}, or 2.3cm^{-1}. A cork top was designed to keep the thermocouple in the center of the chocolate for accurate reading. CAD drawings of the designed capsule and cork are shown in Figures 16 and 17.

The container and chocolate were placed inside a teapot filled with water, submerging the container so that the chocolate would be under water level, but the container would not be completely submerged. The teapot was then placed on a hot plate. The water barrier's purpose was to provide a slow and even heating to the chocolate, as opposed to quicker heating if placed directly on the hot plate.

X-Ray Diffraction was chosen to aid in the determining of the main ingredients that effect chocolate. The chocolate was placed in a holder so that the x-ray would hit the chocolate at the center of the piece. Only larger pieces of chocolate could be used for the x-ray diffraction, which limited the amount of diffraction runs that could be done.

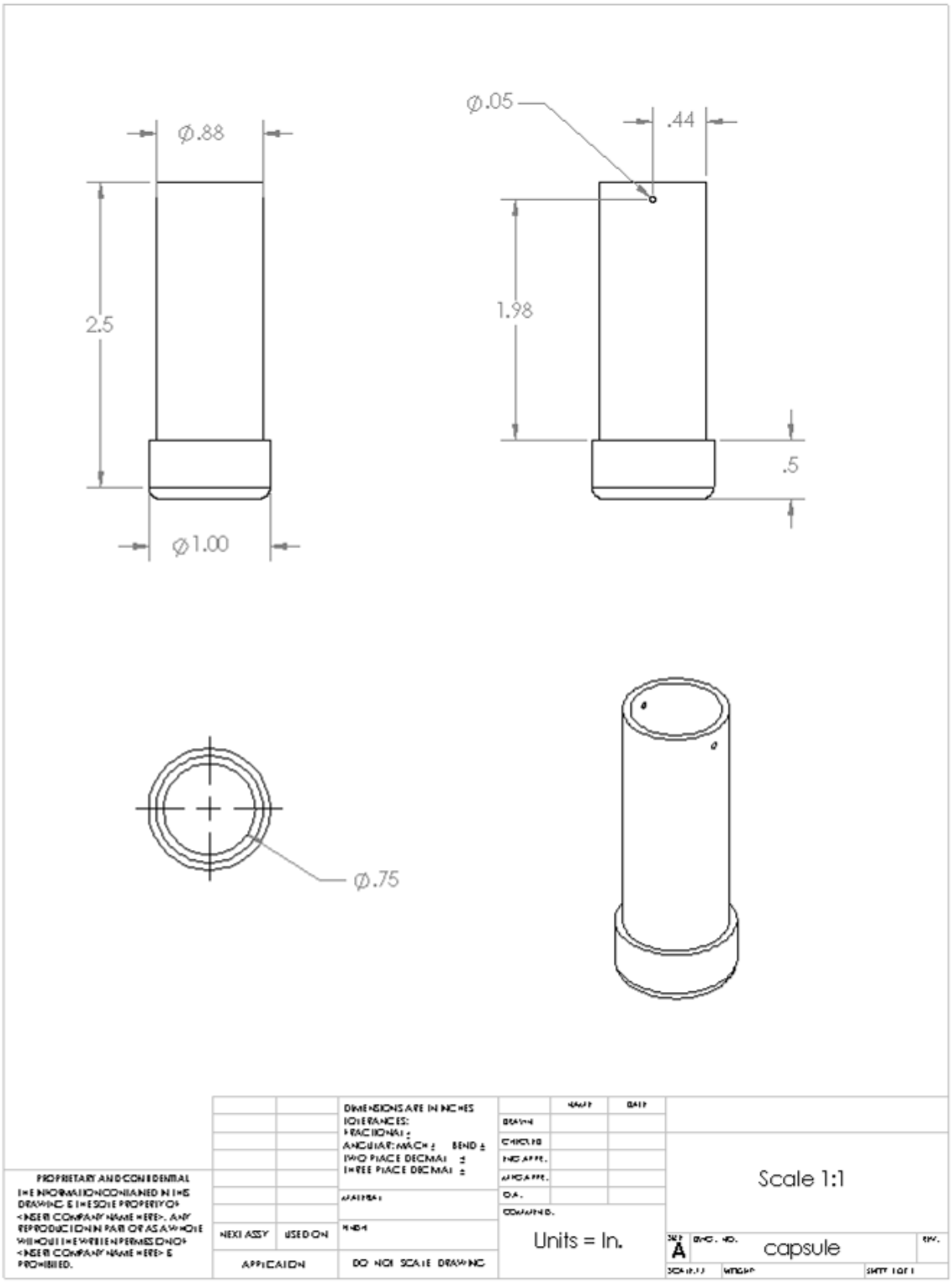

Figure 16: CAD drawing of copper capsule

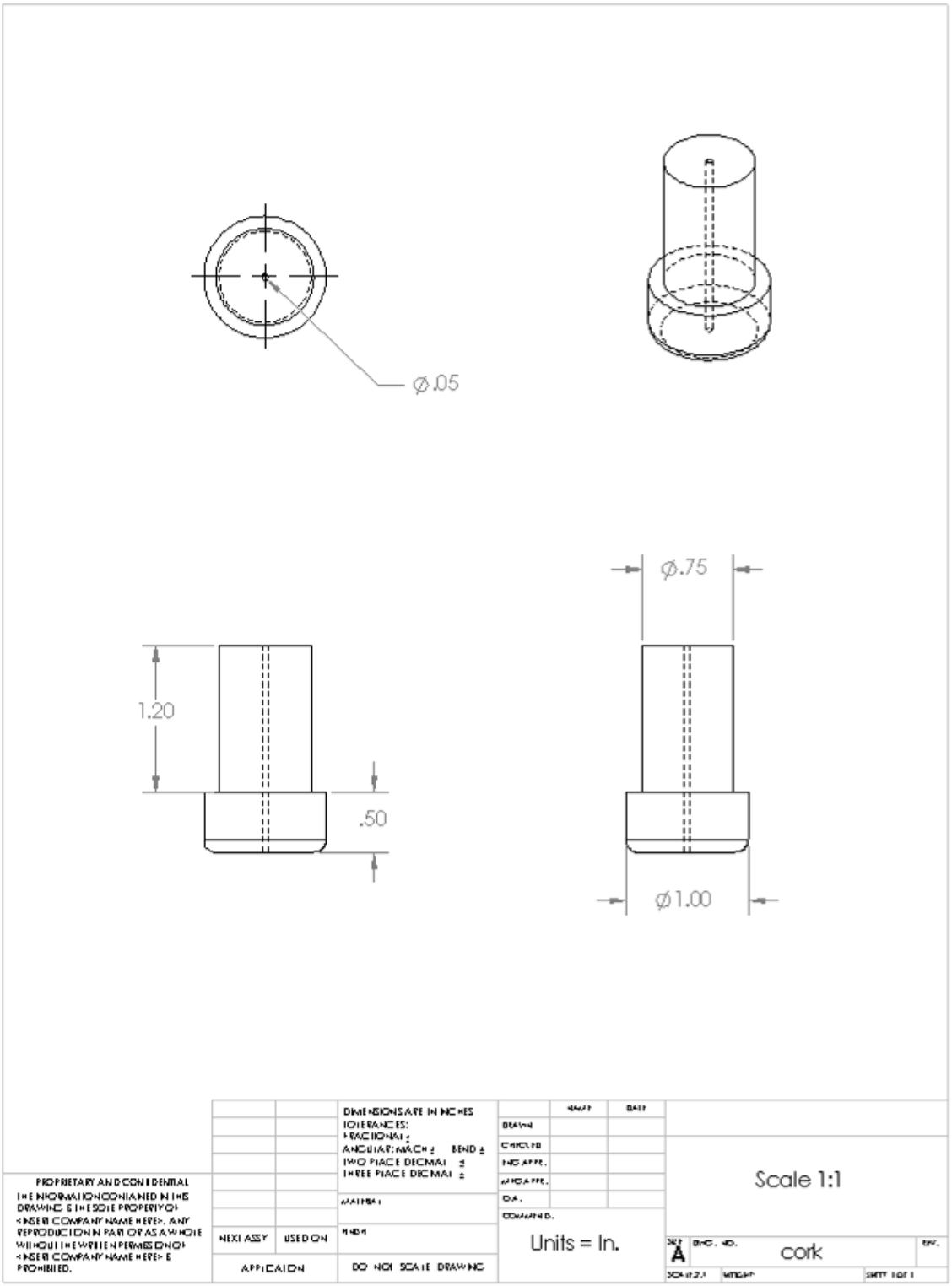

Figure 17: CAD Drawing of cork top

Chapter 5: Experimental Procedure

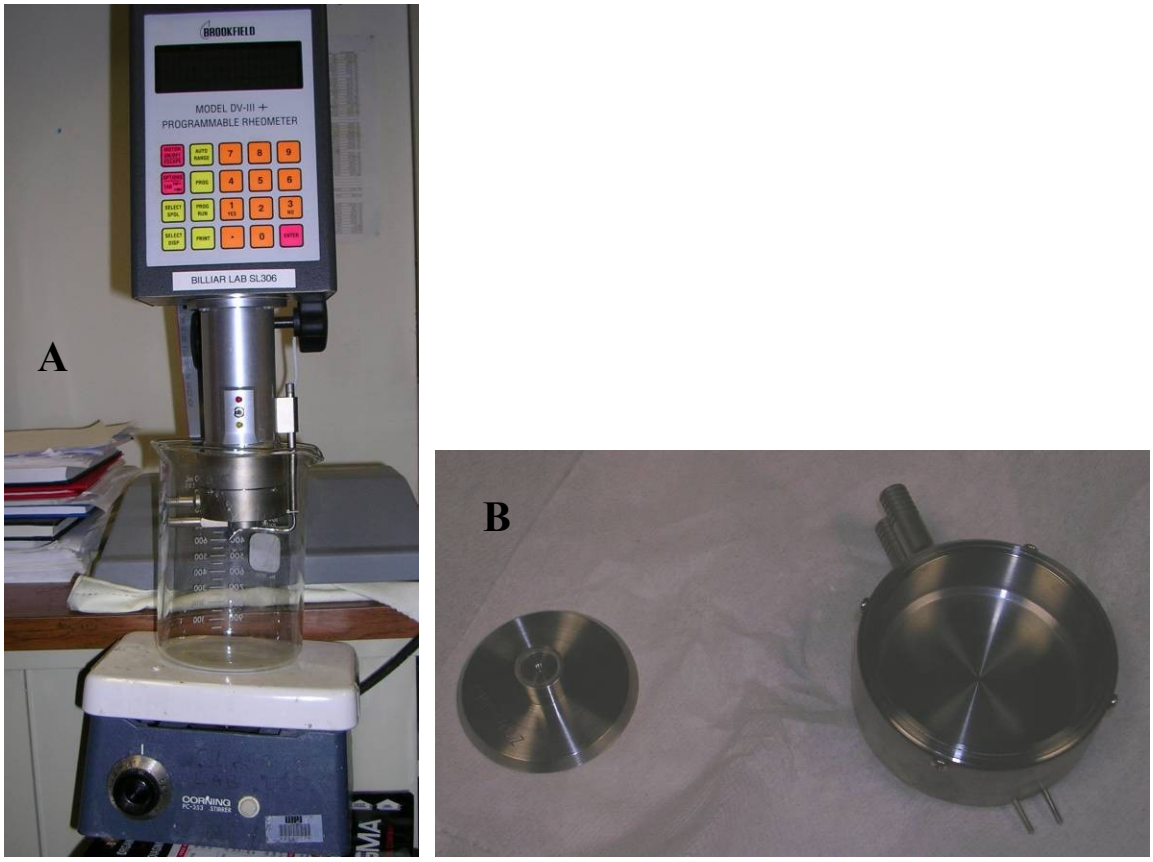

Figure 18: Brookfield Programmable Rheometer Model DV-III+
With A) Beaker and hot plate set up B) Cup and disk

5.1 Procedure for Rheometer

Samples were taken from the original chocolate by finely shaving portions with a razor blade. The samples were weighed using a Denver Instrument Company (A-250) scale, with the target weight 0.95g +/- 0.05. The sample was then placed into the cup of the Brookfield Programmable Rheometer (Model DV-III+), with a diameter of 5.3cm and a depth of 0.6cm. A rheometer would be the equipment used to administer the shear rates. However, the rheometer only allowed the input of a value in RPM, so the final shear rates

had to be adjusted to account for this limitation. The final shear rates used were 10.5 s^{-1}, 20.3 s^{-1}, 29.2 s^{-1}, 40.5 s^{-1}, and 50.3 s^{-1}. These values were obtained using the following linear equation, which was created based on data gathered from the rheometer.

$$y = (0.135)x - 0.42 \quad (5)$$

In this case, y is in RPM and x is s^{-1}. Each shear rate was applied to the largest sample size the rheometer could accommodate, which was 0.95g, for three cycles. The shear rate was administered for 400s based on a study that showed that samples held at a shear rate over 400s had the greatest crystal formation[12]. In order for the rheometer to apply the chosen shear rates and length of time, the chocolate must be in a liquid state. A beaker of water was placed around the cup for heating. The water was heated with a hot plate to 50°C and kept above that temperature for 20 minutes. After that period, the rheometer applied the specified shear rate for 400s. The disk attached to the rheometer used for shearing was 4.75cm in diameter, leaving a .28cm gap around the circumference. The water was removed and the cup was taken off of the rheometer, letting the chocolate sample cool to room temp, or approximately 20°C. The cooled samples are scraped from the cup and are stored in a zip block bag at room temperature. A flow chart for this procedure is shown below in Figure 19.

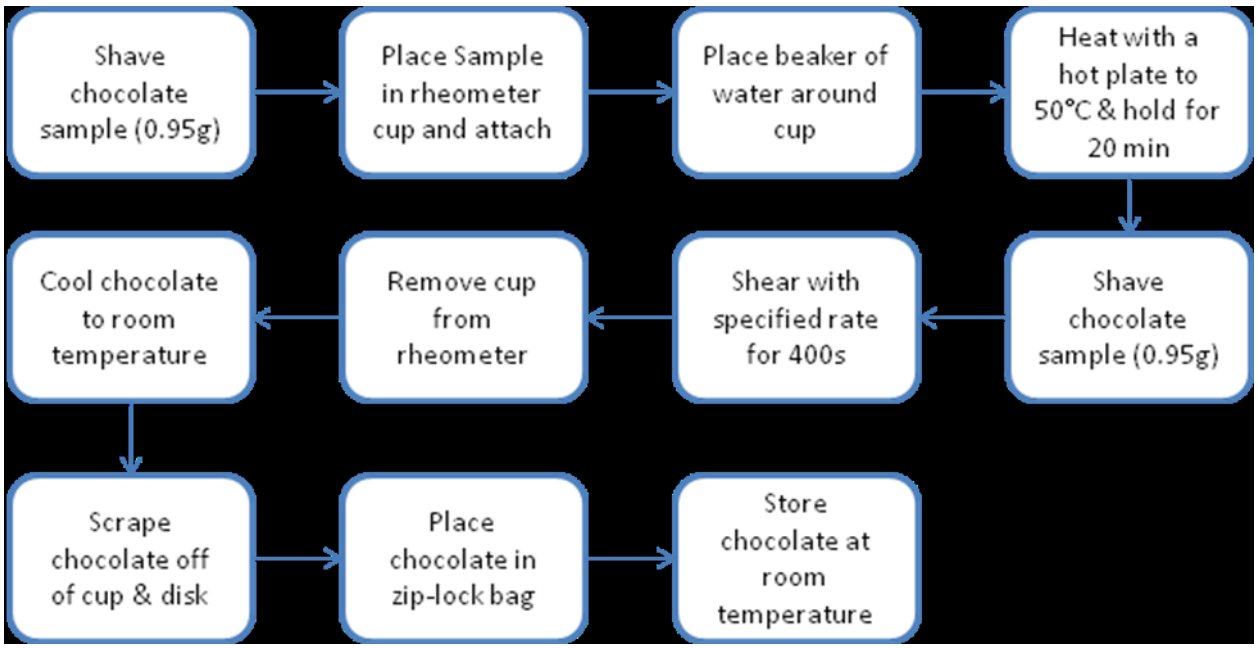

Figure 19: Flow Chart for Rheometer Procedure

5.2 Procedure for Thermocouple Data

Sample was prepared and placed in the copper tubing as shown in Appendix C. The copper tubing was placed in a teapot full of water, which was on a hot plate. A drawing of the set up can be seen in Figure 20. The thermocouples are labeled 1 and 2 in the figure, where 1 measures the room temperature and 2 the temperature of the chocolate.

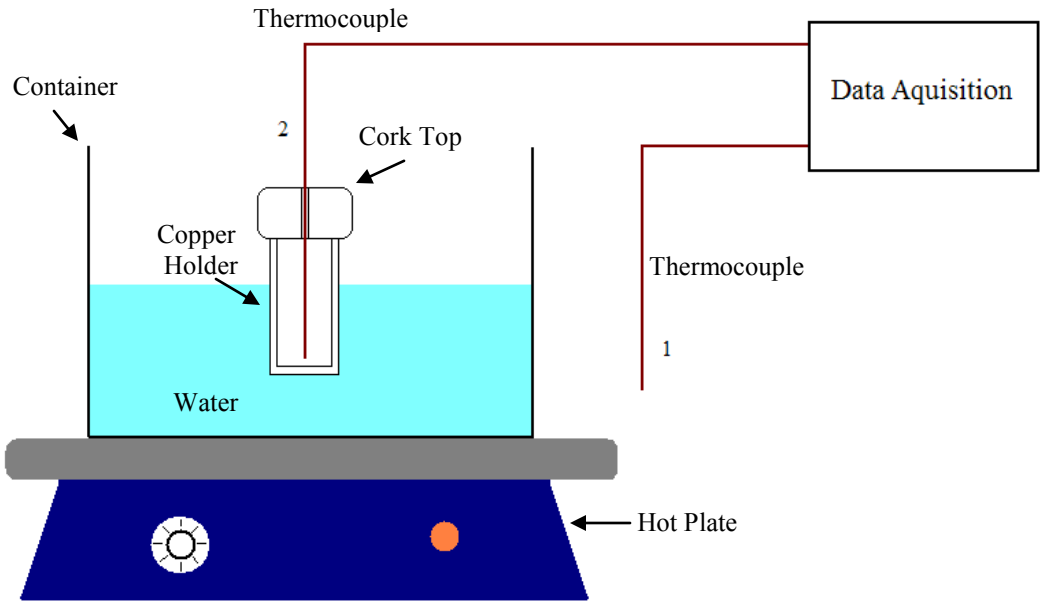

Figure 20: Set up for Thermocouple Procedure
1)Thermocouple measuring room temperature 2)Thermocouple measuring chocolate temperature

The hot plate was turned to its mid heat setting to allow the chocolate to heat to 55°C. After reaching this temperature, the heat was turned off and the chocolate was allowed to cool to room temperature. The heating and cooling of the chocolate was recorded using the data acquisition software LabVIEW 7 in a program specifically written for this project (Appendix I).

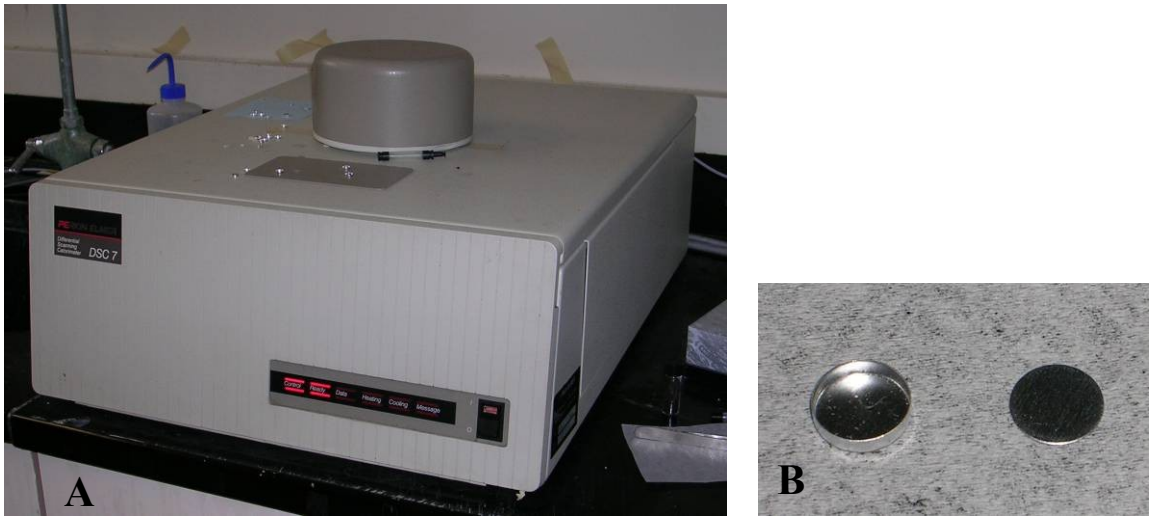

Figure 21: A) Perkin-Elmer DSC 7 B) Aluminum cup

5.3 Procedure for Differential Scanning Calorimetry (DSC)

Samples are prepared by placing pieces of chocolate weighing 6-10 mg are placed in an aluminum cup with a lid. The samples are then placed into the machine, a Perkin-Elmer DSC 7, and heated in the temperature range 25°C to 50°C at a heating rate of 5°C/min. The thermal transitions occurring within this temperature range were recorded and plotted. The transformation temperatures and change in enthalpy were calculated.

5.4 Procedure of X-Ray Diffraction

To investigate the chocolate using x-ray diffraction, a GE/Diano X-Ray Diffractometer utilized a copper tube. The X-Ray Diffractometer was powered through pulling the main power on from the transformer box. The water line was turned on and the line button was pressed. After two minutes, the X-Ray "on" button was pressed and the tube amperage knob was moved from 1 to B for 15 mA of current. The shutter box was turned on and pressed open for the first time. The key for the blue controller box was then turned to on. After the Tube L key was illuminated, the Chan B, Counts/sec and Print buttons were pressed. Worcester Polytechnic Institute's XRD program was opened

on the computer. This system was then allowed to warm up for a minimum of thirty minutes before readings are taken of the sample.

The sample was prepared by taking a large piece of the cooled shear chocolate and placing it in the holder of the machine. The holder is tightened and the safety panes on the machine are closed. The shutter is locked opened and the XRD program is started.

Chapter 6: Results

6. 1 Optical Microscope

Chocolate is made of many different ingredients including cocoa butter, cocoa powder, and sugar crystals. The following pictures are taken at 20-x magnification with an optical microscope. The observations made were based on a comparison of the photographs. White bands are assumed to be fat accumulations, large clear crystals are assumed to be sugar crystals, and small black particles are assumed to be cocoa powder.

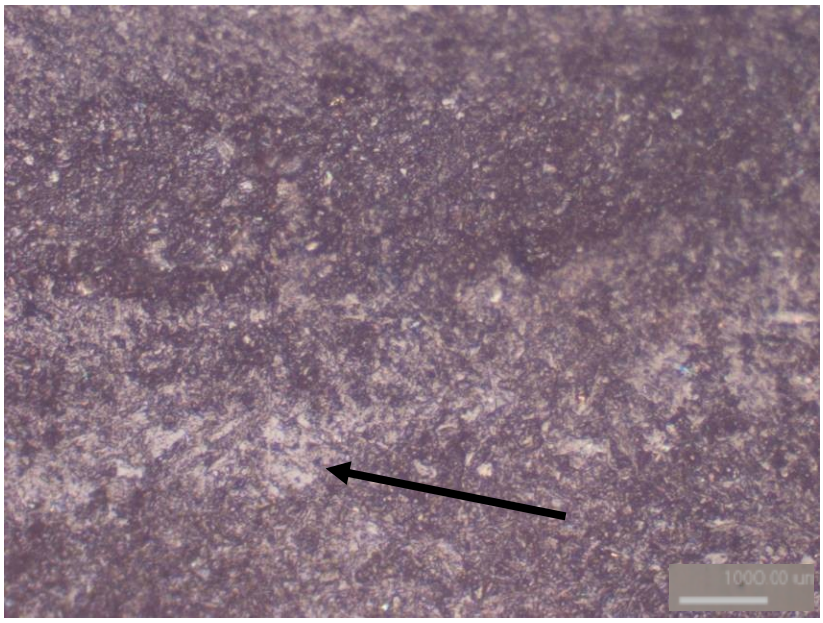

Figure 22: Unsheared Chocolate with fat bloom band (shown by arrow)

The unsheared chocolate in Figure 22 shows tiny sugar particles that formed along the surface of the chocolate. Across the chocolate is a white fat band that has begun to form. Bands of fat are not favorable for the structure of the chocolate should be uniform.

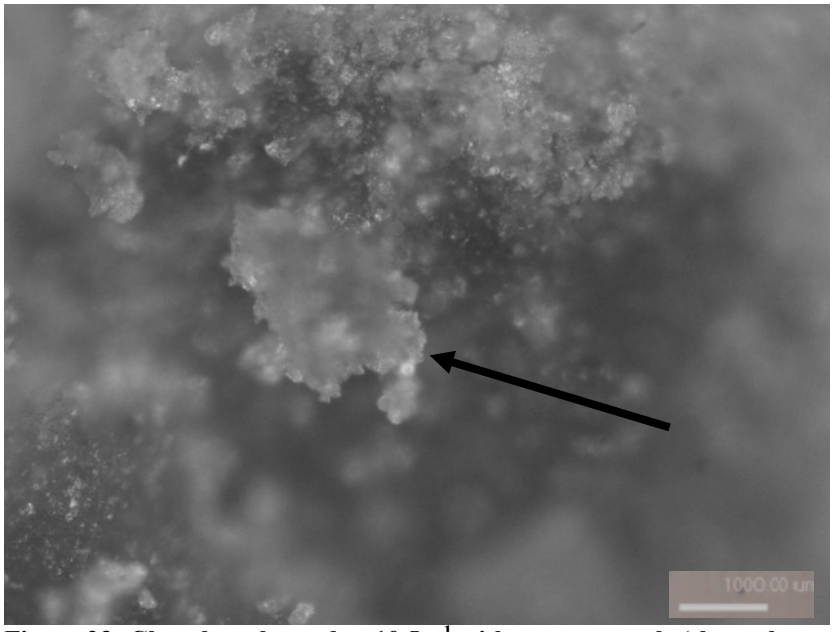

Figure 23: Chocolate sheared at 10.5 s^{-1} with sugar crystals (shown by arrow)

Figure 23 depicts the sugar crystal formation on the surface of the chocolate. The unfocused sections show that this piece has an uneven surface, meaning that the sugar crystals are forming on different layers than the cocoa crystals. A build up of sugar crystals is not desirable, and the chocolate should not have a noticeable separation of layers.

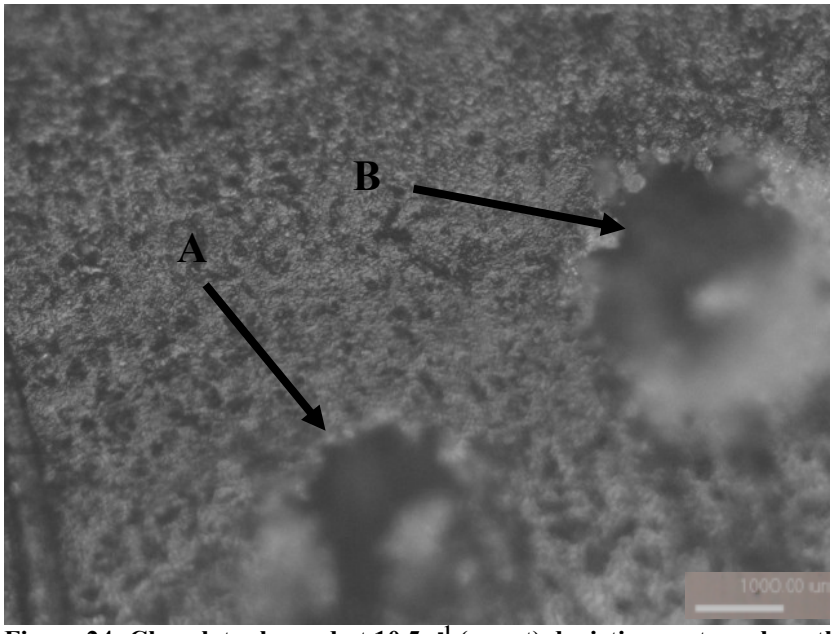

Figure 24: Chocolate sheared at 10.5 s^{-1} (uncut) depicting craters along the surface (Shown by Arrows A & B)

Figure 24 depicts an uncut surface of the 10.5s^{-1} chocolate. There are deformities along the surface of the chocolate that resulted in 'craters'. These voids could be a result of air pockets that were formed during shearing. These pockets have created a place for sugar crystals to collect and should be avoided when processing chocolate.

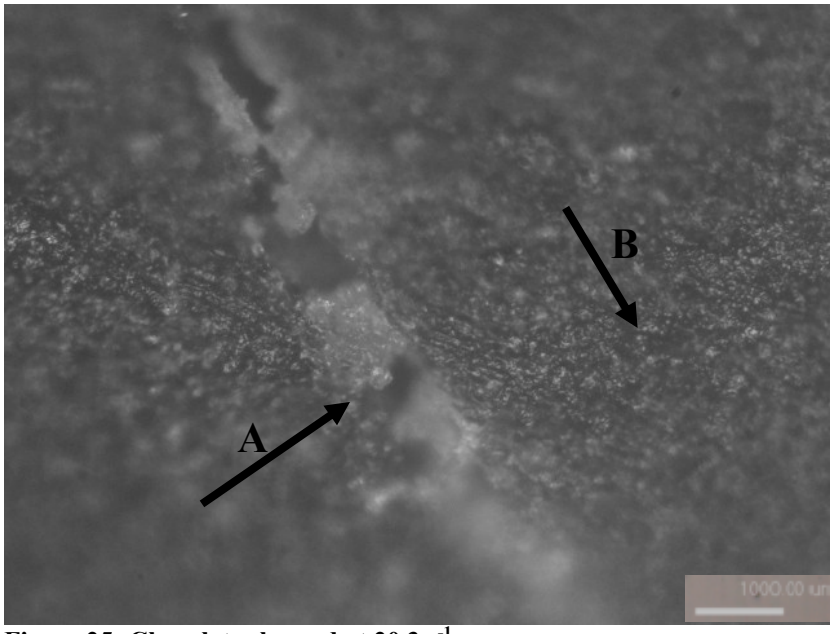

Figure 25: Chocolate sheared at 20.3 s^{-1}
Arrow A shows sugar crystal formations along a fracture in the chocolate; Arrow B shows uniform cocoa crystals

The chocolate sample in Figure 25 has a defect of a cluster of sugar crystals along a crack in the surface. However, the cocoa crystals are uniform beside the crack, which is considered a favorable structure.

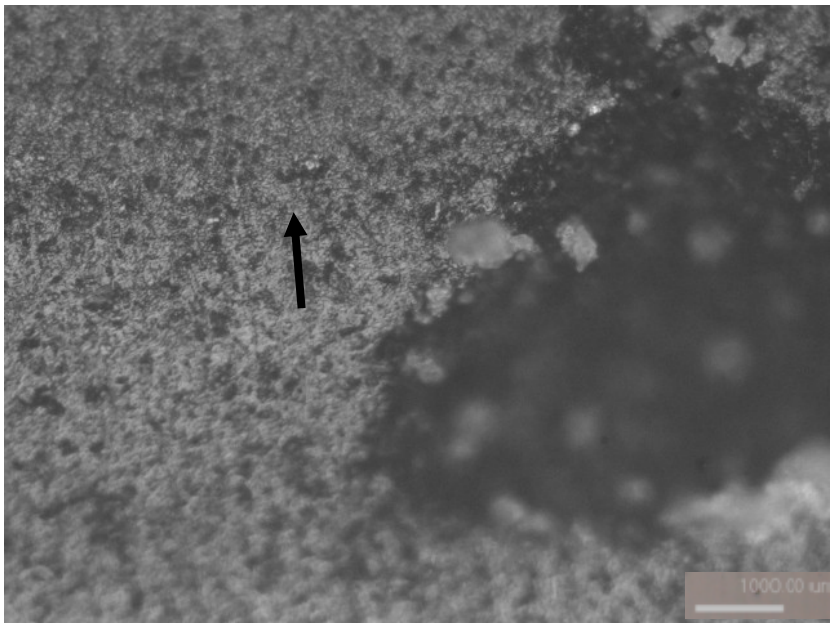

Figure 26: Chocolate sheared at 20.3 s^{-1}; Arrow shows the even cocoa crystals across surface of chocolate

The cocoa crystals are small and uniform along the even surface of the chocolate in Figure 26, which is a desirable structure. However in this section there is a void in the chocolate sample, which may result in fat bloom in the future.

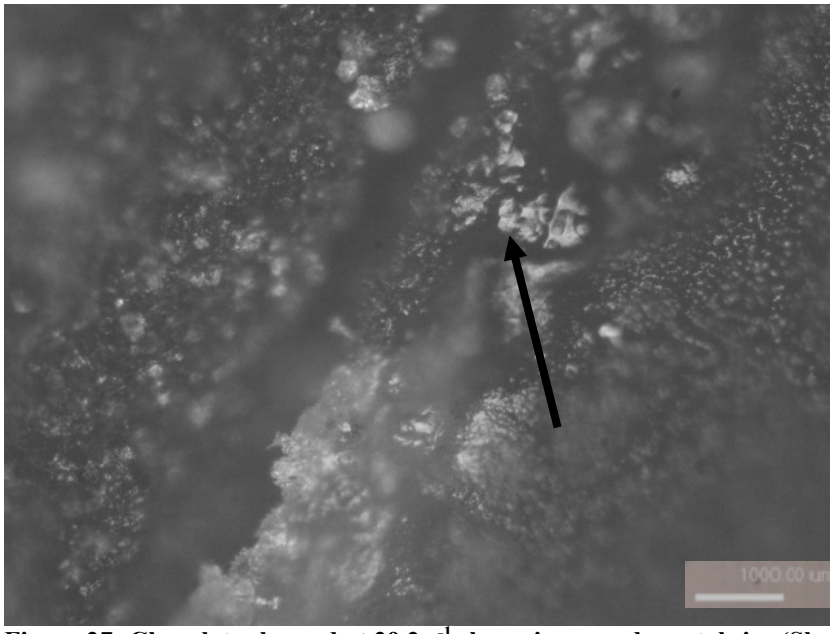

Figure 27: Chocolate sheared at 29.2 s^{-1} shows increased crystal size (Shown by Arrow)

Along the gap in Figure 27, the 29.2s^{-1} sheared chocolate has a greater amount of larger crystal formation. In the areas on the outskirts of this sample, the crystals become small and uniform. The crystals should be uniform without the chocolate,

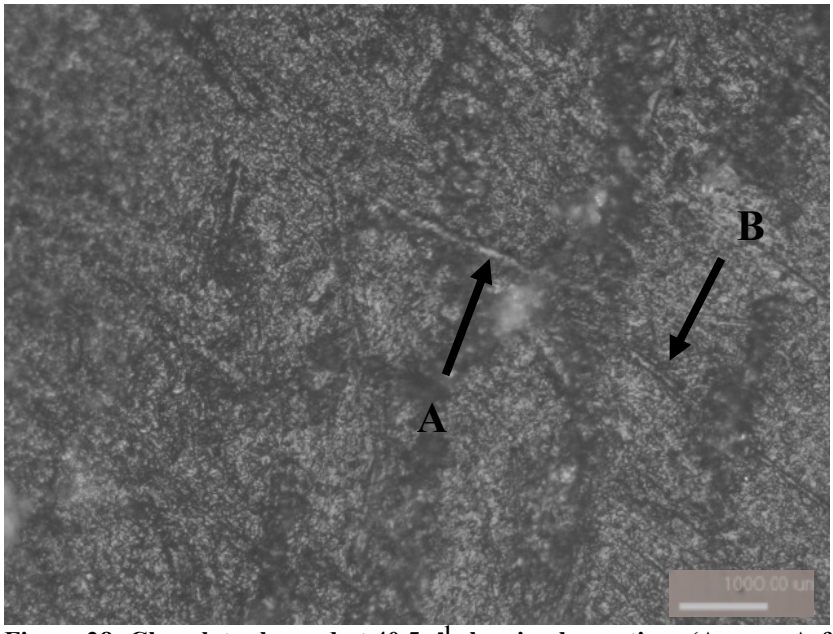

Figure 28: Chocolate sheared at 40.5 s^{-1} showing lacerations (Arrows A & B)

In Figure 28, the cocoa crystals appear to be small, but striations can be seen throughout the chocolate. This could be due to shearing with a razor blade to expose an

even surface of chocolate. The striations could also be a result of a conglomeration of sugar or cocoa crystals.

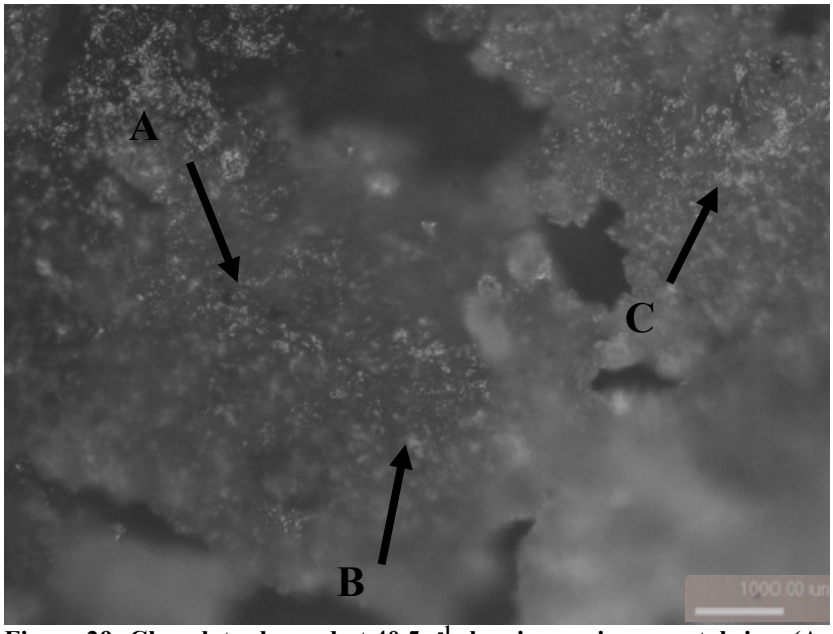

Figure 29: Chocolate sheared at 40.5 s^{-1} showing various crystal sizes (Arrows A, B, & C)

The cocoa crystals vary in size throughout the sample shown in Figure 29. This sample was not cut with a razor blade which could explain why the surface is in multiple planes, as the picture is not focused in all areas. There are also many gaps along the surface of the chocolate. This type of structure is not desirable since the gaps leave an opportunity for fat bloom to occur.

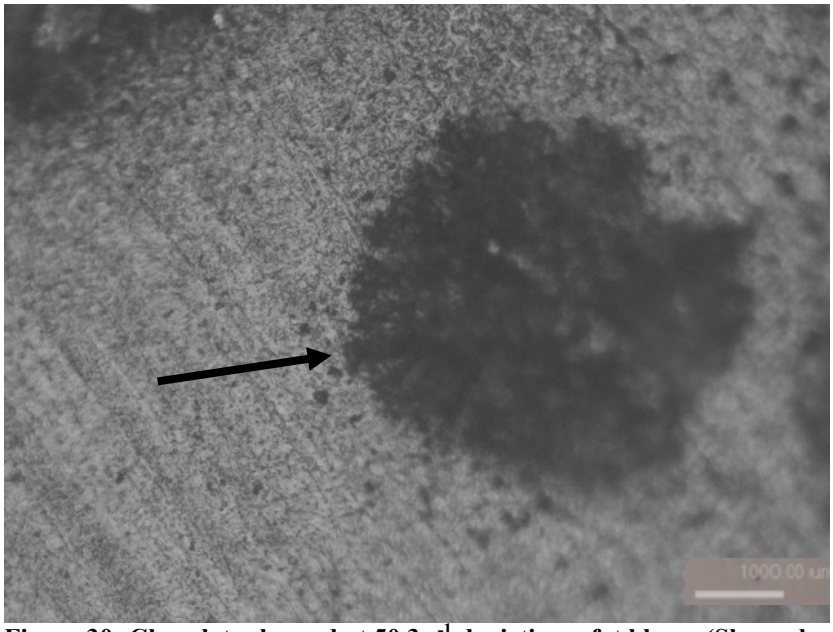

Figure 30: Chocolate sheared at 50.3 s^{-1} depicting a fat bloom (Shown by Arrow)

Figure 30 shows an example of fat bloom in the chocolate sample, which is categorized as a defect in chocolate and should be avoided. Since fat bloom occurs in voids, the chocolate sheared at the rate of 50.3s^{-1} had an increased number of voids after shearing. This could be due to a higher incorporation of air into the chocolate when the shear rate was applied.

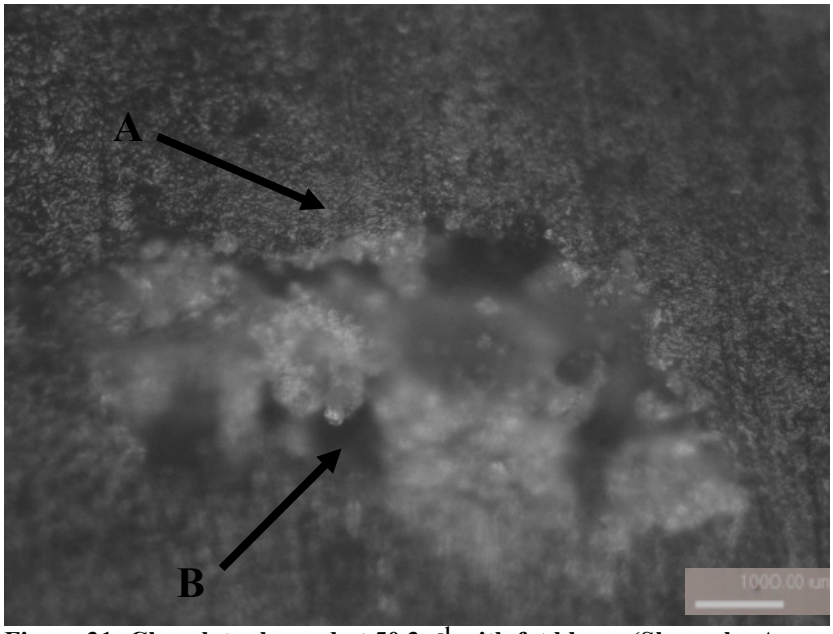

Figure 31: Chocolate sheared at 50.3 s^{-1} with fat bloom (Shown by Arrows A & B)

Another example of a fat bloom on the chocolate is shown in Figure 31. The cocoa crystals outside of the fat bloom are small and uniform. This shows a favorable structure if the fat bloom was eliminated.

Fat blooms occurred in greater frequency at $40.5s^{-1}$ and $50.3s^{-1}$ than the other three shear rates. This suggests that when chocolate is sheared at the higher shear rates the chocolate is more apt to fat bloom formations. This is an undesirable trait for chocolate, leading to the conclusion that $40s^{-1}$ and $50s^{-1}$ shear rates should not be used in the tempering process for chocolate.

A Scanning Electron Microscope (SEM) was used to view the chocolate samples. However, the samples melted due to the high temperatures and the technique of freezing the chocolate was not available. Therefore, SEM data could not be used to analyze the chocolate samples.

6.2 Thermocouple Data Readings

The thermocouple data was inconclusive. As shown in Figures 26 to 21, the results of the thermocouple data were filled with noise, making valid conclusions difficult to access. Because of these base readings, no further investigation was completed.

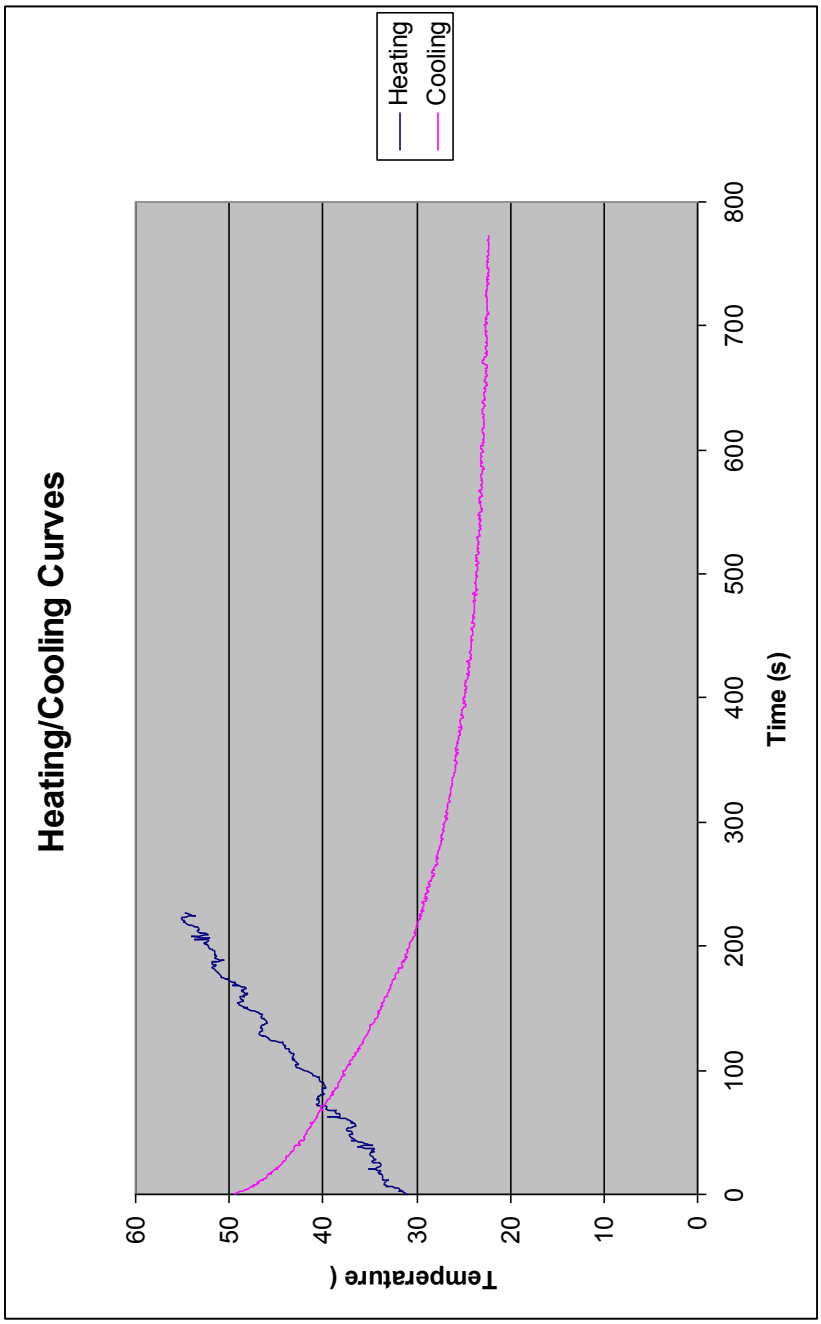

Figure 32: Heating and Cooling Curve Trial 1

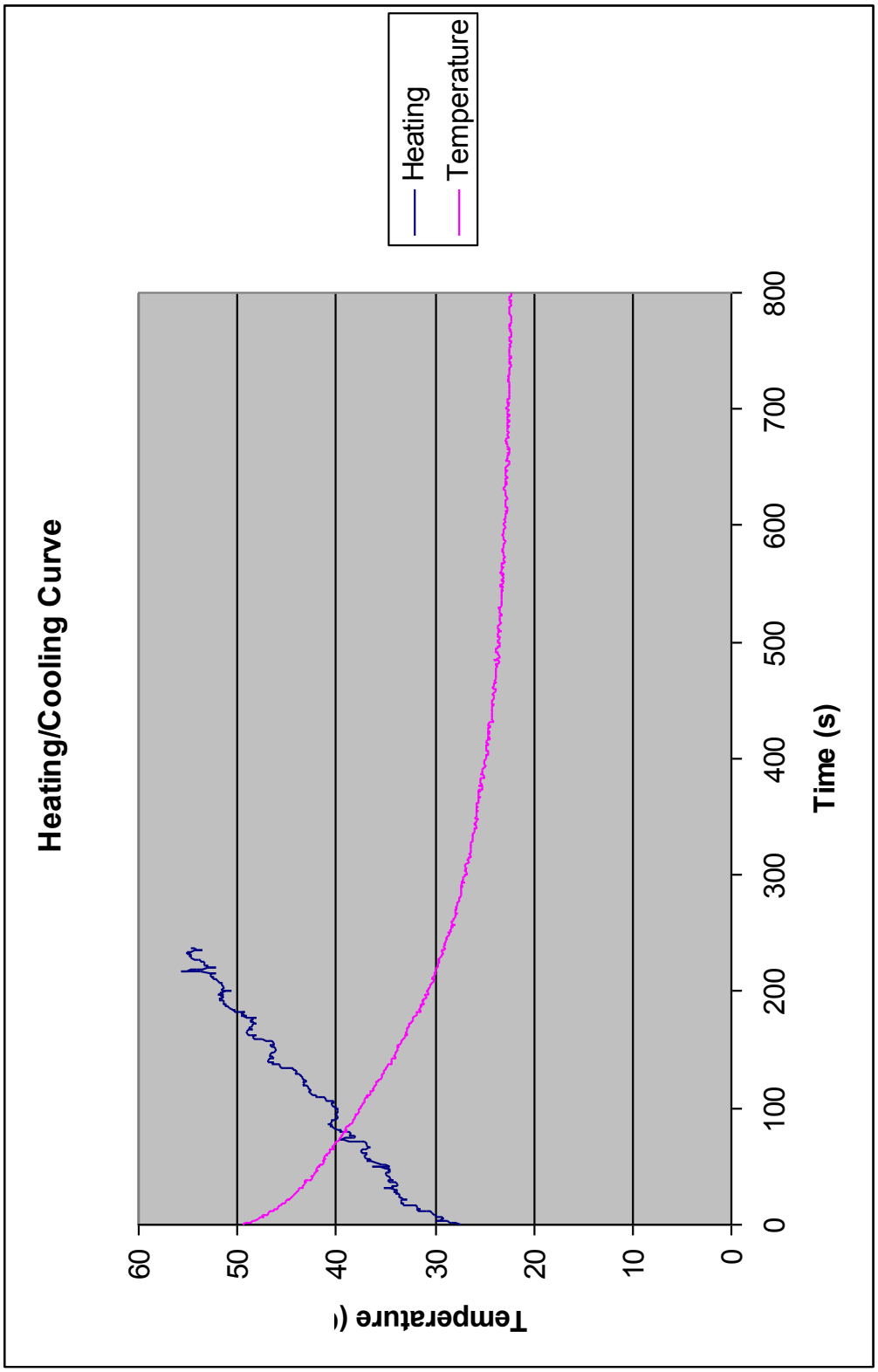

Figure 33: Heating and Cooling curve Trial 2

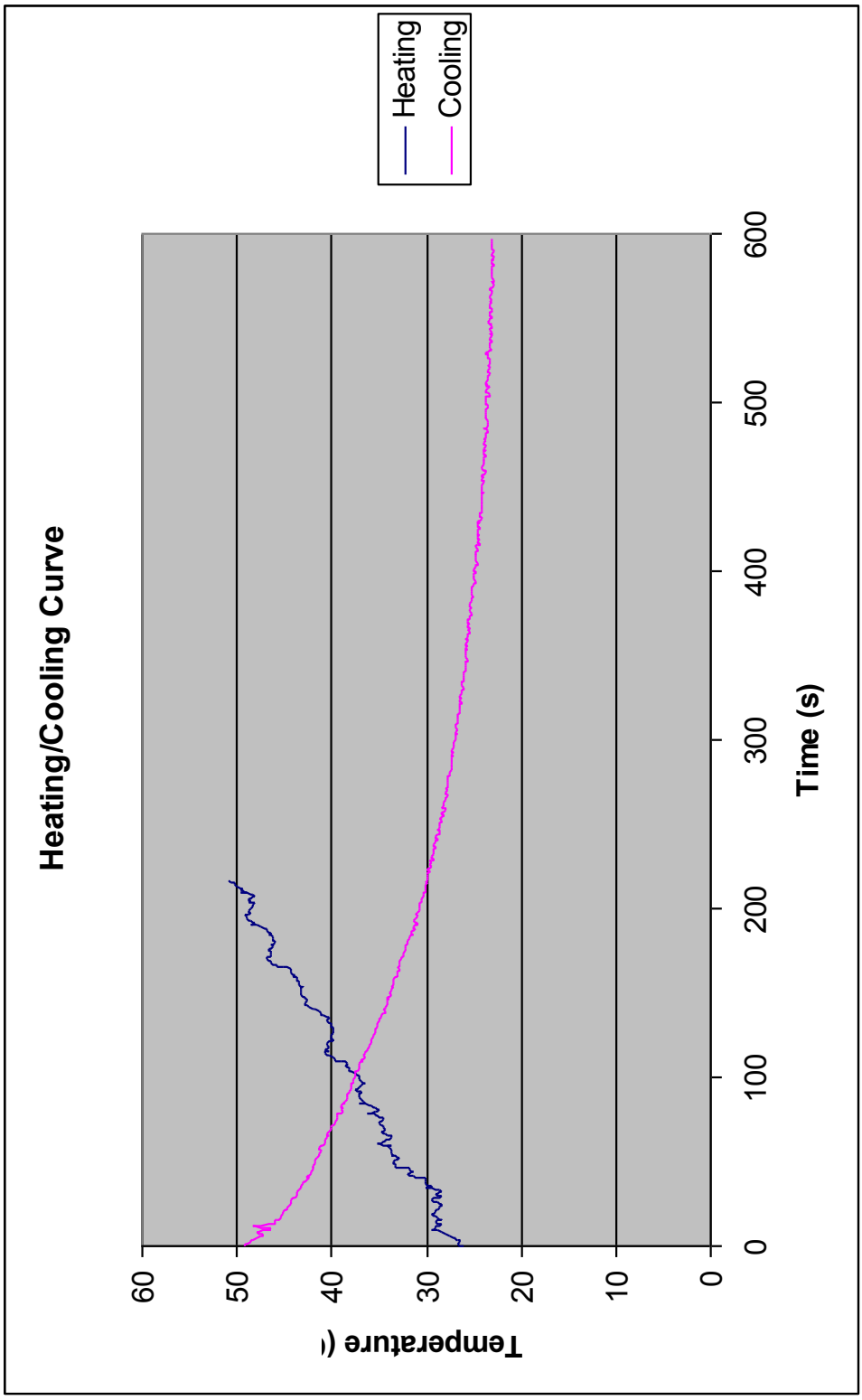

Figure 34: Heating and Cooling curve Trial 3

6.3 Differential Scanning Calorimetry

The effect of shear rate on the crystalline properties of dark chocolate was studied through Differential Scanning Calorimetry (DSC). The resulting graphs are shown in Figures 35 – 40.

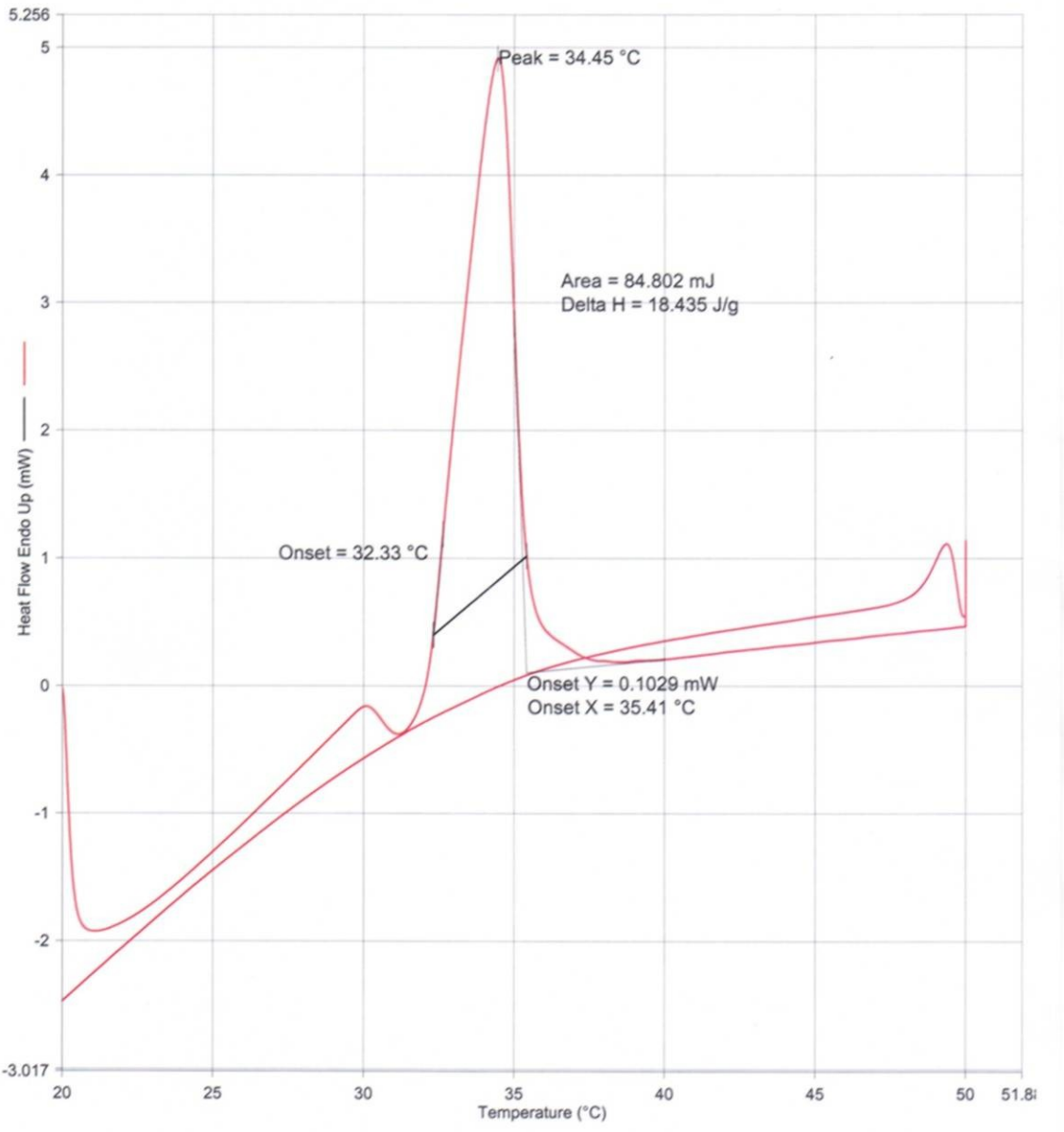

Figure 35: DSC data for unsheared chocolate (Heating rate of 5°C/min)

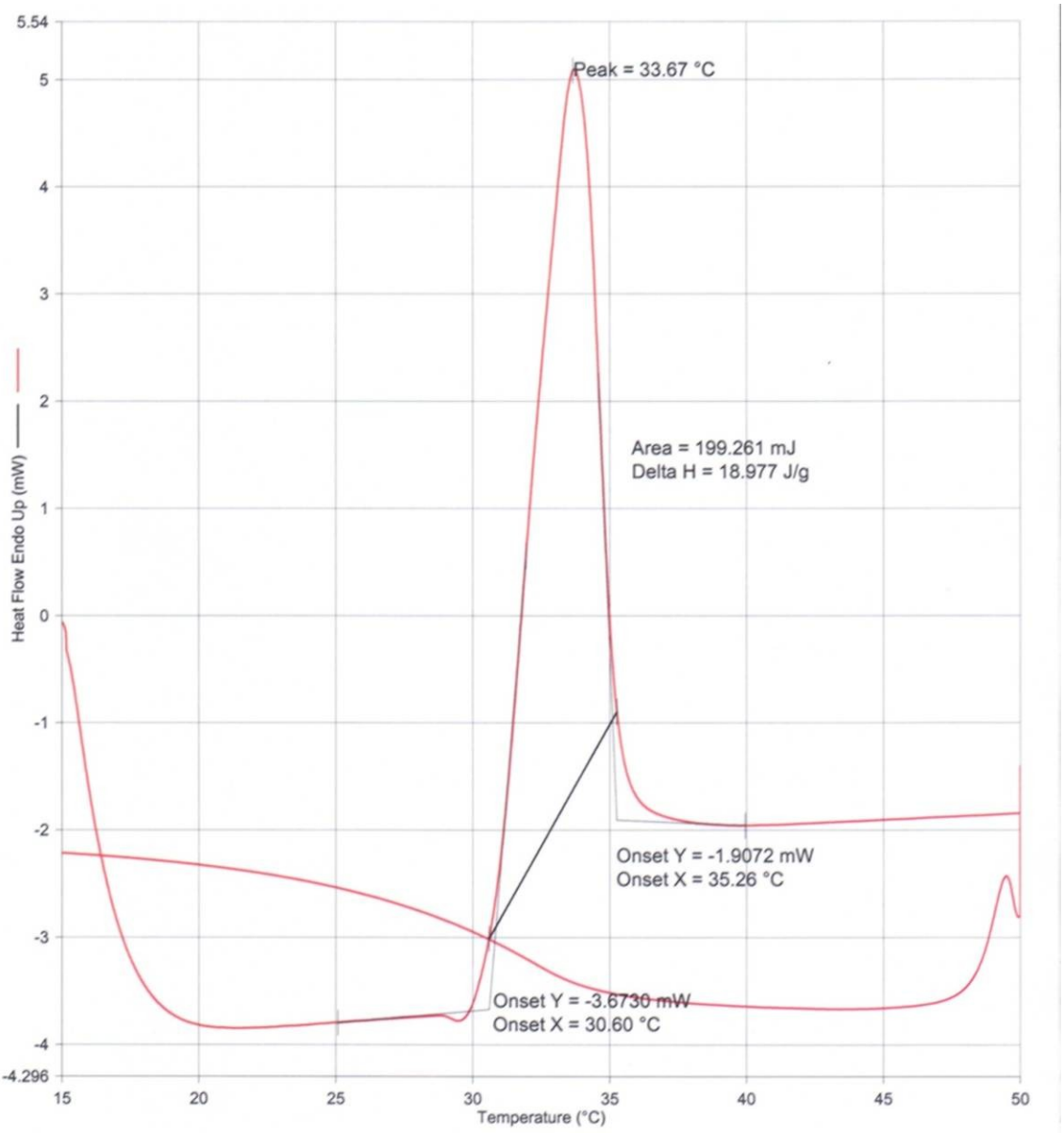

Figure 36: DSC data for shear rate 10.5s^{-1} (Heating rate of 5°C/min)

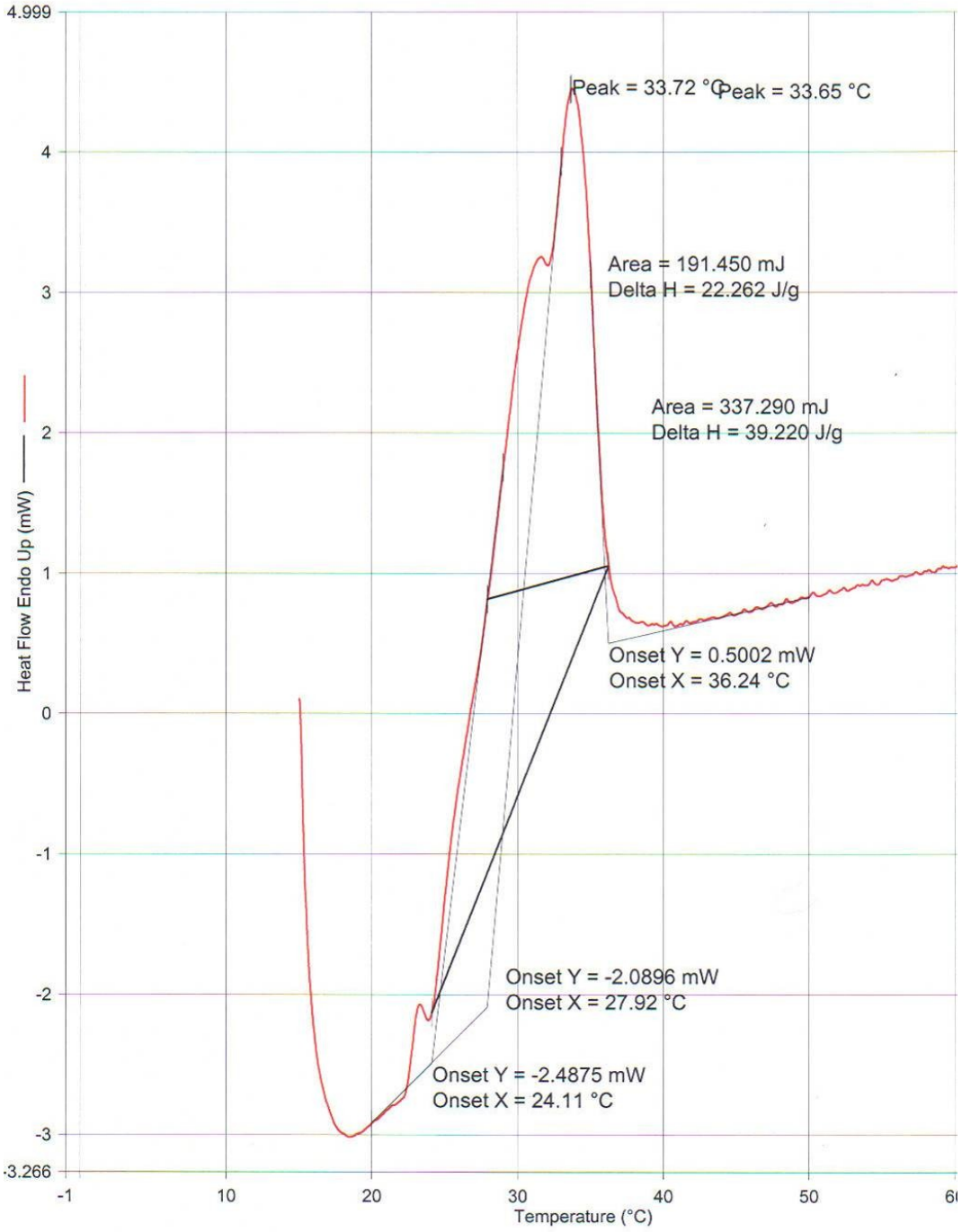

Figure 37: DSC data for shear rate 20.3s^{-1} (Heating rate of 5°C/min)

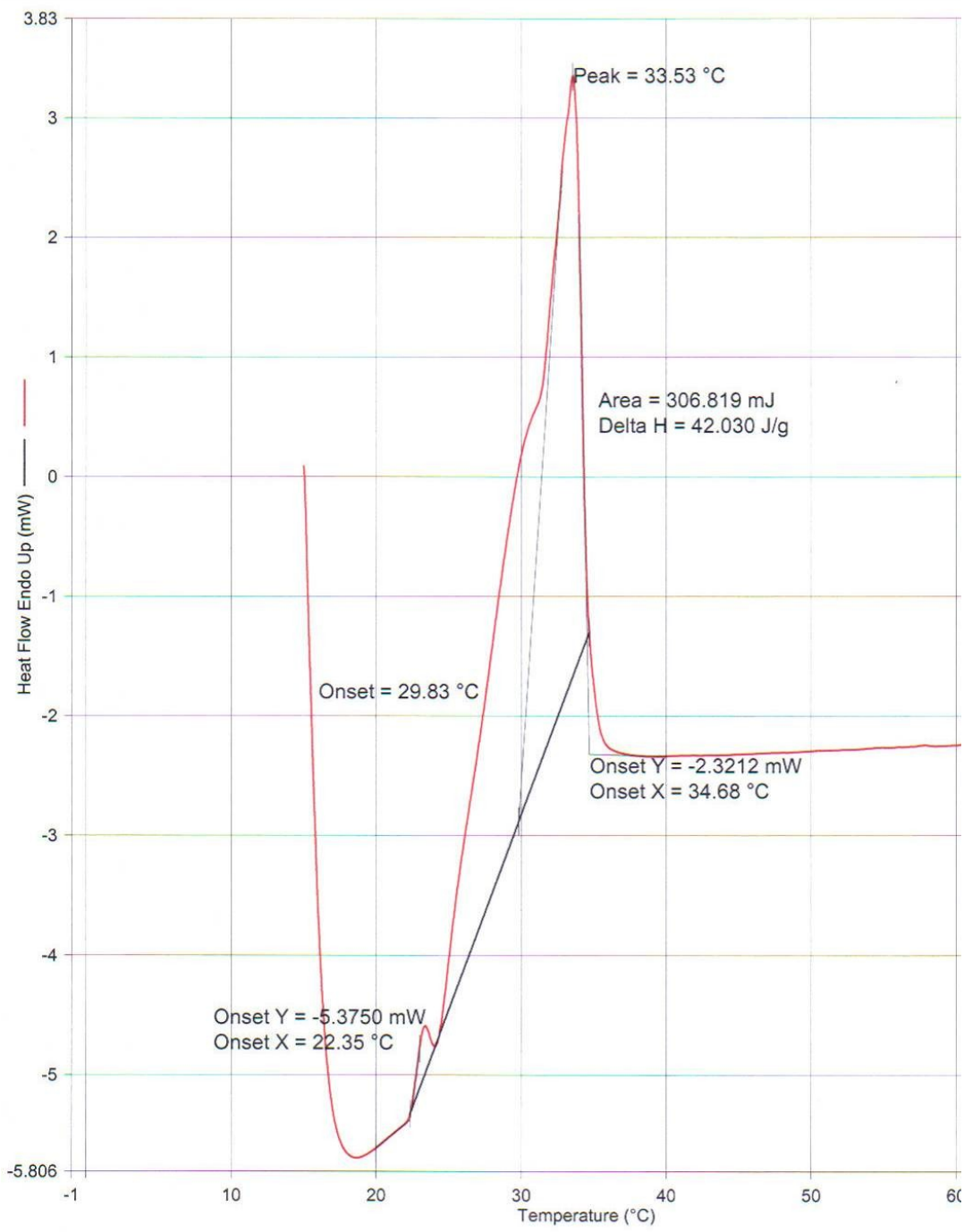

Figure 38: DSC data for shear rate 29.2s^{-1} (Heating rate of 5°C/min)

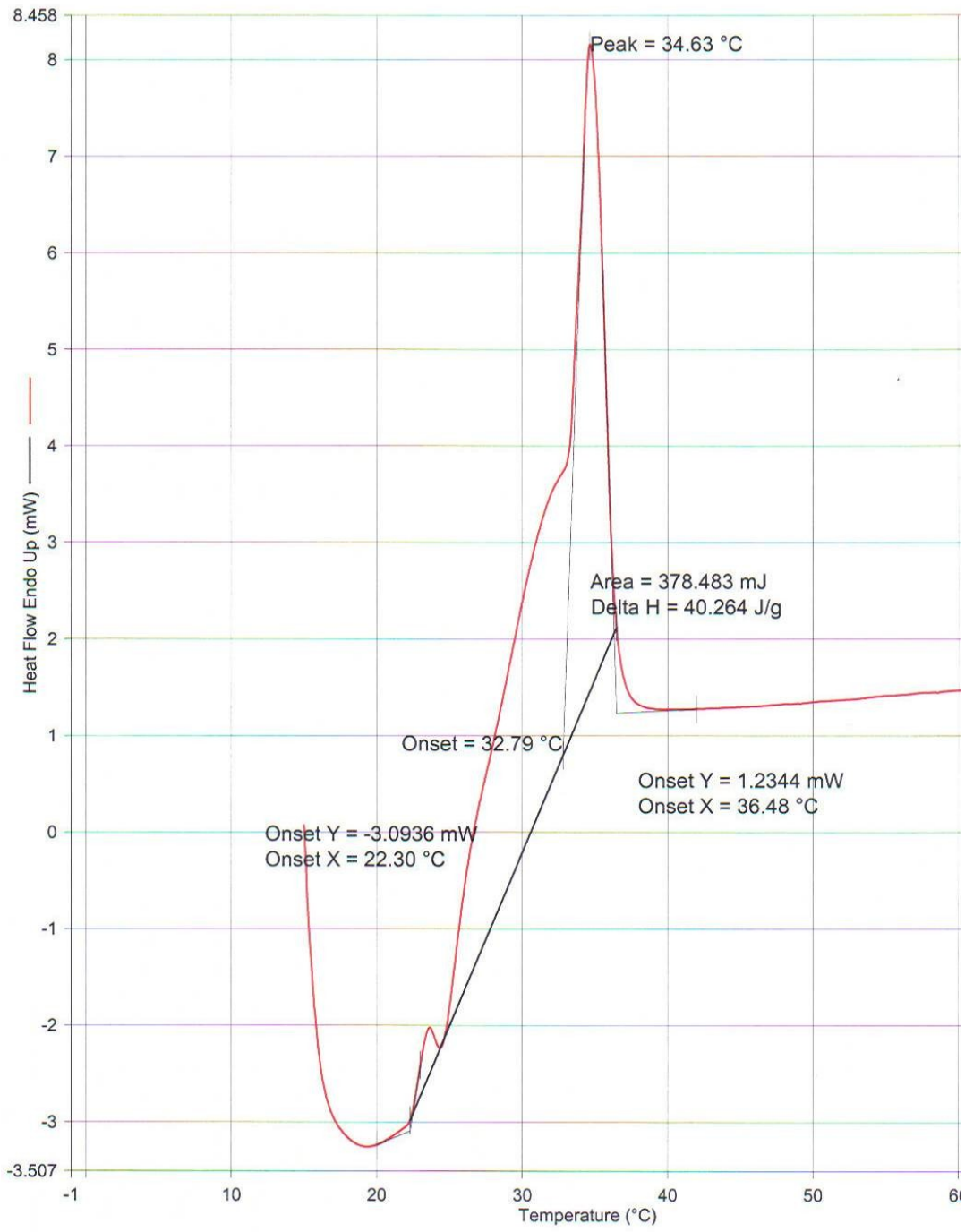

Figure 39: DSC data for shear rate 40.5s^{-1} (Heating rate of 5°C/min)

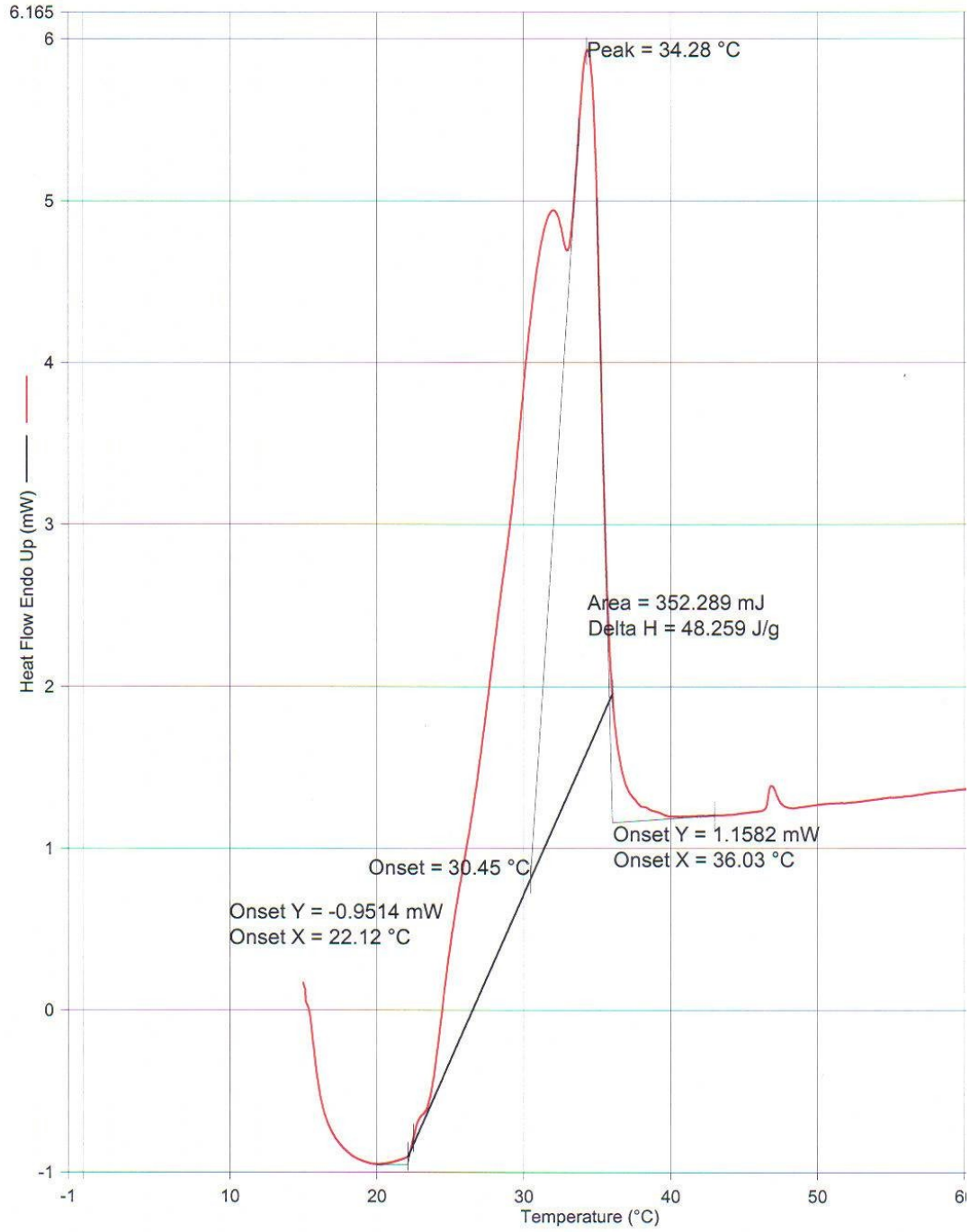

Figure 40: DSC data for shear rate 50.3s^{-1} (Heating rate of 5°C/min)

The results from the DSC graphs vary from shear rate to shear rate. The same basic curve is reflected in each shear rate, with each main curve peaking around 34°C. This can be seen in Figure 38. Similar DSC data for dark chocolate is shown in Figure 7, which shows a peak temperature of 34°C[15]. However, each curve has its own unique shape, yet shows a comparable curve to the one found in Figure 7. The differences could be due to a different heating rate, Figure 7 used a heating rate of 10°C/min and the heating rate used in this experiment was 5°C/min. Also, interference with surrounding equipment, a bad sample, or possibly different crystal structures could account for dissimilar data.

The onset temperature, ΔH, and peak temperature were calculated by the DSC software. The results are shown in Table 4 and graphed in Figures 42 – 44.

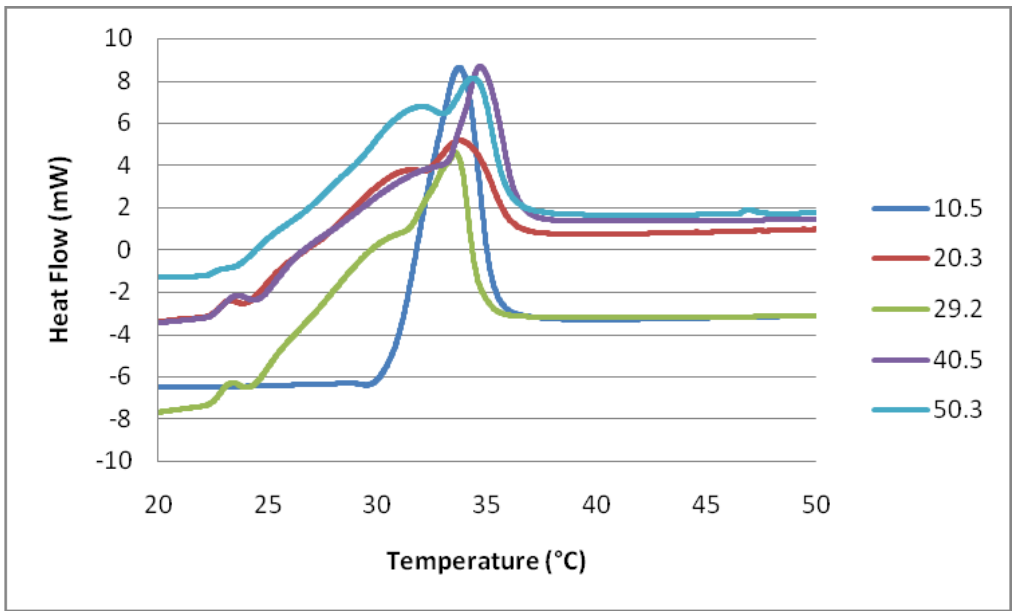

Figure 41: Heat Flow vs. Temperature for all shear rates

Table 4 – DSC Results

SR	onset(°C)	ΔH (J/g)	PeakTemp (°C)
0	32.1	21.4	34.9
10.5	30.5	20.1	33.5
20.3	26.5	41.0	34.1
29.2	29.6	42.7	32.8
40.5	31.2	45.6	34.0
50.3	30.8	45.8	34.0

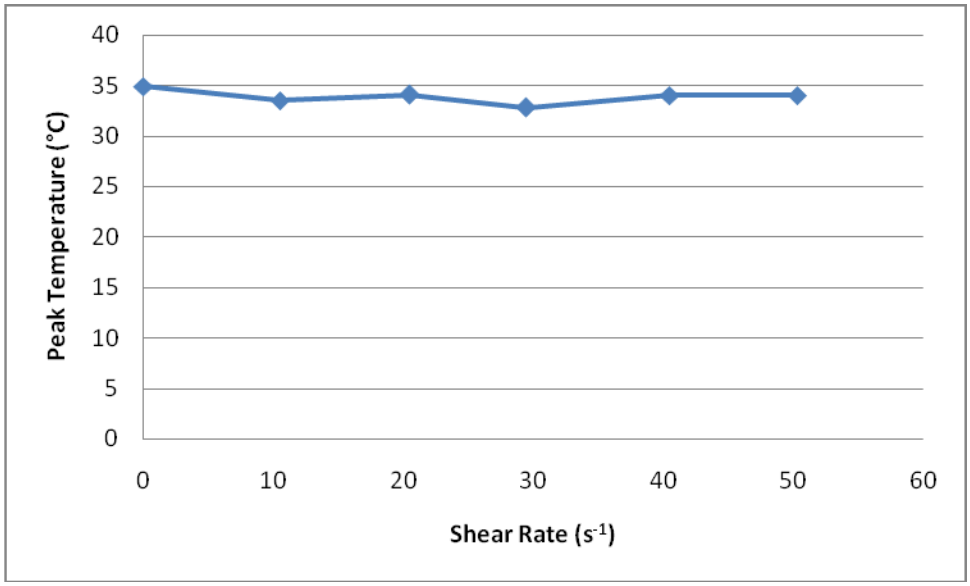

Figure 42: Peak Temperature vs. Shear Rate

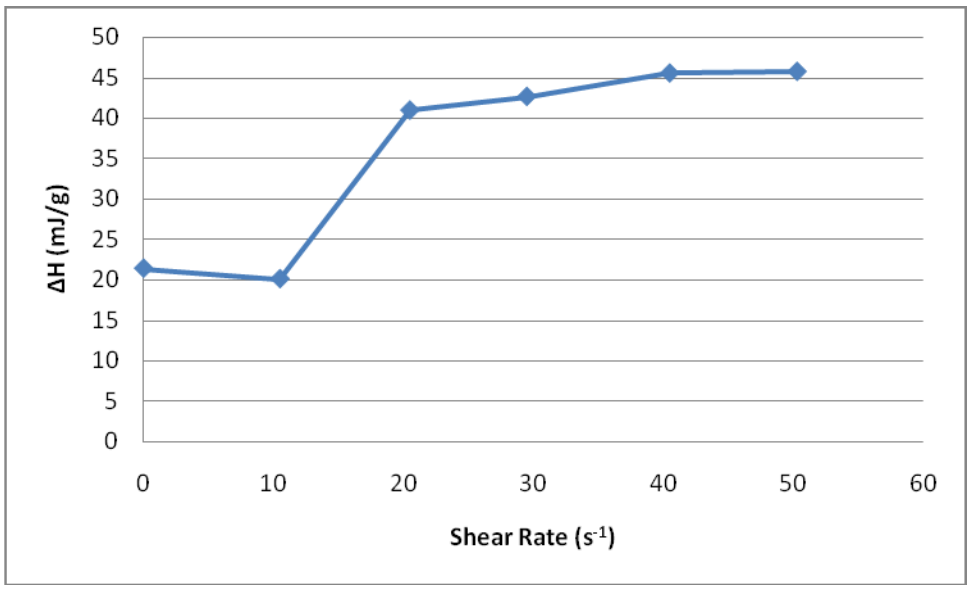

Figure 43: ΔH vs. Shear Rate

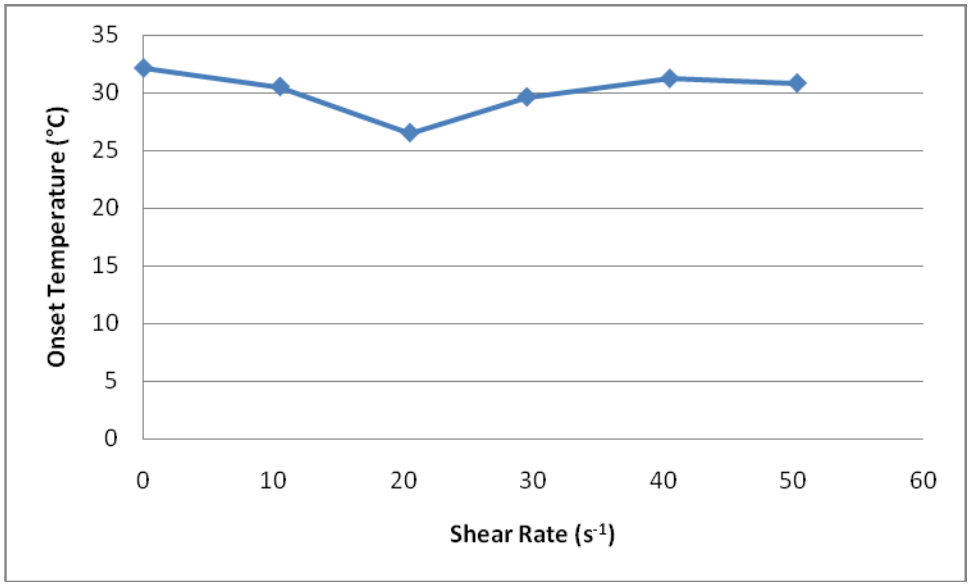

Figure 44: Onset Temperature vs. Shear Rate

The overall trend is ΔH increases with increasing shear rate, which means more energy is needed to melt the chocolate, leading to the conclusion that there are more crystals throughout the chocolate. Based on the curves obtained by DSC, it can be seen that the unsheared chocolate has a slightly higher ΔH (21.4 J/g) than the chocolate that

was sheared at a rate of 10 s^{-1} (20.1 J/g). This could be due to that fact that the assumed unsheared chocolate, used as a baseline, had previously been sheared at a rate higher than 10 s^{-1}. During the heating of the chocolate in the experiment, the crystal history was erased, eliminating the effect of any previous shear. Since the ΔH was smaller at a shear rate of 10 s^{-1} than the baseline, then it can be assumed that the baseline chocolate had been sheared at a rate higher than 10s^{-1} when tempered during manufacturing.

Another point to look at is the onset temperature. The onset temperature average is 30.1°C +/- 1.9. However, there is a noticeable drop in the onset temperature with a shear rate of 20.5 s^{-1}. This onset temperature is 26.5°C, which means the temperature at which the chocolate begins to melt is lower, which translates to a softer chocolate.

The peak temperature is similar for all shear rates. The average peak temperature is 34°C +/- 0.7. Since the peak temperature does not appear to be effected by shear rate, it can be concluded that the onset temperature depends on the type of crystals, not the amount. In this case, the type of crystal should be form V, which has a melting temp of 34°C. This concludes that the chocolate does have the desired form V crystals, which are being analyzed.

Comparing with previous studies, the ΔH values vary. The values in this study range from 21.4J/g to 45.8J/g, as opposed to 130J/g as the mean value found for β forms[15]. The range of the onset temperatures could be an explanation; however they seem to be similar. The range for the onset temperatures for the largest ΔH is 22 - 36°C, a difference of 14°, where the range in Figure 7 appears to be 26 - 38°C, a difference of 12°C. The range in heat flow for the curve also is similar, with 7mW compared to an estimated 6mW from Figure 7. Another explanation could be the shape of the curve, for

a wider curve would result in a larger area. A wider curve and resulting larger ΔH would suggest more crystal formation, which could be due to the fact that the chocolate in the previous study was tempered. Finally, the previous experiment used a rate of 20RPM, which corresponds to a shear rate of $151.3s^{-1}$ using equation 5. The largest shear rate used in this experiment was $50.3s^{-1}$, and following the trend that increasing shear rate increases ΔH, the higher shear rate used in the previous experiment would produce a larger ΔH. The shear rate $151.3s^{-1}$ is roughly 3 times larger than $50.3s^{-1}$. The same is true for the ΔH, with 130J/g being about three times larger than 45.8J/g.

6.4 X-Ray Diffraction

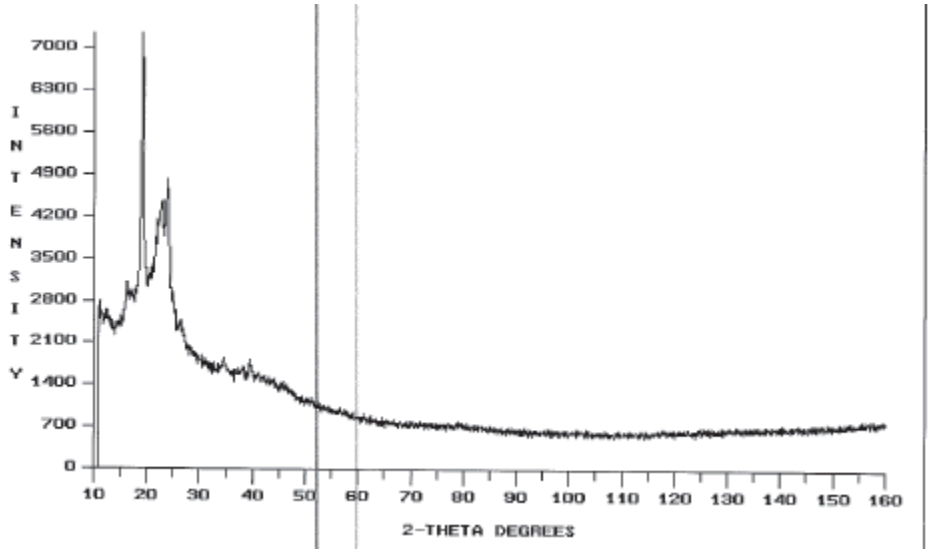

Figure 45: Base X-Ray Diffraction Reading of Unsheared Chocolate

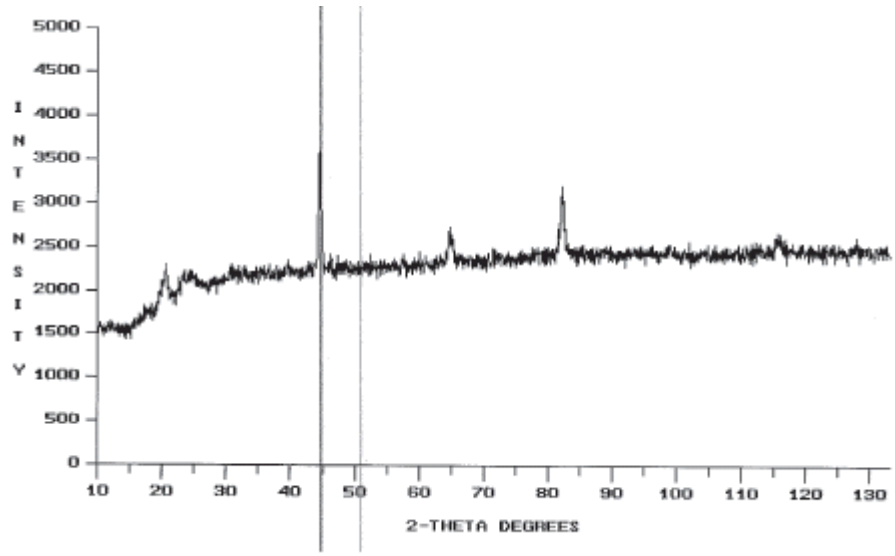

Figure 46: X-Ray Diffraction of Chocolate Sheared at 10.5s^{-1}

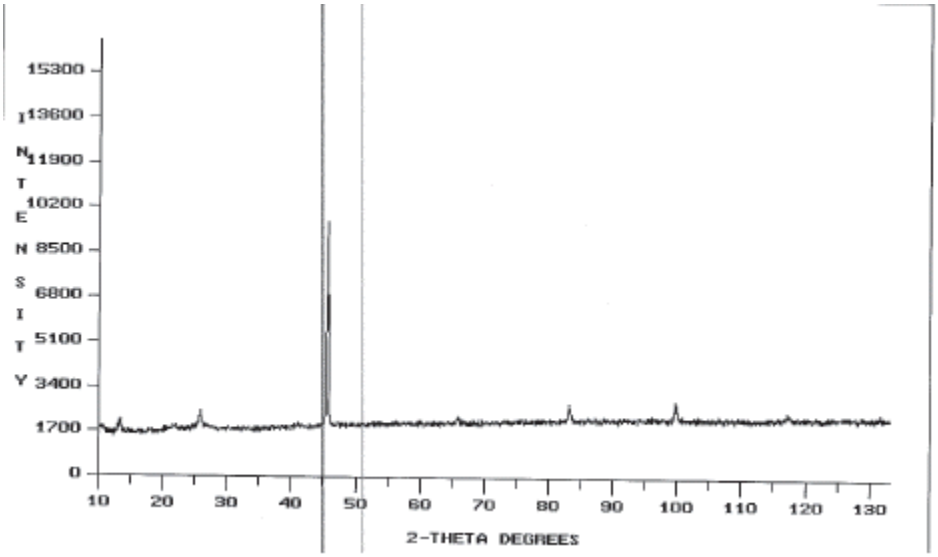

Figure 47: X-Ray Diffraction of Chocolate Sheared at 20.3s^{-1}

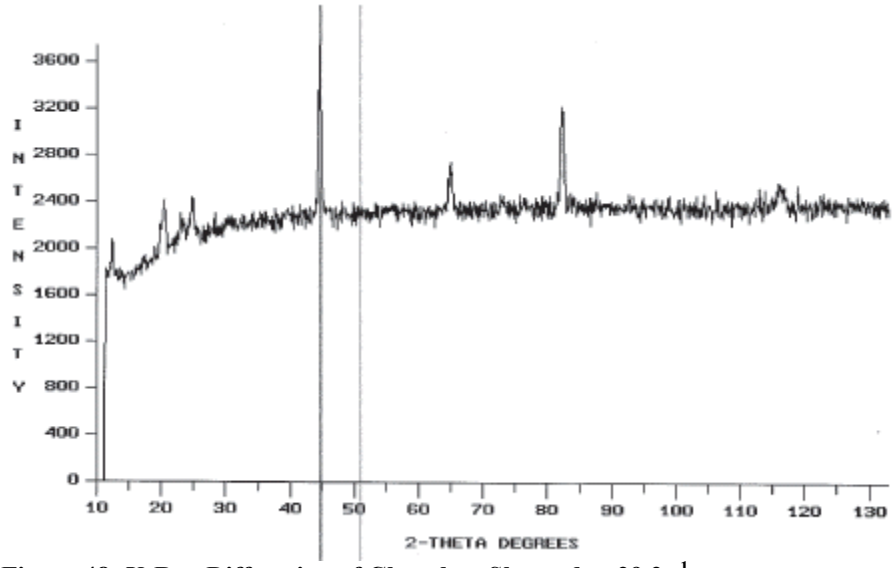

Figure 48: X-Ray Diffraction of Chocolate Sheared at 29.2s^{-1}

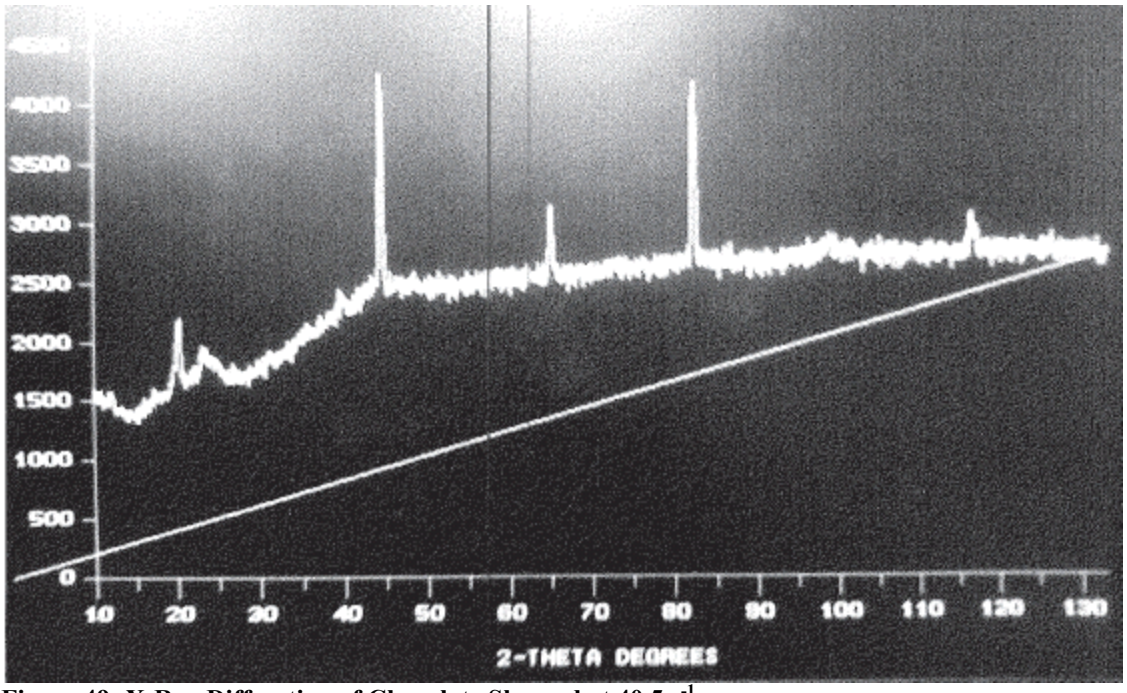

Figure 49: X-Ray Diffraction of Chocolate Sheared at 40.5 s^{-1}

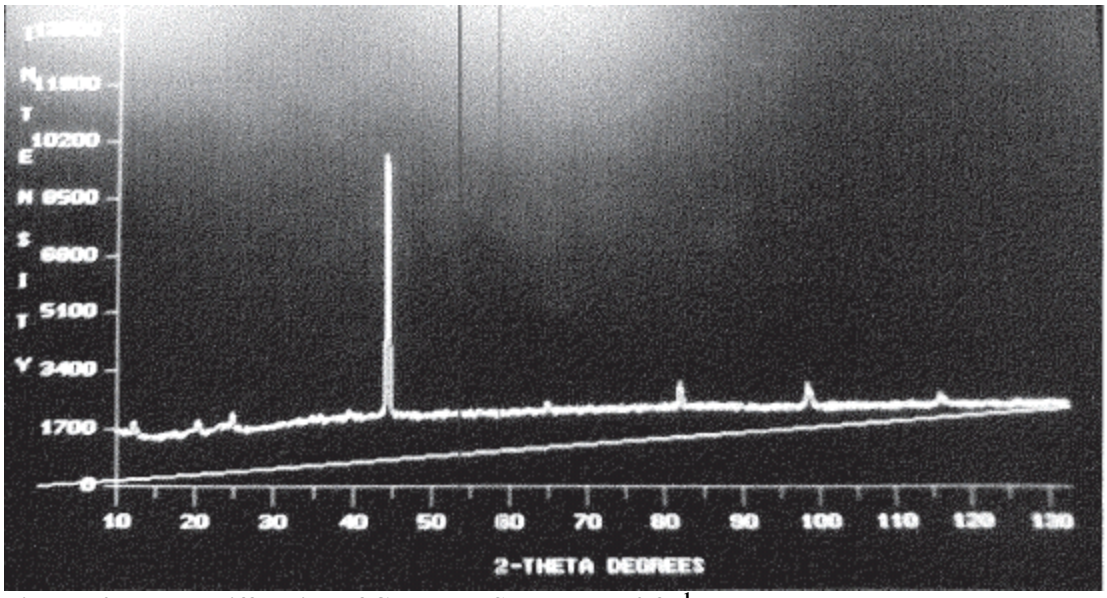

Figure 50: X-Ray Diffraction of Chocolate Sheared at 50.3s^{-1}

Table 4: Angle of Peaks for X-Ray Diffraction of Chocolate

Base	10.5 s^{-1}	20.3 s^{-1}	29.2 s^{-1}	40.5 s^{-1}	50.3 s^{-1}
11	12	14	13	22	13
13	*45*	26	22	24	22
16	66	*46*	24	*46*	26
19	83	66	26	66	*45*
24	116	84	*46*	83	66
25		99	66	118	83
35		118	83		99
45			117		117

Table 4 lists the angles at which there was a peak in intensity for the base and sheared chocolate samples. The italicized angles depict the angle with the largest intensity in height. This angle occurred at 46° for 20.3s^{-1}, 29.2s^{-1}, and 40.5s^{-1}, while occurring at 45° for 10.5s^{-1} and 50.3s^{-1}. Each sheared chocolate had peaks at 66°. 20.3s had a slight shift for a peak at 84° in comparison to the others' 83° peak.

The unsheared chocolate had different intensities than the sheared chocolate samples overall. This could show that the crystal structures of the sheared chocolate changed to a different structure.

Chocolate contains many different acids and alkaloids making it hard to determine the exact composition of the chocolate, due to differences in Cocoa Beans. Table 5 lists common ingredients in chocolate and the angles of high intensities. Tryptophane has intensities greater than 57 from 4.9° to 31.387° thus many of those angles are left of the table.

Table 5: Chocolate Ingredients with corresponding X-Ray Diffraction angle & intensity

Ingredient	2-theta	Intensity
α-Palmitic Acid	21.675	100
	24.386	30
	36.403	20
	41.458	20
Sucrose	18.856	100
	19.627	80
	24.793	100
	25.221	45
	38.317	40
Caffeine	11.799	100
Tryptophane	17.915	96
	18.299	100
α-Oleic Acid	20.559	80
	22.567	80
	23.986	80
Stearic Acid	21.122	55
	21.219	97
	21.648	358
	24.198	102
β-Glucose	16.415	81
	19.253	68
	23.472	100
Theobromine	13.375	80
	27.019	100

Each of the sheared chocolates had peaks between 20° and 28°, which aligns with peaks of the main ingredients in chocolate. Each of the sheared chocolate samples had major peaks at 46°, which are not explained when comparing to the known ingredients of

chocolate. Loisel's[15] study also produced similar peaks to the known Chocolate ingredients JC Pedia files, with peaks between 10° and 15°. The XRPD diffraction patterns of the chocolate in Schenk's study had peaks between 19° and 24°, which aligns with minor peaks found in this studies' sheared chocolate. The peaks for the sheared chocolate are consistent which suggests that the chocolate has similar crystal structures to each other.

Chapter 7: Conclusions

The microstructure of chocolate is complex. The cocoa butter in chocolate is an integral part, resulting in the formation of six different crystal structures. Theses six crystal structures are what give chocolate its properties. Cocoa butter is comprised of three main saturated triacylglycerols (TAGs); stearic, palmitic, and oleic. Each of the TAGS have the same components, but their different combinations of branch lengths make them unique. The presence of the three TAGs in the chocolate samples used in this study were confirmed with X-Ray diffraction. The combinations of these TAGs in cocoa butter create the butter's low melting temperature of 37°C. Since this is the overall melting temperature, each crystal structure has its own defined melting temperature below 37°C. Crystal form V has a melting temperature of 34°C, which was confirmed with data found using DSC. The average peak melting temperature was found to be 34°C+/- 0.7. This confirms that form V was in fact formed and was being measured by DSC. It was also observed that the lowest onset temperature was 26.5°C for a shear rate of $20.3s^{-1}$, which means the chocolate starts to melt at a lower temperature. The low melting temperature is desirable for chocolate, because a low melting point correlates to a softer, betting tasting chocolate. To aid the formation of structure V crystals and elimination of the other forms, the chocolate is tempered.

When tempering is done correctly, the chocolate will have a uniform structure. The effect of shear during the tempering process was investigated using a Brookfield Programmable Rheometer (Model DV-III+). This machine was available to shear the dark chocolate at various rates. Before shearing, any previous crystal history was erased.

This effect can be seen with the difference between the unsheared chocolate and the chocolate sheared at $10.5s^{-1}$. The ΔH for the unsheared was higher than the chocolate sheared at $10.5s^{-1}$, caused by higher crystallization, which means it was previously sheared at a higher rate than $10.5s^{-1}$.

From the ΔH measured for each curve it can be concluded that there is an increase in ΔH with an increase in shear rate. Since ΔH is the amount of energy needed to melt the sample, the greater the energy, the more crystallization there is in the chocolate. The measured crystal form is form V based on the peak temperature, so there are more form V crystals in the chocolate with increasing shear rate.

The results of X-Ray Diffraction were consistent among the different shear rates. This suggests that the chocolate has similar crystal structures to each other, meaning that the same crystal form was produced in each sample. DSC data shows that the crystal for is form V. Each sample had similar angles for peaks in intensity; however, the angles were inconsistent with the angles of similar studies, which had peaks at approximately 10°. The difference of X-Ray diffraction methods could explain the errors in the peaks of known chocolate samples.

The optical microscope was used to view the structure of the chocolate at different shear rates. It was noted that the chocolate sheared at $40.5s^{-1}$ and $50.3s^{-1}$ had a greater percentage of fat blooms than the chocolate sheared at $10.5s^{-1}$, $20.3s^{-1}$, and $29.2s^{-1}$. Fat bloom occurs when form V transforms into form VI, creating a discolored blemish on the surface of the chocolate. Pores in the chocolate increase the chance of fat bloom formation. The higher shear rates may incorporate a greater amount of air in the chocolate, creating the increased chance for fat bloom. These blemishes can be avoided

with a good tempering process. Shear can be used in the tempering process to aid in the creation of a uniform structure. Inducing a shear rate when the chocolate is melted aligns the crystals, as well as reduces their size. The shear rates $20.3s^{-1}$ and $29.2s^{-1}$ had the most consistent structures throughout the chocolate with small, uniform cocoa crystals and little fat blooming.

This study showed no point at which the increase of shear rate was detrimental to the formation of crystals based on the calculations of ΔH from DSC data, however the optical microscope found an increase in fat bloom with shear rates $40.5s^{-1}$ and higher. This data shows that although crystallization increases with increasing shear rate, shear rates above $40.5s^{-1}$ may incorporate too much air into the chocolate, creating pores. An increase in pores increases the occurrence of fat bloom in chocolate. Since the optical showed little to no fat bloom for the shear rate of $29.2s^{-1}$, which had the greatest amount of crystallization below $40.5s^{-1}$, it is concluded that a shear rate of $29.2s^{-1}$ is the optimal shear rate for the tempering of dark chocolate.

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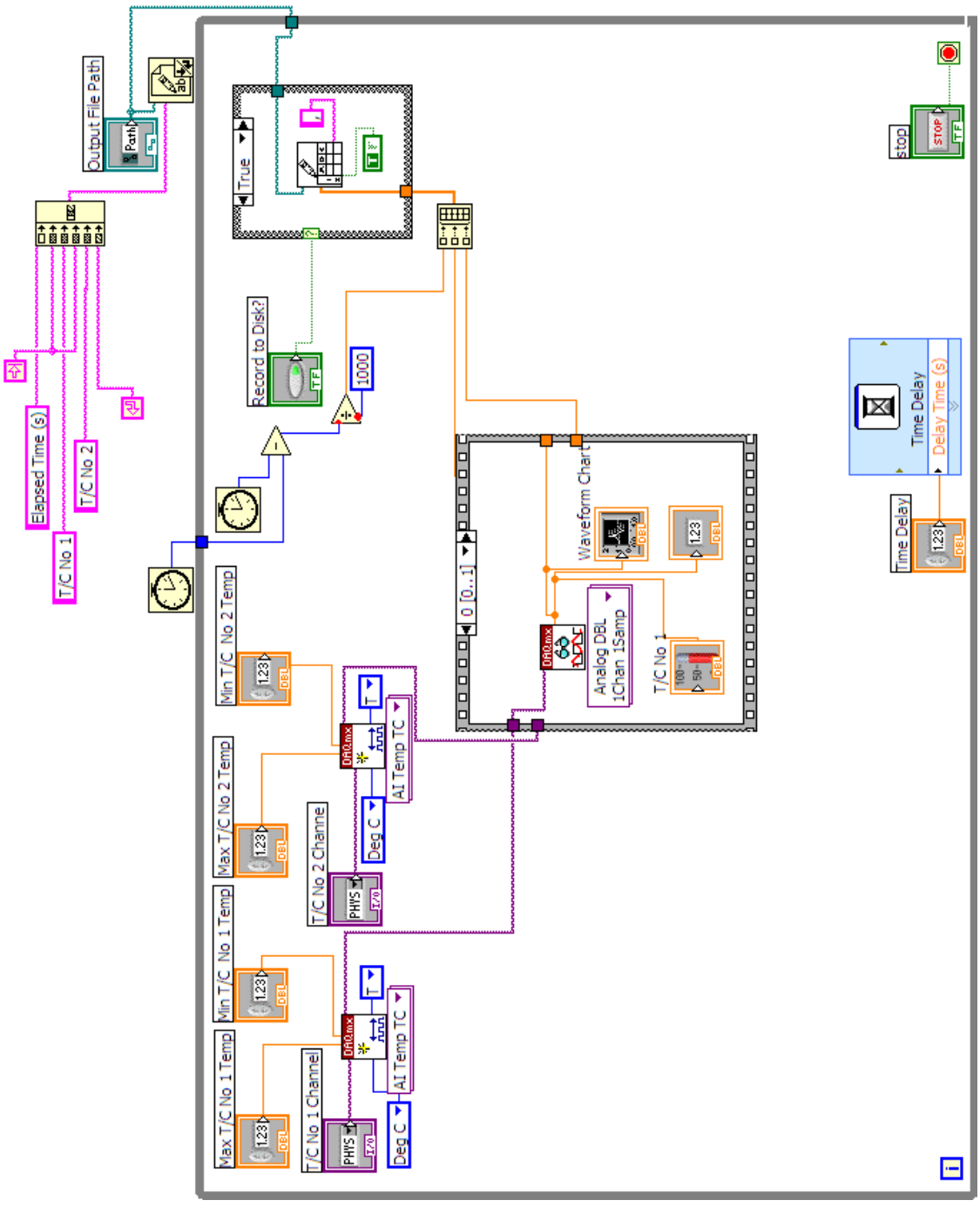
Appendix I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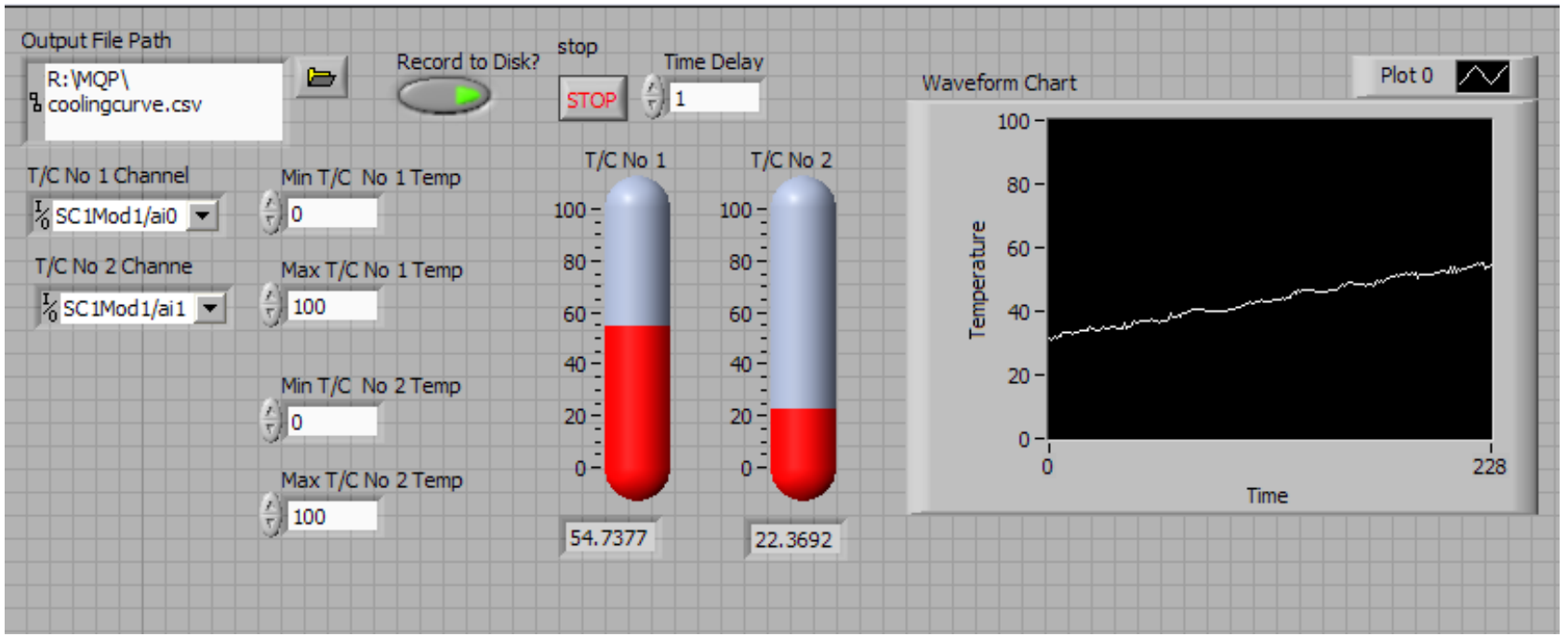
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