The effect of chocolate components and tempering on resistivity and viscosity

THESIS

Presented in Partial Fulfillment of the Requirements for the Degree Master of Science in
the Graduate School of The Ohio State University

By

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2016

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Abstract

A continuous coating layer around food prevents food contacting the environment and extends shelf life. Changing the ingredients in chocolate can change the rheological properties and achieve smaller droplet which makes a thinner continuous barrier with less cost. The objective of this research was to determine the effect of each ingredient in chocolate (cocoa liquor, cocoa butter, sucrose, milk powder) and the effect of tempering on rheological properties of chocolate. The concentration of cocoa liquor (9.5-29.5%), cocoa butter (25-45%), sucrose (0-45%) and milk powder (0-45%) were varied in chocolate samples. The viscosity was measured using a Brookfield Viscometer and the electrical resistivity was measured using an electrometer and voltmeter. The viscosity and resistivity are both affected by ingredients. As cocoa butter increased, the viscosity decreased. The resistivity showed a local peak at 35% cocoa butter. As cocoa liquor increased, the resistivity first decreased and then increased, while the viscosity only decreased. Similarly, as sucrose decreased and milk powder correspondingly increased, the resistivity decreased and then increased. The viscosity did not change. The viscosity of chocolate increased due to tempering, but the resistivity did not change in a clear pattern. Keeping an intermediate cocoa liquor, cocoa butter and sucrose decreases resistivity. Increasing cocoa butter and cocoa liquor decreases the viscosity.

**Keywords:** viscosity, resistivity, ingredients, tempering
Practical applications

Electrohydrodynamic (EHD) spraying of chocolate is an effective and economic method for chocolate coating. Keeping an intermediate cocoa liquor, cocoa butter and sucrose decreases the resistivity. Increasing cocoa butter and cocoa liquor decreases the viscosity. Lower viscosity and resistivity make thinner and more even coating, thus improving the texture and sensory perception while maintaining good barrier properties and reducing cost.
Dedication

This paper is dedicated to all people who love life and science.
Acknowledgments

The first people I need to thank is Dr. Sheryl A. Barringer. As an advisor, processor and department chairman, she spent a lot of time and energy on my class and research. It is her guidance, patience and support that makes me become a qualified master and scientific researcher. Thank her for providing good lab environment and study resources for my entire master period.

In addition, I would like to thank Dr. Kwang Teerarat for her help in the research method. Thank all my committee members Dr. Farnaz Maleky and Dr. Luis Rodriguez-Saona for their help in my classes.

Last, thank my parents for their love and sponsorship throughout my entire studies.
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Table of Contents

Abstract............................................................................................................................................. ii

Practical applications ......................................................................................................................... iii

Dedication............................................................................................................................................... iv

Acknowledgments.............................................................................................................................. v

Vita...................................................................................................................................................... vi

List of Tables ..................................................................................................................................... xi

List of Figures .................................................................................................................................... xii

Chapter 1: Introduction.................................................................................................................... 1

Chapter 2: Literature Review........................................................................................................... 4

2.1 Chocolate Spraying Technology ............................................................................................... 4

2.1.1 Chocolate coating .................................................................................................................. 4

2.1.2 Electric charge ....................................................................................................................... 5

2.1.3 Powder electrostatic spray .................................................................................................... 6

2.1.4 Liquid electrostatic spray ...................................................................................................... 6

2.1.5 Reproducibility ..................................................................................................................... 7
2.2 Charge to mass ratio ................................................................. 8

2.3 Making chocolate ........................................................................ 8

2.4 Methodology ............................................................................... 9

2.4.1 Viscosity Measurement ............................................................ 9

2.4.2 Resistivity measurement ........................................................... 12

2.5 Factors that influence spray quality ............................................. 13

2.5.1 Ingredients ............................................................................. 13

   2.5.1.1 Sweetener ........................................................................ 13

   2.5.1.2 Lecithin .......................................................................... 14

   2.5.1.3 Fat ................................................................................. 16

   2.5.1.4 Salt ................................................................................. 16

2.5.2 Physical properties ................................................................. 17

   2.5.2.1 Temperature .................................................................... 17

   2.5.2.2 Water content ................................................................. 18

   2.5.2.3 Conching time ................................................................. 18

   2.5.2.4 Effect of vibration ............................................................. 18

2.5.3 Quality .................................................................................. 19

   2.5.3.1 Droplet size ..................................................................... 19

   2.5.3.2 Viscosity ......................................................................... 20

   2.5.3.3 Resistivity ....................................................................... 21

2.6 Tempering .................................................................................. 22
Chapter 3: Methods and Materials

3.1 Sample preparation
3.2 Resistivity
3.3 Viscosity
3.4 Spraying
3.5 Statistics

Chapter 4: Results and Discussion

4.1 The effect of cocoa butter versus sugar and milk concentration
4.2 The effect of cocoa liquor versus sugar and milk concentration
4.3 The effect of sucrose versus milk concentration
4.4 The effect of tempering

Chapter 5: Conclusions

References

Appendix A: Raw Data for the Effect of Ingredients on Rheological Properties

A.1 The effect of sucrose on rheological properties
A.1.1 The effect of sucrose concentration on resistivity
A.1.2 The effect of sucrose concentration on viscosity
A.2 The effect of cocoa butter on rheological properties
A.2.1 The effect of cocoa butter on resistivity
A.2.2 The effect of cocoa butter on viscosity ......................................................... 50
A.3 The effect of cocoa liquor on rheological properties ........................................ 51
  A.3.1 The effect of cocoa liquor on resistivity..................................................... 51
  A.3.2 The effect of cocoa liquor on viscosity...................................................... 52
List of Tables

Table 1. The ingredients for cocoa butter effect .......................................................... 25
Table 2. The ingredients for cocoa liquor effect .......................................................... 25
Table 3. The ingredients for sucrose effect ................................................................. 25
Table 4. Resistivity for chocolate at 125 V and 30°C ............................................... 47
Table 5. Viscosity for chocolate at 30°C using RV spindle #4 .................................. 48
Table 6. Resistivity for chocolate at 125 V and 30°C ............................................... 49
Table 7. Viscosity for chocolate at 30°C using RV spindle #4 .................................. 50
Table 8. Resistivity for chocolate at 125 V and 30°C ............................................... 51
Table 9. Viscosity for chocolate at 30°C using RV spindle #4 .................................. 52
List of Figures

Figure 1. The effect of cocoa butter versus sugar and milk powder on viscosity and resistivity................................................................. 29
Figure 2. The effect of cocoa liquor versus sugar and milk powder on viscosity and resistivity................................................................. 32
Figure 3. The effect of sucrose and milk powder on viscosity and resistivity........... 35
Figure 4. The effect of tempering on resistivity. Samples in different data sets with different letters are significantly different. ................................................. 37
Figure 5. The effect of tempering on viscosity. Samples in different data sets with different letters are significantly different. .......................... 38
Chapter 1: Introduction

Chocolate is one of the most popular snacks around the world. It has a smooth texture and good taste, so it is widely used as a coating material in the snack food and confectionary industries. Edible films play an important role in food shelf-life by preventing food contacting its environment. Films can stop moisture migration, improve sensory attributes and decrease the growth of microbes. Food additives, such as antioxidants, pigments and sweeteners, can also be added into food by adding into the edible films (Bravin and others 2006; Diab and others 2001). Besides chocolate, proteins, polysaccharides and lipids are also used as coating materials to isolate water and air exchange (Chiumarelli and Hubinger 2012). The main ingredients of chocolate include sucrose, cocoa butter, cocoa liquor, milk powder and lecithin, which all influence its cost. Therefore, weight control should be accurate during the coating processing in order to reduce cost (Beckett 2000).

Electrohydrodynamic spraying (EHD) is a technology used to spray liquid into small droplets by electrostatic force. Electrostatic coating of liquid seasonings produces more uniform coating and higher flavor intensity than non-electrostatic coating (Evans and Reynhout 2000). Besides chocolate, EHD is used to coat food with oils, emulsifiers and flavors (Marthina and Barringer 2012). The electrostatic spraying droplet size for liquid
chocolate varies from 0.1 to 1,000 μm (Gorty and Barringer 2011). Using finer droplets increases coverage evenness and reduces waste, therefore reducing cost (Aykas and Barringer 2012).

Among the physical properties, resistivity and viscosity are the two most important parameters to affect the spray quality (Gorty and Barringer 2011). The electrostatic spray quality is determined by the resistivity and viscosity of the sample, which are determined by the ingredients of the chocolate.

Resistivity influences the spray quality. Resistivity is affected by temperature and ions in the chocolate (Aykas and Barringer 2012). The resistivity is lower when the ions move easier. The resistivity is also affected by the ingredients in the samples. Increasing sugar content in chocolate increases resistivity (Luo and others 2012). Increasing cocoa liquor and decreasing cocoa butter increases resistivity (Gorty and Barringer 2011). Increasing the resistivity of chocolate increased coating thickness (Marthina and Barringer 2012). In one study, the oil only atomized when the resistivity of the liquid was between 105 and 109Ω·m (Abu-Ali and Barringer 2005). In order to achieve this range, emulsifiers such as lecithin and alcohols can be added into the liquid to decrease the resistivity. The resistivity for chocolate is about 109Ω·m (Gorty and Barringer 2011), which is in the correct range to atomize.

The coating thickness of chocolate decreases with decreasing viscosity, and viscosity decreases with increasing cocoa butter (Marthina and Barringer 2012). Cocoa butter decreases the viscosity (Gorty and Barringer 2011). Fat in chocolate is the continuous phase in which particles are suspended, thus increasing fat increases
continuous phase and decreases viscosity (Castro and others 2003). Increasing sugar content in chocolate increased the viscosity (Luo and others 2012).

Tempering is an important process to create the correct crystallization forms of cocoa butter in the chocolate suspension. The viscosity of tempered chocolate is increased by increased crystal type V (Servais and others 2004). There are six crystal forms for fat in cocoa butter. The main purpose in tempering progress is to produce fat in crystal form V which has the most desirable stable texture and appearance. When chocolate was added with small fat crystals (seeds) at 34°C, the plastic viscosity increases (Chevalley 1975).

The objective of this research is to determine the effect of varying the concentration of each chocolate ingredient and the tempering on rheological properties of chocolate. Viscosity and resistivity of the chocolate were measured to determine their effect on the spray quality. A lower resistivity and viscosity indicates better spray quality.
Chapter 2: Literature Review

2.1 Chocolate Spraying Technology

Short shelf-life is a common problem in fruits and vegetables. During handling or processing, damaged skin and cell wall can cause the loss of nutrients, minerals and accelerate enzymatic reactions or other chemical reactions which results in microbial growth, production of undesirable volatile compounds, color and texture change, and weight loss. The most practical and common methods used to overcome these problems and to prolong the shelf-life of fresh-cut products are modified atmosphere packaging, dipping in solutions of antimicrobials and antioxidants, or storage at low temperature (< 5 °C). However, in last few years, edible coatings became an alternative approach and gained more and more attention from people.

2.1.1 Chocolate coating

Chocolate is the mixture of cocoa solids, sucrose, cocoa butter, milk powder and surfactant, such as lecithin. The moisture content of chocolate is usually between 0.4 to 1.0 g H₂O/100g dry solids. Its water activity generally varies from 0.2 to 0.4 (Biquet and Labuza 1988). The moisture sorption isotherm of chocolate had been studied by many scholars (Kim and others 1999). From their results, good moisture barrier properties of chocolate could be expected. Many dry and semi-moist products coated with chocolate
have considerable shelf-life unpackaged which provides convincing proof for this hypothesis. In addition, some researchers have studied the efficiency of chocolate and cocoa butter coatings as moisture barriers. The scholars used the cup method and saturated salt solutions to determine the water vapor transmission rate (WVTR) and permeability constants of cocoa butter, chocolate liquor and chocolate milk films (Landman and other 1960). The result showed that chocolate was a good moisture barrier and they also mentioned that the cocoa butter continuous phase was the important reason for it.

2.1.2 Electric charge

Electric charge exists anywhere, such as lightning, dust and gas in volcano and geysers, aurora borealis, snow-flakes and rain, and even fog droplets (Clarke 1968). Charge properties include negative (the air above and around water falls) and positive (on the wet rocks). It is easy to generate, so electrostatic coating has been widely used in the automotive painting industry for years. In 1965, an electrostatic salter was introduced for salt coating of potato chips, crackers and pretzels (Matz 1984). This machine induces negative charge on the surface of salt and then the salt is pulled off the rotating cylinder by the attraction of the positively charged dispersion rod. When the salt fell down from the salter, the negatively charged particles repelled each other to generate uniform separation. From then, some companies also introduce electrostatic spray machines used in liquid smoke to meat and food powders to snack foods. Candy and chocolate in confectionary industry also started to apply electrostatic coating to reduce the waste of required flavor (Clarke 1968).
2.1.3 Powder electrostatic spray

Electrostatic powder coating is widely used in food industry. It has advantages in three basic regions: charged powder source, transportation and deposition adhesion (Bailey 1998). Electrostatic spray would result in an even coating of seasoning particles and less dust because charged powders repel each other and seek the nearest target object rather than staying suspended in the air (Bailey 1998; Clark 1995; Madl 2000; Pannell 1980). During the powder deposition, aerodynamic and electrostatic forces play an important role. Aerodynamic force brings particles closer to the target area and electrostatic forces affect powder deposition (Mazumder and others 1997).

2.1.4 Liquid electrostatic spray

Electrostatic coating (electrostatic hydrodynamic spray, EHD) applies charge to promote spraying and now was mainly applied in pharmaceutical and paint industries (Prajapati and Patel 2010). Although it is a novel and cost effective technique, it does not frequently occur during food products processing (Bose and Bogner 2007). Its principle is easy to understand. When a droplet is charged, its surface will accumulate electric charge which could decrease the surface tension. As a result, the surface becomes unstable, and then the droplet spontaneously breaks up into fine and relatively monodisperse charged droplets. Because these broken fine droplets have the same charge, they do not coalesce in the air. They will follow a trajectory to the nearest grounded surface, being the target object. Charged items are easier to be electrostatically attracted to grounded object, so electrostatic spraying has higher transfer efficiency than nonelectrostatic spraying (Luo and others 2012; Maski and Durairaj 2010; Oh and others
When the droplets hit the target surface, such as glass slide, they will start to release their charges to the target surface. Thus, the subsequent droplets can impact freely and will not be influenced by charge. Since electrostatic spraying may produce well-defined and small droplets with the help of electric charge, it could generate more smooth and air-tight coating on the food surface. It is valuable to develop this technique in food industry.

2.1.5 Reproducibility

Reproducibility is the ability for the researcher or other scholars to reproduce the experiment or study in different conditions. An optimal charge concentration must be present to produce efficient, reproducible coating. Both the reproducibility and efficiency were influenced by operating conditions. Voltage had the most significant effect on reproducibility for electrostatic spraying of oils, followed closely by resistivity and then flow rate (Abu-Ali and Barringer 2008). The reproducibility increased with voltage when the voltage was below 35 kV and then decreased. This was because high voltage had little effect on resistivity (Abu-Ali and Barringer 2008). Viscosity had the least significant effect on coating reproducibility for oils and it worked only through interaction with other factors (Aykas and Barringer 2012). When the voltage increased, the effect of viscosity on reproducibility decreased (Abu-Ali and Barringer 2008). Increasing flow rate decreased reproducibility because high flow rate spread charges into more particles which reduced momentary charge concentration. However, the decrease became smaller with increasing voltage (Abu-Ali and Barringer 2008). Increasing the concentration of
emulsifiers first increased and then decreased the reproducibility (Abu-Ali and Barringer 2008).

The reproducibility was not affected by the type of oils. However, addition of an emulsifier into oil caused greater reproducibility than pure oil, because emulsion decreased resistivity and improved spraying quality. Adding additives into water portion of the emulsion did not have much influence on reproducibility (Abu-Ali and Barringer 2005).

2.2 Charge to mass ratio

The optimum conditions for liquid electrostatic coating have been studied. During electrostatic spraying, most droplets will carry the same charge. As the charge to mass ratio increases, the droplets will repel each other and break into lots of small droplets and the droplets size will decrease. Smaller droplets should produce more reproducible coating. Decreasing resistivity and flow rate increases the charge to mass ratio on the droplets of pesticide (Gaultney and others 1987). For the water droplets, when the voltage was lower than 4 kV, charge to mass ratio increases linearly with increasing voltage. Then when the voltage was above 7.5 kV, the charge to mass ratio decreased due to corona discharge (Marchant and Green 1982).

Resistivity had most effect on charge to mass ratio (Wilkerson and Gaultney 1989). Increasing voltage increased charge to mass ratio until the voltage arrived to 30kV (Abu-Ali and Barringer 2008).

2.3 Making chocolate
Before spraying, the first step is to make chocolate with desired ingredients. Most scholars make chocolate by the order of mixing ingredients, conching, tempering and storage. Some scholars produced chocolate by a laboratory ball mill rather than concher (Nebesny and Zyzelewicz 2004).

There are a lot of factors influencing the rheological behavior of chocolate, such as fat content, lecithin or emulsifier content, water content, conching time, particle size, temperature, degree of temper and vibration (Chevalley 1975). Each factor is interdependent to influence the quality of chocolate electrostatic spray.

2.4 Methodology

Spray quality is influenced by many parameters, such as viscosity and resistivity. Viscosity of chocolate is important in determining the coating thickness and the yield value is important in determining how easily the chocolate flows (Beckett 2000). Fat content, lecithin and temperature have a significant effect on both viscosity and yield value. Atomization during EHD is affected by voltage, viscosity and electrical resistivity of the liquid (Wilkerson and Gaultney 1989).

2.4.1 Viscosity Measurement

Different people measure the viscosity at different conditions. A study measured the viscosity at various speeds within the range 5 to 60 sec$^{-1}$ rate of shear when chocolate has reached 40$^\circ$C (Barringer 1972). The shear rate should first ascend then descend. At each speed, the reading is taken when the viscometer has settled down to a steady scale reading. The final viscosity is the mean values of the readings obtained in both ascending and descending order for each speed. To avoid error, use only those results
which lie between 10% and 95% of the total scale. To be more accurate, each chocolate needs to be repeated three times and their results need to conform with the limits of accuracy. The coefficient of variation between replicate determination of yield value and plastic viscosity should not exceed 10%.

A new method to measure the viscosity of chocolate was used in 2004 (Servais and others 2004). The new method is validated for the viscosity of chocolate and related cocoa products using factory grade viscometers. This method needs to record three data. First, record the value of the stress at a shear rate of 5 s⁻¹ to represent the yield stress of chocolate. Second, record the value of the viscosity at a shear rate of 40 s⁻¹ to represent the high shear viscosity. Finally, record the difference between the viscosity measured at a shear rate of 40 s⁻¹ during the ramp up and down in shear rate to represent thixotropy.

The effect of lecithin concentration on properties of sucrose-free chocolate masses sweetened with isomalt has been studied by Nebesny and Zyzelewicz (2005). They measured the viscosity using OICC (Office International du Cacao et du Chocolate) method. Casson viscosity were determined at 40°C, in the range of shear rates of 5–60 s⁻¹, and for the exponent m in the Casson-Steiner’s equation of 0.5 (Nebesny and Zyzelewicz 2005). They have done this operation in triplicate by using a HADVIII+ rheoviscosimeter equipped with the co-axial rotor (SC4-27) and stator, and a small volume sample accessory. The results were processed with Rheocalc V2.0 computer program.

The viscosity of chocolate could be measured by using a Brookfield HB DV II+ Digital Viscometer (Gorty and Barringer 2011). They used a small sample adapter and spindle 27. The sample was pre-sheared for 3 min at 50 rpm before recording the shear
stress values. The spindle was rotated at 5, 10, 20, 50 and 100 rpm. The shear stress values were recorded twice by decreasing the spindle speeds and then increasing it. The average shear stress values were used to calculate the viscosity. The viscosity was measured at 35, 40, 45 and 50°C. The temperature was controlled by water bath. They also measured the viscosity of cocoa butter by using a Brookfield LV DV Π+ Digital viscometer, but they used spindle 1 and a guard leg, because cocoa butter has a lower viscosity than the range of Brookfield HB DV Π+ viscometer. The viscosity was noted at speeds of 20, 50 and 100 rpm and at temperatures of 35, 40, 45 and 50°C.

In Aykas and Barringer (2012)’s researches about the effect of temperature, lecithin content and voltage on droplets during electrostatic spraying of oil, they measured the viscosity of 590 μL oil using a rheometer at 4, 22 and 47°C (Aykas and Barringer 2012). They also measured the surface tension of 4 mL of sample using a Drop Shape Analysis System at 4, 22 or 47°C. They have found that viscosity is affected by both temperature and lecithin content.

The research about confectionary coating with electrohydrodynamic system has been done recently. They mixed sucrose with cocoa powder, and then they heated the samples to 45 to 50 °C in a water bath (Marthina and Barringer 2012). During coating, the samples were sprayed at 60 °C at 0 or 25 kV. The apparent viscosity for samples with different lecithin content was measured at shear rate 40 s\(^{-1}\). The apparent viscosity correlated to droplet size, thickness, and flow rate was reported at the nominal shear rate calculated to occur in the nozzle during spraying. From the result, the Casson model
seemed not to be a good model to measure the apparent viscosity of confectionery coating.

2.4.2 Resistivity measurement

The resistivity of different chocolates at four different temperatures 35, 40, 45, 50°C has been studied (Gorty and Barringer 2011). The electrical resistivity was measured using a resistivity cell, electrometer and a voltmeter (Gorty and Barringer 2011). The sample and sample cell were heated in a hot air oven to achieve the desired temperature. Five milliliters of the sample was put in the resistivity cell each time. To avoid air gaps, a syringe was used to input sample. The voltage was set up using the voltmeter and the current was measured with the electrometer.

The resistivity of the sample was calculated using:

\[
\text{Resistivity} = \frac{k \times V}{I}
\]

where \(k\) is 0.014, the cell constant of the cell. The resistivity measurement was repeated three times for every sample. The unit of the current was chosen differently with different samples.

Electrostatic spray of chocolate is a relatively new research for many professors and scholars; however, electrostatic spray of oil has been studied by a lot of people. Aykas and Barringer (2012) have done some researches about the effect of temperature, lecithin content and voltage on droplets during electrostatic spraying of oil. The oil was sprayed onto the targets by a TDC liquid electrostatic coating machine at six different voltages: 0 kV and electrostatic voltages -15, -20, -25, -30 and -40 kV (Aykas and Barringer 2012). The oil was sprayed at 4, 22 and 47°C. Five grams sample was put in a resistivity cell at 4,
22 and 47°C to measure the resistivity of the oil. To make sure the accuracy, the resistivity of 5 g flake salt [Alberger Untreated Flake Salt, Cargill Salt, Minneapolis, MN, USA] was measured before the sample. Its resistivity was $1.458 \times 10^{10} \, \Omega \text{m}$ which was matched with the expected value.

The resistivity was also tested using a 3200 conductivity meter equipped with model 3256 conductivity dip cell (Abu-Ali and Barringer 2005). The comparative transfer efficiency of the spraying process was calculated by weighing the targets before and after coating to calculate the weight of coating per piece.

2.5 Factors that influence spray quality

2.5.1 Ingredients

2.5.1.1 Sweetener

As sucrose concentration increased from 30-55%, the resistivity increased from $4.17 \times 10^{-4}$ to $3.70 \times 10^{-3} \, \Omega \text{m}$ (Luo and others 2012).

Dark and milk chocolate masses sweetened with isomalt displayed higher Casson viscosity than their sucrose containing counterparts (Nebesny and Zyzelewicz 2005). The viscosity increased with increasing sucrose concentration (Luo and others 2012).

When sucrose concentration in the chocolate suspension increased, the droplets size of electrosprayed chocolate particles increased (Mohos 2010). Luo and others found that when sucrose concentration was below 40% w/w, droplets sizes were small (0.15mm) and increased slowly. When sucrose concentration was higher than 45% w/w, droplets size was about 0.3mm (Luo and others 2012). Sucrose concentrations of 30–35%w/w resulted in very fine relatively monodispersed chocolate particles, and the particle
distribution range broadened with increasing sucrose concentrations. The reason why sucrose concentration could influence spray quality may be because sucrose increases viscosity and surface tension and decreases electrical conductivity of the chocolate suspensions.

2.5.1.2 Lecithin

Lecithin concentration can affect the spray quality. As lecithin content increases from 0.1 to 1.0 g/100 g, Casson viscosity of chocolate mass decreases (Nebesny and Zyzelewicz 2005). When the lecithin concentration was elevated to 0.5 g/100 g, Casson viscosity decreases to a considerable low value (2-4 Pa.S) in dark and milk chocolate masses supplemented with isomalt. As lecithin concentration continues increasing from 0.5 g/100 g to 1.0 g/100 g, no changes in the viscosity were found. The same dependence was observed for the dark chocolate mass sweetened with sucrose. As for the sucrose-containing milk chocolate masses, the greatest decreases in Casson viscosity occurred within lecithin concentrations ranging from 0 to 0.3 g/100 g. An increase in lecithin content from 0.3 to 0.5 g/100 g caused a further decrease in viscosity of sucrose-containing milk chocolate masses. These relationships and minimal changes in viscosity at lecithin concentrations above 0.5 g/100 g reflected the character of lecithin function in emulsion formed by chocolate ingredients. Hydrophilic fragment of lecithin molecule anchors sucrose or isomalt molecule and its lipophilic part will bind the fat. Therefore lecithin reduces internal friction of chocolate masses. Beside the sucrose, the hydrophilic part of lecithin could also bind water, molecules of which are absorbed on sucrose crystals. Because this portion of water can attract only a definite number of lecithin
molecules, an excess of the lecithin imposes no effect on chocolate mass viscosity. An addition of 1.5% lecithin decreases the viscosity and electrical resistivity, thus, adding lecithin concentration lower than 1.5% could produce better spray quality.

Decreasing lecithin concentration could decrease the viscosity. Lecithin reduces the surface tension. In terms of transfer efficiency and reproducibility, 13% lecithin is the ideal level for electrostatic spraying of oils (Abu-Ali and Barringer 2005). When the concentration of lecithin is higher than 5%, voltage had the greatest effect, followed by temperature, and the lecithin content has the least effect on viscosity and resistivity. However, neither temperature nor lecithin content had a large effect on surface tension. Addition of lecithin decreases the electrical resistivity (Gorty and Barringer 2011). As the lecithin content increased, the resistivity of all samples decreased.

Lecithin could decrease the viscosity in a great degree. Very small quantities of lecithin could produce an immediate lowering of viscosity when added to liquid chocolate. This function of lecithin is very obvious at low concentrations. When the lecithin concentration is about 0.143%, more than 10 times its weight in cocoa butter could obtain the same viscosity reduction (Stanley 1941). The reason why the lecithin reduces the chocolate viscosity is that lecithin interacts with the sucrose particles (Harris 1968). Lecithin used in chocolate is a natural soya lecithin which contains about 65-70% phospholipids. Phospholipids act as a kind of emulsifier which has both hydrophilic tail and hydrophobic tail. The hydrophilic tail could combine with non-fat particles such as sucrose and the hydrophobic tail would combine with fat such as cocoa butter. Thus, the chocolate will be more stable and have less resistance to flow.
2.5.1.3 Fat

Fat content has a great influence on chocolate viscosity. In 1941, a study showed that the MacMichael value from a rotational viscometer decreased with the cocoa butter content (Stanley 1941). In the next several years, studies found that the apparent viscosity changes when the fat content varies (Ardakani and others 2014). High fat content in chocolate decreases Casson viscosity (Nebesny and Zyzelewicz 2005). The apparent viscosity significantly increased with a decrease in the fat content. Low viscosity is expected to generate good spray quality; therefore, chocolate samples with high fat produce the best spray quality with EHD. Increasing fat content decreases apparent viscosity of dark chocolate, but has less effect when the fat content was between 30 % to 35%. As fat content increased from 25% to 30%, the plastic viscosities decreased at all particle sizes. However, when fat content was above 30%, the plastic viscosities did not change much (Afoakwa and others 2008).

An increase in fat content decreased the electrical resistivity. The resistivity increased significantly as the fat content decreased from 100 to 53% (Gorty and Barringer 2011). This was because that fat could generate a continuous phase of particulate suspension. When the content of fat decreased, other increased solids content would disrupt this phase and cause drag for ions movement. Therefore, the resistivity increased (Palaniappan and Sastry 1991).

2.5.1.4 Salt

Luo and others (2012) did some research about how salt affects the spray quality. NaCl was used in this work to study the effect of a small amount of an electrolyte
(between 1% and 3%w/w) in the chocolate samples on the droplets size of electrospayed chocolate. In this study, every chocolate sample has similar contents and only salt contents vary from 0, 1 to 3%w/w. The results showed that the presence of 1% w/w of NaCl in the suspension narrowed the droplet distribution range and decreased the average droplets size diameter when sucrose concentration was between 30-45% w/w. The addition of 1%w/w NaCl not only significantly increased the conductivity of the samples, but also slightly increased the surface tension of the samples. However, it did not have much influence on the viscosity. When NaCl was increased to 3%w/w, particle diameter did not further decrease. On the contrary, too much NaCl led to unstable jetting during electrostatic spray and fewer droplets could be collected. The average diameter of the droplets collected from samples with 3%w/w NaCl was 0.16 mm, higher than that from 1%w/w NaCl, 0.11 mm. This is because too much salt increases electrical conductivity and slightly elevates surface tension of samples.

2.5.2 Physical properties

2.5.2.1 Temperature

Increasing temperature decreases the viscosity of chocolate (Nebesny and Zyzelewicz 2005). When lecithin is present, temperature had a slightly greater effect than lecithin content (Gorty and Barringer 2011). Some scholars also found increasing temperature decreases the viscosity (Wilkerson and Gaultney 1989) and decreases the surface tension of most liquids including chocolates (Kahl and others 2003). As the temperature increases, the plastic viscosity will decrease. This effect begins at about 40°C
for milk chocolate without lecithin and at about 60°C for chocolate with lecithin (Stanley 1941).

Electrical resistivity of chocolate decreased with increasing temperature (Nebesny and Zyzelewicz 2005). Increasing temperature from 35-50°C, the resistivity significantly decreased (Gorty and Barringer 2011). When the temperature increased, the kinetic energy of molecules increased. The drag for the movement of ions decreased, so the resistivity decreased. The drag for ionic mobility may depend on size, shape and orientation of particles (Palaniappan and Sastry 1991)

2.5.2.2 Water content

The apparent viscosity of chocolate increases with the water content (Stanley 1941). A research controlled the range of water contents in chocolate in a very low content 0.1-0.4%, and then a sharp increase in the apparent viscosity was observed only when the concentration of water between 0.1-0.2% (Chevalley 1975).

2.5.2.3 Conching time

It is generally recognized that conching could reduce the viscosity of chocolate. If the lecithin was added into the chocolate mixture as soon as it started conching, the viscosity would not have significant decrease (Chevalley 1975). The viscosity depends on the water content, which also decreases with the conching time. The viscosity decreased most after 10 h, but it is nearly constant after 24 h (Chevalley 1975).

2.5.2.4 Effect of vibration

The rheological properties of chocolate during the moulding and spray operations are influenced by vibrations. Increasing amplitude of vibration could decrease the
apparent viscosity (Bartusch and Heiss 1961). Rostagno (1973) used Brookfield viscometer fixed on a vibrating table and reported his results in 1973 which confirmed this result. The product of the vibration amplitude and frequency act as the determinant factor for changing rheological quality.

2.5.3 Quality

2.5.3.1 Droplet size

Beside viscosity and resistivity, many other factors, such as flow rate, sucrose concentration and the presence of trace amounts of electrolyte NaCl also have significant influence on the average diameter and percentage area covered. Average particle diameter increased and the size distribution range broadened with increasing sucrose concentration (Luo and others 2012).

There are a lot of factors having a dramatically significant effect on droplet size and spray quality of oils, including resistivity, voltage, mass flow rate, temperature, viscosity and surface tension (Abu-Ali and Barringer 2008). Among all of these factors, resistivity has the greatest effect and surface tension has the least significant effect on droplet size of vegetable oil (Wilkerson and Gaultney 1989). The electrostatic spraying droplet size of vegetable oil increases with increasing electrical resistivity (Wilkerson and Gaultney 1989). Under EHD, it is the resistivity, instead of the apparent viscosity, that significantly affected the 2-dimensional area representing droplet size (Marthina and Barringer 2012).

An increase in viscosity is directly related to an increase in average droplet size and the observation of satellite particles (Jayasinghe and Edirisinghe 2002). The electrostatic
spraying droplet size of vegetable oil increases with increasing viscosity (Wilkerson and Gaultney 1989).

The applied voltage, electrical resistivity, viscosity and surface tension of the liquid determine the formation of droplets in electrostatic spraying (Aykas and Barringer 2012). Addition of surface-active agents, such as lecithin, decreases droplet size at a given voltage (Nawab and Mason 1958). What’s more, decreased viscosity or surface tension of the liquid significantly increases the number of droplets and decreases the droplets size (Matthews 1979). With the addition of lecithin, increasing voltage increases the number of droplets, decreases the average drop size which means more even coating could be produced. The maximum number of droplets occurs when the temperature is 47°C and voltage is 40 kV with 10% lecithin. Increasing temperature and voltage also reduce the droplet size.

2.5.3.2 Viscosity

The viscosity of chocolate will increase with the decreasing particle size of other ingredients, such as cocoa butter, cocoa liquor, sucrose and so on, if other conditions keep constant (Chevalley 1975). Decreasing particles size of the sucrose-cocoa butter and cocoa mass-cocoa butter systems increased the viscosity of chocolate (Chevalley 1975). The percent area covered decreases with increasing viscosity. It is the size and shape of the suspended particles instead of the difference in fat content of the samples that has more effect on the difference of viscosity, although fat content could influence viscosity (Nebesny and Zyzelewicz 2005). On the other side, viscosity also could influence other spray quality.
Apparent viscosity is affected by fat content, temperature and lecithin. Decrease fat increased the viscosity (Gorty and Barringer 2011). Fat could generate a continuous phase of particulate suspension. When the fat decreased, other solid contents could disrupt this continuous phase which decreased the viscosity (Chevalley 1994). High temperature increases the kinetic energy of chocolate molecules, so increasing temperature decreases viscosity (Nik and others 2007). Lecithin molecule has two tails. The hydrophilic tail interacts with sucrose and lipophilic tail interacts with lipid. Therefore, lecithin acts as emulsifiers to reduce internal friction and further to reduce viscosity (Nebesny and Zyzelewicz 2005).

2.5.3.3 Resistivity

Electrical resistivity is an important parameter for electrospraying, which should normally be between $1 \times 10^5 \Omega \cdot m$ and $1 \times 10^{10} \Omega \cdot m$ for successful atomization of water in oil emulsions (Khan and others 2013). Yurteri reported that only when samples had resistivity between $1 \times 10^5 \Omega \cdot m$ and $1 \times 10^{10} \Omega \cdot m$, they could atomize (Yurteri 2003). High resistivity has insufficient electrical stress build-up in the spraying material, therefore limits atomization (Khan and others 2012), while low resistivity could cause unstable cone-jets (Luo and others 2012). Electrical resistivity is affected by temperature, viscosity and type and concentration of ions in the solution (Adamczewski 1969). The percent area covered decreases with increasing electrical resistivity (Gorty and Barringer 2011). In EHD electrostatic spraying, the resistivity of the additive has a dramatic impact on the efficiency of the process (Burayev and Vereshchagin 1972). At high voltages, the resistivity of the emulsion decreases so that good atomization occurs.
Abu-Ali and Barringer (2005) has studied the method for electrostatic atomization of emulsions in an EHD system. The main factor affecting the suitability of a solution for EHD types of electrostatic atomization is the electrical resistivity (Buraye and Vereshchagin 1972). At high resistivity, atomization doesn’t occur because the insufficient charge builds up on emulsions; while at low resistivity, the liquid conducts the charge back along the feed line, causing a short to the nearest ground. Some materials, such as alcohols, emulsifiers, seasonings and coloring agents, are suggested to decrease the resistivity (Evans and Reynhout 2000).

Decreased resistivity could bring more benefits for spray quality. During EHD coating, when the resistivity of the samples decreased, charges could move faster through the liquid (Marthina and Barringer 2012). Thus, the mobility of charge-carriers increases which leads to good atomization. The droplets size would become smaller with more charges on the surface which producing more repulsion between the droplets. Therefore, it was able to spread over a wider area. On the other hand, resistivity would result in poor atomization, which means it causes larger droplet size and narrow width of spraying (Marthina and Barringer 2012). The larger the droplets and narrower the spray width, the thicker the coating becomes.

2.6 Tempering

Tempering is the final process of making chocolate. There are six crystal forms for chocolate. The more type V crystals exist, the better the chocolate is. Crystal type V provides the best appearance and texture and creates the most stable crystals, so the texture and appearance will not degrade over time. The crystallization types of chocolate
change with temperature. During the process, the chocolate is firstly heated to 45 °C to melt all six forms of crystals. Then, the chocolate is cooled to about 27°C which will allow type IV and V form. At this temperature, the chocolate is agitated to create many small crystal "seeds" which will serve as nuclei to create small crystals in the chocolate. The chocolate is then heated to about 31 °C to eliminate any type IV crystals, leaving just type V.

Tempering is a very important step during chocolate making. It is necessary and the last step before molding. By adjusting the temperature, cocoa butter could generate many little crystal seeds and only have crystal type V. A study showed that chocolate was seeded by adding small fat crystals at 34°C and the plastic viscosity increased. This increase in apparent viscosity is proportional to the amount of fat crystals added in the chocolate (Chevalley 1975). Many scholars used this result to determine the degree of tempering. Thickening occurs for the milk chocolate when the temperature is between 28 and 30°C (Chevalley1975).
Chapter 3: Methods and Materials

3.1 Sample preparation

Chocolate was made with different proportions of the key ingredients. The lecithin (American Lecithin Company, Oxford, CT, USA) was controlled at 0.5% for all samples. The cocoa butter (SaaQin Inc., Hicksville, NY, USA) was melted in a hot water bath at 55 to 60°C and transferred into a concher (Alchemist’s Stone Chocolate Melanger, Oakland, OR, USA) along with the lecithin, sucrose (Domino Sugar Factory, Brooklyn, NY, USA), cocoa liquor (Kraft Food, Northfield, IL, USA), and nonfat milk powder (The Kroger Co., Cincinnati, OH, USA), and conched for 8 h. The finished product was poured into a Pyrex glassware storage container and cooled in the refrigerator. The cooled sample was then cut into pieces and stored in a ziplock bag at 4°C. Each batch was 1500g. For tempered samples, chocolate was tempered using a temperer (ChocoVision Corp, Poughkeepsie, NY, USA). Hershey’s milk chocolate (The Hershey Company, Derry Township, PA, USA) was used as seed chocolate. Four ounces seed chocolate and 400g untempered chocolate were added each bath. The ingredients for each sample are showed in table 1-3.
Table 1. The ingredients for cocoa butter effect

<table>
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<tr>
<th>Ingredient Abbreviation</th>
<th>Cocoa butter (%)</th>
<th>Cocoa liquor (%)</th>
<th>Sucrose and Milk (1:1) (%)</th>
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Table 2. The ingredients for cocoa liquor effect

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<th>Cocoa liquor (%)</th>
<th>Sucrose and Milk (1:1) (%)</th>
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Table 3. The ingredients for sucrose effect

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<th>Cocoa liquor (%)</th>
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3.2 Resistivity

The electrical resistivity was measured using a resistivity cell, electrometer (614 Electrometer, Keithley Instruments Inc. Cleveland, OH, USA) and a voltmeter (ABC 125-1DM, KEPCO Programmable Power Supply, Seoul, Korea). Approximately 125g milk chocolate was placed into a 250ml beaker (about half of the volume) and heated by hot plate to the desired temperature (30°C) and then put into the resistivity cylinder. The cylinder was filled carefully to avoid any air gaps. The voltage was adjusted to 125V and the current was read from the electrometer after the reading stabilized, which took 10 to 30 sec. Three replicates were tested.

The resistivity of the sample was calculated using:

\[
\text{Resistivity} = \frac{k \times V}{I}
\]

where \(k\) is 0.014, the cell constant of the cell, \(V\) is the voltage applied and \(I\) is the current.

The bulk density of chocolates were measured by using a 10ml volumetric flask and balance. It was calculated using:

\[
\text{Bulk density} = \frac{w}{v}
\]

Where \(w\) is the weight of sample and \(v\) is the volume.

3.3 Viscosity

Viscosity was measured using a Brookfield RVDV- II + Viscometer (Brookfield Engineering Laboratories Inc., Middleboro, MA, USA) using spindle 4. 400g sample was put in a 600ml beaker and was pre-sheared for 3 min at 50 rpm before recording the viscosity values. The spindle was rotated over all speeds. The viscosity value was recorded by decreasing the spindle speeds from 100 to 0 rpm followed by an increase.
The viscosity was measured at 30°C. The temperature of the sample was maintained by controlling the temperature of the water bath. The viscosity for all samples was compared when the speed of spindle is at 10 rpm (average value for increasing and decreasing speed). Three replications were performed.

3.4 Spraying

The samples were coated using a TDC Liquid Electrostatic Coater (Terrronics Development Corporation, Elmwood, IL, USA). The samples were sprayed at -25 kV. The sample was pumped to the nozzle using a variable speed pump (Cole-Parmer Instrument Company, Vernon Hills, IL, USA). The speed is controlled at the maximum flow rate of 250 mL/min. The inlet and outlet tubes of the pump were insulated and heated to 30°C by a variable autotransformer (The Superior Electric Co., Bristol, CT, USA). The samples were sprayed onto a 16 × 18 cm glass slide, maintained at room temperature, placed on a conveyer belt moving at a speed of 1.7 cm/s. Three replications are performed for each sample.

3.5 Statistics

Error bars represent standard deviations of three replications for each sample. The Figure 4 to 6 were analyzed using paired t-test by SPSS. P value below 0.05 is used to determine significant difference for viscosity and resistivity of different samples.
Chapter 4: Results and Discussion

4.1 The effect of cocoa butter versus sugar and milk concentration

When considering about the effect of cocoa butter on spray quality, the cocoa butter increased from 25 to 45% in the chocolate, the sucrose and milk powder mixture (1:1 proportion) decreased in the same proportion and the cocoa liquor remained constant. The resistivity and viscosity were analyzed by the trend.
Figure 1. The effect of cocoa butter versus sugar and milk powder on viscosity and resistivity.

The resistivity increased as cocoa butter increased from 25 to 35% and then decreased as cocoa butter further increased from 35 to 45% (Figure 1). The initial increase in resistivity was probably mainly affected by the effect of sugar on resistivity. As cocoa butter increased from 25 to 35%, both the sucrose and milk concentrations decreased from 27.5 to 22.5%. Decreasing sucrose from 27.5 to 22.5% increased the
resistivity from $0.79 \times 10^{10}$ to $1.1 \times 10^{10}\Omega \cdot \text{m}$ (Figure 3). However, decreasing the milk powder from 27.5 to 22.5% did not change the resistivity. Therefore, the decrease in sucrose likely caused the initial increase in resistivity. This was proved by the results in 4.3. As cocoa butter continued to increase from 35 to 45%, the resistivity decreased. The resistivity of pure cocoa butter is measured as $5.65 \times 10^9 \Omega \cdot \text{m}$, while the resistivity of pure sugar and milk powder are almost ten times higher at $2.31 \times 10^{10}$ and $4.81 \times 10^{10} \Omega \cdot \text{m}$. The other study also found that the resistivity of pure cocoa butter was as low as $1.0 \times 10^9 \Omega \cdot \text{m}$ (Gorty and Barringer 2011). Thus, further increasing the cocoa butter decreased the resistivity. The electrical resistivity decreased significantly when the fat content increased from 53 to 76% (CL + CB + S versus CL + CB) and from 76 to 100% (Gorty and Barringer). Cocoa butter generated a continuous fat phase which suspends all other ingredients in the chocolate. Other solid contents cannot break up this phase when there is enough fat and these solids cannot generate enough drag to slow down the ionic movement (Castro and others 2003). Thus, increasing cocoa butter, the resistivity decreased.

The viscosity decreased as cocoa butter increased (Figure 1). Other scholars also had similar results. The apparent viscosity changes when the fat content varies (Ardakani and others 2014). The cocoa butter forms a continuous phase which suspends the solids in the chocolate thus adding additional cocoa butter decreases the viscosity of chocolate (Chevalley 1994). In one study, as the cocoa butter increased from 53 to 100% (CL+CB versus CB), the viscosity decreased from 0.48 to 0.01 Pa·s (Gorty and Barringer 2011). When cocoa butter increases, the continuous phase is better maintained and is not
interrupted by other solids content, therefore, the viscosity decreases (Castro and others 2003). High fat content in chocolate decreases Casson viscosity (Nebesny and Zyzelewicz 2005). In dark chocolate (without milk powder), as fat content increased from 25 to 30%, the plastic viscosity decreased (Afoakwa and others 2008). Free fat in dry whole-milk powder becomes part of the continuous fat phase reducing chocolate viscosity during conching (Verhey 1986).

4.2 The effect of cocoa liquor versus sugar and milk concentration

As the cocoa liquor concentration increased from 0 to 29.5% (CL0 to CL 29.5, Table 2), the sucrose and milk powder mixture (1:1 proportion) decreased from 32.25 to 17.5% in the same proportion and the cocoa butter remained constant.
As cocoa liquor increased, the resistivity first decreased from $2.03 \times 10^{10}$ to $1.41 \times 10^{10} \Omega \cdot \text{m}$ and then increased from $1.41 \times 10^{10}$ to $2.16 \times 10^{10} \Omega \cdot \text{m}$ (Figure 2). The initial decrease in resistivity was likely because of both milk powder and sucrose decreasing...
and cocoa liquor increasing. As sucrose decreased from 32.25 to 27.5%, the resistivity increased from $0.78 \times 10^{10}$ to $0.9 \times 10^{10} \Omega \cdot \text{m}$ (Figure 3). As milk powder decreased from 32.25 to 27.5%, the resistivity decreased from $1.18 \times 10^{10}$ to $1.05 \times 10^{10} \Omega \cdot \text{m}$ (Figure 3). Therefore, the resistivity decreased. Other study also showed that decreasing milk powder (CL+CB+S+M versus CL+CB+S) decreased the resistivity from $7.0 \times 10^{10}$ to $6.0 \times 10^{10} \Omega \cdot \text{m}$ (Gorty and Barringer 2011). The cocoa liquor contains 53% cocoa butter. As the cocoa liquor increased from 0 to 9.5%, the total cocoa butter in the system increased from 35 to 40% and increasing cocoa butter over 35% decreased the resistivity (Figure 1).

As the cocoa liquor continued to increase from 9.5 to 29.5%, the resistivity increased (Figure 2). Cocoa liquor has an extremely high resistivity compared to other ingredients in chocolate. The electrical resistivity of pure cocoa liquor was measured as $5.49 \times 10^{10} \Omega \cdot \text{m}$ at 30°C compared to $0.952 \times 10^{10} \Omega \cdot \text{m}$ for the chocolate with only 9.5% cocoa liquor. The resistivity of pure cocoa liquor was $1.8 \times 10^{10} \Omega \cdot \text{m}$ at 35°C, which was significantly higher than the samples containing cocoa butter, sucrose, milk powder and lecithin (Gorty and Barringer 2011). Similarly, the resistivity increased when cocoa liquor was used to replace other ingredients such as milk or sugar (Gorty and Barringer 2011). When adding 24% cocoa liquor into pure cocoa butter, the resistivity increased significantly (Gorty and Barringer 2011). As the cocoa liquor concentration increases, the solids in the cocoa liquor break up the continuous phase of the cocoa butter. Thus, the movement of the electrons in the liquid is slowed down by the increasing solids (Castro and others 2003).
As the cocoa liquor increased, the viscosity decreased (Figure 2). The cocoa liquor includes roughly 53% cocoa butter, 17% carbohydrates, 11% protein, 6% tannins and 1.5% theobromine (Healthy Eating @ Rebound Health 2012). As cocoa liquor increased, the fat in the system increased, which decreases the viscosity. Similarly, as the cocoa liquor increased from 0 to 24% to replace cocoa butter, the viscosity increased significantly from 0.01 to 0.1 Pa·s at 35°C (Gorty and Barringer 2011).

4.3 The effect of sucrose versus milk concentration

Sucrose was increased from 0 to 45%, while milk powder was decreased from 45 to 0% and cocoa butter and cocoa liquor were kept constant.

The resistivity decreased and then increased as sucrose increased and milk decreased (Figure 3). The resistivity is affected by particle size, moisture content, bulk density and constituents of food materials (Jha and others 2011). When the sucrose and milk powder were mixed together, the bulk density of the chocolate changed, thus, there was an interaction between sucrose and milk powder that changed the resistivity of the chocolate. The higher the bulk density, the lower the resistivity (Jha and others 2011). The bulk density for the sample with 0% sugar and 45% milk powder was 1.15g/ml, for the sample with 30% sugar and 15% milk powder, it was 1.21g/ml, and for the sample with 0% milk powder and 45% sugar, it was 1.17g/ml. As sucrose concentration increased from 30-55% in an aqueous system, the resistivity also increased (Luo and others 2012). The resistivity increased when 40% sucrose and milk were added into samples of chocolate (Gorty and Barringer 2011).
Figure 3. The effect of sucrose and milk powder on viscosity and resistivity.

The viscosity did not change greatly as sucrose versus milk powder concentration changed (Figure 3). The viscosity decreased with decreasing sucrose concentration in one study that replaced sucrose with distilled water, which has a much lower viscosity compared to other ingredients (Luo and others 2012).
4.4 The effect of tempering

Tempering decreased or increased resistivity in no clear pattern (Figure 4). The tempered chocolate has lower resistivity, such as 0 and 19.5% cocoa liquor (Figure 4). The resistivity for both the tempered and untempered chocolate decreased and then increased with liquor content, but they were offset with different liquor contents as the lowest value. Tempering creates many small crystal seeds which serve as nuclei to create small crystals in the chocolate (Loisel and others 1998). These small crystals aligned in order and had closer packing which made them have lower resistivity (Comerford 2012). When the cocoa liquor increased, the fat content also increased, because the cocoa liquor contains 53% cocoa butter. Increased fat generated more closed packed small crystals, thus, the resistivity decreased after tempering. However, when cocoa liquor continued to increase, the resistivity increased because of the high resistivity of pure cocoa liquor.
Figure 4. The effect of tempering on resistivity. Samples in different data sets with different letters are significantly different.

Tempering slightly increased the viscosity (Figure 5). The viscosity increases after tempering (Briggs and Wang 2004). When chocolate was added to temper with small fat crystals (seed chocolate) at 34°C, the plastic viscosity of tempered chocolate increases (Chevalley 1975). Tempering creates many small crystal seed which serve as nuclei to create small crystals in the chocolate. These small crystals generate harder chocolate with high viscosity (Loisel and others 1998).
Figure 5. The effect of tempering on viscosity. Samples in different data sets with different letters are significantly different.
Chapter 5: Conclusions

Increasing cocoa butter and cocoa liquor decreases the viscosity. Keeping an intermediate cocoa butter (35%), cocoa liquor (9.5 to 19.5%), sucrose (30%) and milk powder (15%) decreases the resistivity. Commercial milk chocolate typically contained around 19% cocoa butter, 12% cocoa liquor, 20% milk powder and 48% sugar. Compared with laboratory samples with the best rheological properties, commercial samples have less cocoa butter and more sugar. The high percentage of sugar and milk powder brings better flavor and the low cocoa butter is mainly decided by cost. Tempering slightly increases the viscosity, but influences the resistivity in a no clear pattern.
References


Chiumarelli M, Hubinger MD. 2012. Stability, solubility, mechanical and barrier properties of cassava starch – carnauba wax edible coatings to preserve freshcut


Ratanatriwong P. 2004. Sensory evaluation of electrostatically coated chips and powder physical property effects (size and food composition) on electrostatic coating improvement (Doctoral dissertation, Ohio State University).


Appendix A: Raw Data for the Effect of Ingredients on Rheological Properties

A.1 The effect of sucrose on rheological properties

A.1.1 The effect of sucrose concentration on resistivity

Table 4. Resistivity for chocolate at 125 V and 30°C

<table>
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<th>Resistivity 1 (Ω*m)</th>
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A.1.2 The effect of sucrose concentration on viscosity

Table 4. Viscosity for chocolate at 30°C using RV spindle #4

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A.2 The effect of cocoa butter on rheological properties

A.2.1 The effect of cocoa butter on resistivity

Table 5. Resistivity for chocolate at 125 V and 30 ℃

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<th>Resistivity 1 (Ω*m)</th>
<th>Resistivity 2 (Ω*m)</th>
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<td>B40</td>
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<td>1.01E+10</td>
<td>1.08E+10</td>
<td>1.04E+10</td>
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<tr>
<td>B45</td>
<td>9.89E+09</td>
<td>9.72E+09</td>
<td>9.94E+09</td>
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### A.2.2 The effect of cocoa butter on viscosity

Table 6. Viscosity for chocolate at 30°C using RV spindle #4

<table>
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<th>Speed (RPM)</th>
<th>B25</th>
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<th>B35</th>
<th>B40</th>
<th>B45</th>
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<td>9100</td>
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<td>30700</td>
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<td>12650</td>
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A.3 The effect of cocoa liquor on rheological properties

A.3.1 The effect of cocoa liquor on resistivity

Table 7. Resistivity for chocolate at 125 V and 30°C

<table>
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<tr>
<th></th>
<th>Resistivity 1 (Ω*m)</th>
<th>Resistivity 2 (Ω*m)</th>
<th>Resistivity 3 (Ω*m)</th>
<th>Average (Ω*m)</th>
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<td>2.03E+10</td>
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### A.3.2 The effect of cocoa liquor on viscosity

Table 8. Viscosity for chocolate at 30°C using RV spindle #4

<table>
<thead>
<tr>
<th>Speed (RPM)</th>
<th>L0</th>
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<th>L14.5</th>
<th>L19.5</th>
<th>L24.5</th>
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