ABSTRACT
Flint, Mandy, Pauline. Comparison of Sweetened Condensed Skim Milk and Whey Protein Ingredients in Caramels. (Under the direction of Edward Allen Foegeding.)

Caramels may be described as 'soft glasses' that are viscous in nature and contain a dispersion of milk protein and an emulsion of fat. Milk proteins have traditionally been used in the confectionary industry for contributing distinct flavor, color, and texture, with sweetened condensed milk and milk powders being among the most popular. There are two main types of proteins in milk: caseins and whey proteins. Two popular ingredients made from whey proteins are whey protein isolates (WPI) and concentrates (WPC). Whey protein concentrates (WPC) contain between 25 and 80% protein and whey protein isolates (WPI) contain approximately 90% protein, with the remaining constituents being water, ash, lipid, and lactose. The goal of this research was to evaluate the acceptability and functionality of using whey protein ingredients in caramel confections by replacing the sweetened condensed skim milk with an imitation sweetened skim milk made with whey protein ingredients.

A control formula containing sweetened condensed skim milk (SCSM) and one with an imitation sweetened condensed skim milk made with whey protein isolate (I-SCSM) were evaluated. Formulations were cooked to 113°C, 116°C, and 119°C. Properties of both treatments were highly influenced by cook temperature. Creep recovery testing was used to evaluate viscoelastic properties of caramels. All caramels showed minimal recovery, indicating they were mainly viscous (fluid) in nature. Cold flow, the flow of caramels at room temperature over time under the force of gravity, was evaluated by measuring sample area over time. Minimal cold flow was seen in caramels

cooked to 116 and 119 ºC. However, caramels cooked to 113°C showed cold flow in both formulations, with caramels made with WPI exhibiting more cold flow than the control caramel. There were perceptible color differences between control and those made with WPI processed to 119°C; however, few differences were seen at 113°C and none were seen at 116°C. The relationship between glass transition temperature and maximum compliance was similar between both caramel treatments, suggesting no change in the mechanism responsible for rheological properties. Based on all of the properties measured, whey proteins can be substituted for SCSM in caramels with an endpoint temperature of 116°C. However, color and textural differences were seen at 113°C and 119°C.

Based on the similarity seen in caramels made with WPI and SCSM, three brands of 34% whey protein concentrates (WPC) were explored as a more complex system containing higher levels of lipid, lactose, and minerals. There were no significant effects ($p>0.05$) due to brand of 34% whey protein concentrate (WPC) in compliance from the creep and recovery test, viscosity, percent recovery, glass transition temperature, moisture content or water activity. Differences due to WPC brand were seen in retardation time and color. A consumer acceptance test ($n = 106$) revealed that a caramel formulation made with one brand of WPC was similar to the control caramel with SCSM with the exception of stickiness.

Three brands of commercial caramels were evaluated in order to validate that the data from analytical testing was similar to that found in experimental caramels. Only slight differences were seen in rheological properties amongst commercial caramels and between commercial caramels and experimental caramels. Differences were mostly seen

in color, which may be attributed to by final cook temperature (unknown) or ingredient formulations. Color values did fall within the range of experimental caramel formulations using SCSM, WPI, and WPC.

COMPARISON OF SWEETENED CONDENSED SKIM MILK AND WHEY PROTEIN INGREDIENTS IN CARAMELS

by
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APPROVED BY:

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Chair of Advisory Committee

Dedication

I dedicate this thesis to my family
for always supporting me and
to my friend and co-worker Paige Luck
for encouraging me, teaching me, and
believing in me even when I didn't.

BIOGRAPHY

Mandy Flint was born on December 11, 1977 in Lompoc, California to Norman and Susan Flint. Mandy has two older brothers, Jason and Nathan. Growing up Mandy was active in music and drama. She played the violin for three years and then became active in choir during high school. Mandy also participated on the yearbook staff and in various clubs in high school. She graduated from Lompoc High School in June of 1996 and began attending Allan Hancock Community College in August of 1996. Mandy explored a variety of majors including English, journalism, and psychology. However, she had become very interested in chemistry during high school and knew she was interested in pursuing some aspect of science. After hearing about food science from a friend, she explored this major when applying to California Polytechnic State University in San Luis Obispo. Mandy began at Cal Poly in food science in September of 1998 where she was active in the food science club and InterVarsity. For a summer internship experience in food science, she worked in a frozen strawberry plant in Salinas, California in the quality assurance department. After graduating from Cal Poly in 2001 with her Bachelors of Science in Food Science, Mandy started her graduate program at North Carolina State University. At NCSU Mandy has been active in the food science club in both social and service aspects. Mandy was a co-chair for the outreach committee, participated in intramural volleyball, and the product development team. As a member of the product development team, Mandy helped to develop *Mocha Royale*, a chocolate covered coffee creamer that won NCSU first place in the IFTSA product development competition in Anaheim, California in June of 2002. Currently Mandy is seeking out a product development position that will take her back to the West Coast.

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Introduction

Caramel is a popular and widely consumed confection that produces images of delicious, chewy treats in the minds of consumers. Caramel may be found in a range of textures, colors, flavors and products. This common confection may be consumed alone as or in combination with chocolate, nougat, marshmallows, nuts, and other inclusions. The properties of individual caramels are dictated by ingredient formulation and processing. Some applications include caramels wrapped for consumption, for depositing into chocolate shells, as ice cream toppings, and as an ingredient in other confections or desserts.

The confectionery industry is a successful and ever-growing business in the United States and worldwide. The National Confectioner's Association (NCA) reported that total chocolate consumption was 3.3 billion pounds and non-chocolate consumption was 3.1 billion pounds in 2000 (NCA 2000). These values show that Americans love candy and there is a large market for caramel consumption.

Milk proteins have traditionally been used in the confectionary industry for contributing distinct flavor, color, and texture. Milk proteins are used in a variety of forms with sweetened condensed milk and milk powders being among the most popular (Campbell and others 1987). Proteins, especially casein, create a firm and chewy confection upon heating, heighten moisture retention, and control free and bound water in the system (Campbell and others 1987). Casein and whey proteins also provide emulsion stability when lipids are one of the ingredients in confections (Hugunin and others 1977).

Whey solids have been used in the production of caramel and have been shown to enhance the browning reaction due to the increase in lactose content (Kinsella 1970). The use of whey proteins in the confectionary industry may pose a cost-efficient substitute to other milk ingredients, with potential to show similar flavor, color, and texture characteristics.

The use of whey protein as a functional ingredient has grown tremendously in the food industry. Whey protein has been shown to have foaming, whipping, emulsifying, viscosity-building, and gelling properties. Whey protein ingredients may range in protein content of 25 to 90%. The level of protein purity is a large factor in deciding which ingredient is appropriate for a specific application (Foegeding and others 2002). Whey protein concentrates (WPC) contain between 25 and 80% protein and may be used as nonfat milk substitutes, or in products such as yogurt, infant formulas, and processed cheese (Foegeding and others 2002). Whey protein isolates (WPI) contain approximately 90% protein with the remaining constituents being water, ash, lipid, and lactose (Foegeding and others 2002). Between January 2000 and June 2002, 181 new products have been introduced globally that list WPI on their labels. These product categories are snacks (115), beverages (33), weight control (28), confectionary (4), and novelty (1) (Minitel's Global New Database 2002). The use of whey protein in confectionary products is of interest for flavor, color and structural effects.

The goal of this research is to evaluate the acceptability and functionality of using whey protein ingredients in caramel confections by replacing the sweetened condensed skim milk with an imitation sweetened skim milk made with whey protein ingredients. Typical caramel characteristics for a control caramel formulation and a variety of milk

and whey protein caramel formulations will be assessed and compared through monitoring glass transition temperature, moisture content, water activity, cold flow, color and small strain creep recovery. Product acceptability will be evaluated using consumer testing. These properties are measured in order to determine effects of using whey protein ingredients and their ability to maintain a functional and appealing product.

Caramel Formulation and Ingredient Functionality

Caramels may be described as 'soft glasses' that are viscous in nature and contain a dispersion of milk protein and an emulsion of fat (Jeffrey 2001). Ingredient choices play a large role in the quality of the final product in caramel confections. Cold flow, the tendency for a substance to flow at room temperature under its own gravity, is one of the quality parameters controlled by ingredients (Warnecke 1996). Texture, flavor, color, and potential to grain, indicated by crystal formation, are other important quality issues that are affected by ingredient choices.

Caramel typically consists of sugar, corn syrup, milk protein, and vegetable fat (Jeffrey 2001; Pyrz 1976; Warnecke 1996). Water, salt, vanilla, and emulsifiers are common optional ingredients (Brown 1993). Lecithin and glycerolmonostearate (GMS) are the emulsifiers typically used in caramels at 0.2 to 0.3% of the lipid content (Brown 1993). There is no standard of identity for caramels making it an ideal matrix for ingredient experimentation (Warnecke 1996).

The sugar in caramels is generally sucrose which provides bulking and sweetness properties (Hofberger 1997). The sucrose to corn syrup ratio in caramels is vital in controlling stickiness, cold flow, and chewiness. Typically, with an increase of sucrose comes a decrease in chewy texture of caramels (Pyrz 1976). If there is a higher

proportion of sugar in the formulation, there is an increase in graining potential (Hofberger 1997). Graining occurs when the sugar in a confection crystallizes and causes an appearance that may be desirable or undesirable depending on final application (Jackson 2000). Graining usually appears on the surface of the product first and then progresses inward, creating a short texture which usually leads to a reduction in stickiness (Ledger 1996). A product is said to be "short" when it is not cohesive and does not result in stringing when bitten into (National Starch and Chemical Company 2003).

Corn syrup provides body to caramels as well as adding sweetness and effecting cold flow, chewiness, and graining properties (Hofberger 1997; Ledger 1996). Corn syrup with a dextrose equivalent (DE) of 42 is typically used for caramels (Brown 1993). Dextrose equivalent may be defined as the percentage of reducing sugars in corn syrup, calculated as dextrose, on a dry weight basis (Whistler and others 1985). The DE value will affect the color and texture characteristics of caramels. A high DE corn syrup will result in a darker colored caramel due to the increased content of reducing sugars whereas corn syrup with a low DE will produce a chewier caramel (Brown 1993). In addition to DE value, the amount of corn syrup in a caramel also affects the sensory characteristics of the final product. Corn syrup has the ability to prevent crystallization, thus preventing product dryness while providing characteristic chewiness (Pyrz 1976). However, when used as a large portion of the formulation, corn syrup will produce a product that is undesirably sticky and tough in texture (Ledger 1996).

The ratio of sugar to corn syrup has a significant affect on the graining potential, and thus the shelf life, of a caramel (Ledger 1996). There is some debate as to what proportion of sugar to corn syrup should be used in order to inhibit graining. Guelfi

(1988) stated that when the proportion of sucrose is higher than that of corn syrup the caramel has an increased tendency to grain but also bites more cleanly. If the amount of corn syrup in the formulation is higher there is an increase in browning, stickiness and elasticity (Guelfi 1988). Pyrz (1976) found that a ratio of 40:60 sugar:corn syrup was sufficient to inhibit graining. More recently, Richmond (1998) stated that a ratio of 50:50 is the standard proportion for retail caramels. For an increase in shelf life or if the caramels are made in the summer months, the sugar content may be lowered below 50% and the corn syrup may be increased to over 50% (Richmond 1998). In hard candies, Kitt (1993) stated that corn syrup is normally used in the amount of 35 to 40%, but that the level of corn syrup required was dictated by the type of manufacturing process to be used. However, Kitt also reported that highly viscous candies create a barrier against graining because it is difficult for the sucrose molecules in the candy to order themselves into crystals. Jackson (2000) found that in hard candies 1.5 parts sucrose to 1 part 42 DE corn syrup was sufficient for a storage shelf life of several years. Different ratios of sugar to corn syrup may be used in order to completely change the characteristics and potential applications of the individual confection.

Lipid, from vegetable or milk sources, is a key element in caramel. Lipid content in caramel formulations can range from 5 to 20% with typical values between 10 to 12% (Hofberger 1997). Lipid provides a variety of functional benefits with the most obvious being flavor. Lipid also has a shortening effect on the texture of caramel, as well as, the ability to reduce stickiness (Ledger 1996). Melting points should be between 29.4 and 46.1 °C when vegetable lipids are used (Pyrz 1976). The melting point of the lipid is a quality parameter for the texture of the caramel. Lipid does contribute to a ‘stand-up’

caramel texture; thus lowering the melting point could create a plastic flow to the product, affecting the caramel's ability to retain its shape (Pyrz 1976). A melting point higher than the recommended range could lead to a waxy mouthfeel upon consumption (Pyrz 1976). Lipid may also affect the shelf life stability of a caramel with the potential for rancidity or fat expression. Fat expression is a defect that occurs when there is poor emulsification and results in a greasy caramel surface (Jeffrey 2001).

Sweetened condensed skim milk (SCSM) is used for flavor, color, and cold flow control in caramels. Sweetened condensed milk is most often used due to the lower water content and added sugar creating a more stable product (Ledger 1996; Pyrz 1976). This ingredient also produces a more efficient process because there is less water to be boiled off during cooking. In addition to its functionality, sweetened condensed skim milk is also commonly chosen for its reduced cost in comparison to other milk protein ingredients (Jeffrey 2001).

Milk Proteins

Milk proteins are essential for caramels in the development of flavor, color, and body that occur during heating (De Wit 1989; Southward 1989). In addition, milk proteins interact with the ingredients in caramels to form a characteristic viscoelastic texture (De Wit 1989). There are two main types of proteins in milk: caseins and whey proteins. These proteins are categorized based on their solubility at pH 4.6 at 20 ºC. The proteins that precipitate are caseins, and whey proteins remain soluble (Fox 2001).

Caseins from bovine milk consist of four types of proteins that have different functional characteristics: α_{s1} (38%), α_{s2} (10%), β (36%), and κ (12%) (Fox 2001). αs_1, α_{s2}, and β-caseins all have a rather large amount of phosphate groups that bind polyvalent

cations (primarily calcium) strongly, causing charge neutralization that leads to precipitation at >6mM Ca^{2+} at 30°C (Fox 2001). However, κ-casein only contains 1 PO_4/mol and therefore binds cations weakly and does not precipitate, making it able to stabilize up to ten times its weight of calcium-sensitive caseins through the formation of micelles (Fox 2001). α_{s2} - and κ-caseins contain cysteine which exists as intramolecular disulphide bonds, inhibiting flexibility (Fox 2001). In contrast, αs_1- and β- caseins do not contain cysteine and are more flexible (Fox 2001). All four types of caseins contain high levels of proline, but β-casein contains the highest level which prevents formation of a secondary structures (α-helices, β-sheets, and β-turns) (Fox 2001). In general, caseins have a small molecular mass (~20-25 kDa), are phosphorylated and contain high levels of serine (Fox 2001). Caseins have secondary and tertiary structures and are relatively hydrophobic but do possess high surface hydrophobicity and display genetic polymorphism (Fox 2001). Caseins also have an open-chain structure that enables them to be highly heat stable in a variety of food applications (Reimerdes 1988).

Casein contributes a firm and chewy texture to caramels upon heating, while lacking stickiness and toughness (Kinsella 1984). Large sucrose crystal formation may be inhibited by the ability of caseins to bind water (Campbell and others 1987). Surfactant properties may also be provided by caseins as a result of their amphiphilic structure, aiding in the formation of a homogeneous product (Southward 1989; Swaisgood 1985).

Whey proteins lack the amphiphilic structure that caseins have and thus are considered inferior in their emulsification capabilities (Swaisgood 1985). The whey protein portion of bovine milk consists of four main proteins: β-lactoglobulin (50%), α-

lactalbumin (20%), blood serum albumin (10%), and immunoglobulins (10%) (Fox 2001). Whey proteins differ from caseins in that they have high levels of secondary, tertiary, and often quaternary structures (Fox 2001). In addition, whey proteins are globular proteins that are denatured upon heating, are not phosphorylated, and are not sensitive to Ca^{2+} (Fox 2001).

Whey proteins may be used to make several functional ingredients, including whey protein isolates and concentrates (WPI and WPC). Whey protein concentrates are the dry portion of whey with some of the lactose, fat, and minerals removed to provide a finished product with protein levels ranging from 34% to 80%, typically produced by ultrafiltration/diafiltration (King 1996; Igoe and others 1996; Fox 2001). Whey protein isolates are ingredients processed through ion-exchange and/or membrane processing and are considered to be higher in quality than most WPC ingredients due to their high protein content (~95%) (Fox 2001). Although, the use of WPI is often limited by the high expense associated with production. However, there are a wide range of WPC ingredients with functionality similar to WPI (Fox 2001).

Whey protein concentrates possess a variety of functional characteristics with some of the most important being solubility, emulsification, foaming and whipping ability, gelation, water absorption, and flavor and color development (King 1996). Whey protein concentrates have a high level of solubility at a wide pH range, which allows them to be used under acidic conditions without coagulating (King 1996). WPCs function as emulsifiers by absorbing on the surface of fat globules. The ability of WPC to emulsify may be manipulated through denaturation of the proteins (Campbell and other 1987; King 1996). WPCs (80%) have been shown to make stable foams, providing there

is a low fat content and the proteins have not been denatured (Mulvihill 1992; King 1996). Upon heating, the protein in WPCs form a 3-dimensional gel network (King 1996). Flavor may be provided by WPCs due to its ability to absorb volatile flavor compounds. Flavor compounds are also contributed directly from the whey. In addition, color and flavor formation due to the lactose undergoing Maillard browning resulting in a brown color and aldehyde production (King 1996; Campbell and others 1987). These functional properties make WPC a potential substitute for traditional milk proteins in caramel products.

Water is an important ingredient in confections and its functionality is often overlooked. Water as an ingredient works as a solvent and dispersing medium (Igoe and others 1999). In caramels, water acts to dissolve the sugar and create a syrup in the cooking process (Ledger 1996). Control of the final moisture content is a quality parameter (Jeffrey 2001). The more moisture a caramel has, the softer the texture (Jeffrey 2001). The degree of cold flow also tends to increase with an increase in moisture content (Jeffrey 2001a). Typical moisture levels for caramels range from 6 to 15%, depending on the application (Warnecke 1996).

Emulsifiers "reduce the surface tension between two immiscible phases at their interface, allowing them to become miscible" (Igoe and others 1999). They have five major functions in a food: complexing, dispersing, control of crystallization, wetting, and lubricating (Igoe and others 1999). The primary applications in caramels are controlling crystallization of sugars, dispersing the fat phase, and lubricating the product in order to avoid stickiness. Lecithin is one of the most common emulsifiers used in caramels (Brown 1993). Due to its amino group, lecithin takes part in the Maillard browning

reaction (Davies and others 1997). Typically lecithin ranges from 0.0 to 0.3% in caramel confections (Ledger 1996).

In addition to the above ingredients, there are optional ingredients that various candy manufacturers may choose to add to their caramels. Salt is the most prevalent optional ingredient and is used to enhance the flavors of the other components in the caramel (Kitt 2002). The amount of salt used in caramels ranges from 0.25 to 1.00% of the formulation, with a typical value of 0.50% (Kitt 2002; Pyrz 1976).

Natural and artificial flavors may be added in order to enhance the natural caramel notes or to provide the product with a new flavor (Pyrz 1976). Vanilla, usually in the form of vanillin, is the most common flavor added (Pyrz 1976; Kitt 2002). Vanillin is often chosen over pure vanilla for increased flavor stability and cost efficiency. The addition of flavors should occur during the end of the cooking process in order to avoid degradation of the volatiles and the potential for stickiness due to the added moisture from the vanilla (Pyrz 1976). Other common flavor additions to caramels include licorice, peppermint, and raspberry (Kitt 2002). Honey and molasses may be added for their dual contribution of flavor and color (Minifie 1975).

Inclusions are ingredients that may be added to create a caramel with unique flavor and texture characteristics. Examples of inclusions commonly added to caramels are chocolate, peanut butter, nuts, and marshmallows (Kitt 2002). In essence, these inclusions allow for caramels to fit new product descriptions and allow the confectionary industry to expand its applications.

Caramels may also have ingredients added to modify the textural properties. Egg whites and gelatin function to aerate caramels in addition to creating a more elastic final

product (Minifie 1975). These properties may or may not be desirable depending on the final product application. A variety of starches may be added to caramels in order to provide body (Kitt 2002). Modified starches with a high level of amylopectin may reduce cold flow in caramels. However, this will cause an increase in viscosity, possibly causing processing difficulties. Pectin, gelatin, wheat flour, soy proteins, and alginates are other optional ingredients used to improve the body of caramels (Kitt 2002).

Maillard Browning Reaction

The milky flavor associated with caramels comes from the Maillard reaction occurring among the milk proteins, reducing sugars, and water. The Maillard browning reaction provides not only flavor but color development as well (Jeffrey 2001). This reaction is complex, especially in a multi-component system such as caramel. In confectionary products high temperature and low water activity are two primary conditions that affect the rate of reaction (Edwards 2000). Another important condition for Maillard browning is pH, with very little browning occurring in a product with a pH 6 or less (Ellis 1959).

In the beginning stages of the Maillard reaction a free amino group from a protein condenses with a carbonyl group of a reducing sugar which results in a Schiff base (Edwards 2000). The Schiff base rearranges through the Amadori or Heyns rearrangements resulting in an *N*-substituted glycosylamine and an *N*-substituted fructosylamine (Edwards 2000). The rearrangement products degrade as the reaction progresses by one of three modes: deoxysones, fission, or Strecker degradation (Edwards 2000). The end result is the formation of brown nitrogenous polymers and copolymers (Edwards 2000).

Overview of Caramel Manufacture

The cooking process of caramels serves three main functions: reduction of moisture, development of color and flavor, and development of texture (Guelfi 1988). Caramels are manufactured with a range of different methods, depending on the production scale and the product application. The most traditional and basic method is a batch operation using an open kettle. The kettle may be heated either by steam or gas and is normally made of copper or stainless steel (Kitt 2002). In order to prevent the caramel from scorching, kettles contain mixing blades with scrapers for continuous agitation of the batch (Jeffrey 2001). Batch size ranges from approximately 40 to 500 pounds with the cycle length related to the size, steam pressure and final moisture requirement of the caramel (Guelfi 1988). The practice of rinsing the sides of an open kettle after the boiling point is reached is suggested for reduced graining (Hofberger 1997). When using an open kettle, the average cook time is between 20 and 30 minutes, depending on the desired level of color and flavor development (Hofberger 1997). The agitation of the caramel should be stopped immediately after cooking as a preventative measure for graining (Hofberger 1997). The batch process is disadvantageous due to its labor intensity, inconsistency, and small capacity (Brown 1993).

A continuous process may be advantageous over a batch process when a large capacity is required for production. However, the switch from batch to continuous decreases the amount of cook time required, thus stunting the time for the Maillard reaction to develop color and flavor and resulting in a white caramel (Mermelstein 1999). Continuous, high temperature, short time, high shear (HT-ST-HS) also requires a significant financial investment and an increased skill level for those operating it (Guelfi

1988). The confectionary industry has attempted to correct for the lack of color and flavor development with two approaches. The first is cooking continuously, holding for 10 to 20 minutes, and then cooling the caramel. The second approach has been to use a pressurized system to raise the caramel syrup to above 148.8 °C in order to achieve carmelization quickly, followed by evaporation to reduce the moisture level (Mermelstein 1999). Other new methods in the confectionary industry include using microwaves to vacuum-dry semi-finished products and using liquid jets for cutting confections (Mermelstein 1999).

There are five basic steps involved in the production of caramel: pre-mixing, emulsification, cooking/carmelization, cooling, and forming (Kitt 2002). Pre-mixing involves combining the pre-melted fat with the sugar, corn syrup, emulsifier, sweetened condensed milk, and salt while heating to a temperature above the melting point of the fat. The emulsification step involves agitating the premix at a high speed while temperature remains constant for 10 to 20 minutes. During the cooking stage the heat is boosted and the caramel syrup is brought to a boil until the desired final temperature is reached. After cooking the flavor may be mixed in and then the caramel is cooled, normally between stainless steel slabs on a greased table. Upon cooling, the caramel can be passed through a cut and wrap machine (Kitt 2002).

Quality Control Measurements

There are standard measurements that may be tested in order to monitor the quality and consistency of caramels. Water activity (a_w), moisture, and pH are primary factors that have a significant impact on the final product. Water activity ranges from 0.0 to 1.0 and is an indicator of the amount of water in a food system that is unbound and free

to react biologically and chemically (Potter and others 1995). Most pathogenic bacteria will not grow at a water activity below 0.90 and at 0.65 mold growth is inhibited (Potter and others 1995). In order to avoid microbial spoilage, a_w of caramels is usually kept below 0.68 (Jeffrey 2001). There are several simple analytical machines available to quickly obtain a_w.

Water activity is related to the equilibrium relative humidity (ERH) by multiplying the a_w by 100 (Potter and others 1995). The ERH is a critical factor for preventing both the absorbance of moisture and the drying out of the product due to lack of moisture (Jackson 2000). An ERH of less than 65% is recommended for a shelf life of 6 to 9 months (Jeffrey 2001a).

The final moisture content of caramels has a significant effect on the texture and the potential for graining (Kitt 1993; Ledger 1996; Jeffrey 2001). Moisture content is a function of cook time and temperature. If the moisture content is high, the caramel has a softer texture, whereas if the moisture content is low the candy will be very viscous (Jeffrey 2001; Kitt 1993). The more viscous a caramel is the less prone to graining it will be (Ledger 1996). Cold flow is another factor that is affected by the moisture content. The higher the moisture content the softer the texture and thus the caramel is more susceptible to cold flow (Jeffrey 2001a).

A common and reliable measurement of moisture for confectionary products is the Karl Fischer titration (Beard 2001). This method involves the dispersion of a sample of known mass into an organic solvent. A typical solvent mixture is a 50/50 blend of methanol and formamide. The solvent liberates the moisture in the sample and is subsequently titrated with the Karl Fischer reagent, which contains iodine and sulfur

dioxide, to a visual, potentiometric or conductometric endpoint. The level of Karl Fischer reagent used in the titration and the mass of the sample are factors in calculating the moisture content. Foods that contain ascorbic acid, aldehydes, ketones, or free carboxyl groups cannot be tested using this method due to their reaction with the organic solvent and release of water causing an overestimation of the moisture content (Beard 2001).

The measurement of pH is defined as

$$pH = -\log_{10}[H^+]$$

with $[H^+]$ as the concentration of hydrogen ions in the solution. The pH is an important parameter for foods because it conveys their degree of acidity or alkalinity (Edwards 2000). For the confectionery industry, pH indicates conditions that may or may not be favorable to certain ingredients. In fruity candies, pH is a quality control parameter regarding the degree of acidity. In candies that contain hydrocolloids, pH can be crucial to know in order to avoid precipitation at its isoelectric point (Edwards 2000). In caramel production the pH indicates the level of color and flavor that has been achieved. A high pH reading denotes a strong flavor and color development, while at a neutral pH browning becomes very rapid as the caramel undergoes complex Maillard browning reactions. If the pH of a product is acidic during Maillard browning the sugar in the product may go through inversion, thus increasing the level of reducing sugars which affects the sweetness, color, stickiness, and viscosity (Brown 1993). In addition, a low pH may result in denaturation of the milk proteins that creates a coarser texture in the caramel (Brown 1993). Therefore, the recommended pH range for caramels is 6.0 to 6.7

at the end of the cooking process depending on the desired degree of development (Jeffrey 2001).

Sensory Analysis

The use of sensory analysis is important to the successful development and subsequent improvement of quality food products. Consumer acceptance of products is vital to the overall success of the final product. Sensory evaluation may be defined as a method that scientifically measures, evokes, analyzes, and interprets responses to products through smell, sight, taste, touch, and hearing (Stone and others 1993).

There are several different methods of sensory evaluation that may be used to obtain useful data. The three main categories are discriminative, descriptive, and affective. Discriminative tests are based on the ability for people to correctly identify the product being tested from among a group of similar products (Lawless and others 1999). A commonly used discriminative or difference test is the triangle test in which two products are the same and one is different. The objective of this test for the panelist is to choose the product that is different. Descriptive tests are used to quantify the intensities of select product attributes as perceived by a trained panel (Lawless and others 1999). Affective or hedonic tests are ideally designed to quantify the degree to which a person likes or dislikes a product (Lawless and others 1999). Affective tests are used to determine if a person has a preference for one product over another.

The use of consumer affective or acceptance sensory evaluation is beneficial in determining the probable success of a product. In the food industry consumer sensory testing has two main methods: the measurement of preference and the measurement of acceptance (Jellinek 1964). Consumer acceptance scores may be used to infer

preferences indirectly (Lawless and others 1999). Acceptance testing is typically measured using a hedonic scale with 5, 7, or 9 points. The 9-point or degree-of-liking scale is the most common hedonic scale and was invented in the 1940s at the Food Research Division of the Quartermaster Food and Container Institute in Chicago, Illinois (Peryam and others 1952). The hedonic scale has words associated with the numerical values ranging from 1 relating to dislike extremely to 9 relating to like extremely and these words are chosen on the basis of equal interval spacing, thus giving the scale ruler-like properties (Lawless and others 1999).

Glass Transition

Glass transition temperature (T_g) the temperature at which a highly viscous supersaturated amorphous liquid becomes a glassy solid upon being rapidly cooled to a certain temperature zone, characteristic of the product (Gabarra and others 1998). If the product is below this temperature zone, it is considered to be in the glassy state. For amorphous (non-crystalline) systems, glass transition can be dependent on time or temperature and specific to the composition or material being examined. The glass transition shows the change that occurs in the physical state of a material from the glassy solid form to the rubbery viscous liquid (Ferry 1980; Wunderlich 1990). Another way in which to define glass transition is in relation to the mechanical relaxation of a material (Ferry 1980). Mechanical glass transition is a result of temperature and deformation where a decrease in temperature results in the immobilization of macromolecules (Slade and others 1993).

Dynamic Differential Scanning Calorimetry (DDSC) is an instrument commonly used to detect glass transitions as well as other endothermic and exothermic reactions.

DDSC combines traditional thermal analysis methods and mathematical analysis to determine the specific heat of a sample (DiVito and others 1995). DDSC, in contrast to nondynamic DSC, may also be used to separate specific heat from other reactions, such as loss of moisture, and breakdown or crystallization of a sample (DiVito and others 1995). With the DDSC method, there is a choice between two types of thermal methods, Iso-Scan or Heat-Cool. These thermal methods, as applied to the sample are referred to as the repeating unit. In the Iso-Scan method the repeating units are generally an isotherm followed by a scan segment (DiVito and others 1995). The Iso-Scan method steadily increases the temperature of the samples and is used when analyzing semicrystalline materials within their melting region (DiVito and others 1995). The Heat-Cool method involves a heat step followed by a cool step and is used to obtain the glass transition from other reactions in the material (DiVito and others 1995).

Dynamic Differential Scanning Calorimetry provides quantitative data from which the complex specific heat (C_p) of the material is calculated. The C_p consists of the storage specific heat (C_p') and the loss specific heat (C_p"), which can indicate properties that can help characterize the material (DiVito and others 1995). A tangent delta curve may be derived using the storage and loss specific heat values (C_p"/ C_p'), which monitors the time dependence of transitions in the sample (DiVito and others 1995). A curve of the total specific heat may be used to note the non-dynamic response of a sample (DiVito and others 1995).

Color Measurement

The impact of wavelengths of light in the visible spectrum of 390 to 760 nm on the human eye is known as color (Francis 1995). The color of a food often serves as an

indicator of quality, both to the manufacturer and the consumer. Color serves as an indicator for ripeness and freshness and as doneness in foods such as meat, vegetables, and bread (Lawless 1995). The light reflected from a colored material may be categorized as hue, value, and chroma (Potter and others 1995a). Hue is the predominant wavelength reflected from a colored material, which relates to the color that is perceived (Potter and others 1995a). Value is the lightness or darkness of the color or the ratio of white to black (Potter and others 1995a). Chroma relates the intensity strength of the color (Potter and others 1995).

There are three common instrumental techniques for measuring color in the food industry: the Commission International de I'Eclariage (CIE) system, the Hunter L, a, b system, and the Munsell color solid (Giese 2000). The Commission International de I'Eclariage (CIE) system is based on using a standard source of illumination and a standard observer and produces CIE curves illustrating the visible spectrum for the tristimulus values which relate to X, Y, and Z primaries (Giese 2000). The Hunter L, a, b system quantifies the degree of lightness (L), the degree of redness or greenness (+/- a), and the degree of yellowness or blueness (+/-b) (Giese 2000). The Munsell color-order system specifies colors and evaluates their relationships with each other (Giese 2000). Munsell created numeric standards for hue, value and chroma and a collection of colored chips (the Munsell Color Book) displaying correlations between the chips and the hue, value, and chroma parameters (Giese 2000).

Rheological Testing (Creep and Recovery)

Creep Recovery is a common rheological method for viscoelastic materials in which a constant stress is applied to a sample while the strain is measured as a function of

time (Ferry 1961). The change in strain over time is the creep (Steffe 1992). After the stress is removed, the sample is observed to determine if any recovery occurs (Steffe 1992). For ideal elastic materials, strain would be constant when a sample is subjected to a constant stress and there would be complete recovery to the original shape (Steffe 1992). For ideal viscous materials, a linear response would result from steady flow and there would be no recovery of the material's shape (Steffe 1992). Materials viscoelastic in nature would have a nonlinear response to strain and display a permanent deformation less than the original deformation applied to the sample (Steffe 1992).

Creep data is easily performed on controlled stress rheometers and described with a creep compliance function (Steffe 1992). The equation for the creep compliance function is:

$$J = f(t) = \gamma / \sigma_{constant}$$

where J represents creep compliance as a function of time, γ represents strain, and $\sigma_{constant}$ represents a constant stress (Steffe 1992). Retardation time is another useful value that may be derived from this test to help characterize a material. Retardation time (λ_{ret}) is the time it takes for the delayed strain to arrive at approximately 63.2% of the final value (Steffe 1992). If a material has a large retardation time they will reach complete deformation very slowly (Steffe 1992). The Kelvin and Burgers models may be used to evaluate retardation time (Steffe 1992).

Conclusion

There are a variety of ingredients that may be used in caramels. The effects of specific ingredients in caramel confections may be analyzed through the use of physical and sensorial properties. Rheological testing, differential scanning calorimetry, water

activity, moisture analysis, color, and consumer acceptance may prove to be reliable methods to characterize functionality of ingredients in caramels.

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CHAPTER 2: Comparison of Sweetened Condensed Skim Milk and Whey Protein Ingredients in Caramels

Introduction

Caramel typically consists of sugar, corn syrup, milk protein, and vegetable fat (Jeffrey 2001; Pyrz 1976; Warnecke 1996) and may be classified as an emulsion made up of a dispersed phase of fat globules, and a supersaturated continuous phase comprised of sugars, proteins, and other additions (McMaster and others 1987). There are several common optional ingredients that are used in caramels because there is no standard of identity, including salt, vanilla, and emulsifiers (Brown 1993). The properties of individual caramels are dictated by ingredient formulation and processing parameters and may vary widely in texture, flavor, and color.

Milk proteins are essential for caramels in the development of flavor, color, and body that occur during heating (De Wit 1989; Southward 1989). In addition, milk proteins interact with the ingredients in caramels to form a characteristic viscoelastic texture (De Wit 1989). There are two main types of proteins in milk: caseins and whey proteins. These proteins are categorized based on their solubility at pH 4.6 at 20 ºC. The proteins that precipitate are caseins, and whey proteins remain soluble (Fox 2001). Casein is thought to contribute a firm and chewy texture to caramels upon heating, while lacking stickiness and toughness (Kinsella 1984). Whey proteins differ from caseins in that they have high levels of secondary, tertiary, and often quaternary structures (Fox 2001). In addition, whey proteins are globular proteins that are denatured upon heating, are not phosphorylated, and are not sensitive to Ca^{2+} (Fox 2001).

Whey proteins may be used to make several functional ingredients, including whey protein isolates and concentrates (WPI and WPC). Whey protein concentrates are the dry portion of whey with some of the lactose, fat, and minerals removed to provide a

finished product with protein levels ranging from 34% to 80% (King 1996; Igoe and others 1999; Fox 2001). Whey protein isolates are considered to be higher in quality than most WPC ingredients due to their high protein content (~95%) (Fox 2001). However, "quality" is a subjective term that needs to be evaluated based on ingredient functionality and taste in a specific application. The use of consumer sensory evaluation is one way to predict the probable success of a product. One form of consumer sensory testing is the measurement of acceptance, in which a 9-point hedonic or degree-of-liking scale is the most common scale. This scale has words associated with the numerical values ranging from dislike extremely (1) to like extremely (9) and these words are considered to have equal interval spacing, thus giving the scale ruler-like properties (Jellinek 1964; Lawless and others 1999).

This study was comprised of two sets of experiments. The objectives of the first experiment were to analyze the physical and rheological properties of caramels made with sweetened condensed skim milk (SCSM) and compare those to caramels made with an imitation-SCSM (I-SCSM), formulated using a whey protein isolate (WPI). Caramels were cooked to 113, 116, and 119 ºC to evaluate temperature- based changes. Water activity, moisture analysis, creep and recovery testing, cold flow, and glass transition temperature determination were the parameters chosen to characterize the caramels. The second experiment used 3 brands of 34% (WPC) to formulate I-SCSM for 3 caramel formulations cooked to 116 ºC and compared the physical, rheological, and sensorial properties to a caramel made with SCSM. The overall objective of the study was to determine if whey protein ingredients were an acceptable replacement for SCSM in caramels based on taste and functionality.

Materials and Methods

Caramel Ingredients

Food grade ingredients used were: corn syrup (42 DE/43 baume) and lecithin (Yelkin TS PI-105) (ADM, Decatur, IL, U.S.A.); granulated cane sugar (Dixie Crystals, Sugar Land, TX, U.S.A.); partially hydrogenated palm kernel oil (Paramount C, Loders Croklaan, Channahon, IL, U.S.A.); sweetened condensed skim milk (Level Valley Creamery, West Bend, WI, U.S.A.); whey protein isolate (BIPRO, Davisco Food International, Le Sueur, MN, U.S.A.) (Table 1); whey protein concentrate (34%) (Land O'Lakes, St. Paul, MN, U.S.A.; Glanbia Foods, Gooding, ID, U.S.A.; and Protient, St. Paul, MN, U.S.A.)(Table 1). Alpha-lactose was certified A.C.S. grade purchased from Fisher Scientific (Fair Lawn, NJ, U.S.A.). Deionized water (9.7 megaohms-cm) was used in the formulations.

Caramel Formulation

The standard formulation was a modified version of a commercial caramel formulation from the National Confectioner's Association (Table 2). The standard formula was adjusted to contain less fat, more water, and no salt in order to standardize all formulas. The ratio of sugar to corn syrup was adjusted in order to prevent graining. An "all whey protein" formulation was made by replacing the SCSM with an imitation SCSM (I-SCSM), formulated such that milk protein was replaced with whey protein and the lactose and sucrose content remained constant (Table 3).

Cooking Apparatus

Each caramel formulation was made according to the method of Steiner et al., (2003). Each batch (600g) was cooked in an All-Clad 1.5 quart stainless steel saucepan with an aluminum core (Metalcrafters, Inc., Canonsburg, PA, U.S.A.) placed on a

ceramic hotplate (Fisher Scientific, catalog number 11-500-108H). The caramel was blended with a stainless steel stir-shaft attached to a digital speed mixer (Heidolph, model RZR 2021, Kelheim, Germany). The hotplate surface temperature and caramel cooking temperature were monitored with a type K beaded probe (Fisher Scientific, catalog number 15-077-45) attached to a thermocouple (Fisher Scientific, catalog number 15-078-3A). After the caramel was cooked to the desired endpoint temperature, the caramel was poured into a fabricated rectangular stainless steel mold (30.5 x 15.2 x 0.64 cm) placed on a Silpat® (Demarle Inc., Cranbury, NJ, U.S.A.).

Caramel Preparation and Storage

The surface of the hotplate was heated to 170 ºC (level 5). The partially hydrogenated palm kernel oil and lecithin were combined and melted in the saucepan. The sugar, corn syrup, SCSM, and water were then added simultaneously. The ingredients were pre-mixed at 375 rpm for 20 min. After the pre-mixing stage was complete, the temperature level was boosted to level 7 and the stir speed was lowered to 200 rpm. Caramel formulations were cooked to 113, 116, or 119 ºC and then poured into the rectangular mold on the Silpat® to cool for 1 h at room temperature. Caramels were then stored in airtight Rubbermaid® containers to prevent moisture loss. Each caramel formulation at each cook temperature was replicated three times. All caramel samples were tested within 48 h.

Sample Analysis
Cold Flow

Cold flow describes the tendency for a product to flow over time under the force of its own weight (Warnecke, 1996). Caramels were cooled for 1 h at room temperature in stainless steel molds. A circular cutter (5.08 cm dia, 0.64 cm height) was used to

remove a sample and the sample was placed in Pyrex® Petri dishes (cover: 3.9" dia, 0.52" thick; bottom: 3.5" dia, 0.54" thick**)**. Labeling tape (Fisherbrand, 12-0) was used to create an air-tight seal as well as provide axes from which to take measurements for calculations (Figure 1). Changes in sample shape were measured at 0, 5, 10, 15, 20, 25, 30, 60 min and 2 d, and an elliptical area calculation was used to evaluate cold flow.

Creep Recovery

A controlled-stress rheometer (Stress Tech Rheometer, ATS Rheosystems, Bordontown, NJ, U.S.A.; Reologica Instruments, AB, Lund Sweden) was used to measure creep and recovery of the caramels. A constant stress of 100 Pa was used; this was established to be in the linear viscoelastic region (LVR) based on preliminary stress sweep experiments. A parallel plate attachment (20 mm diameter, 0.5 mm gap) was used. Caramel samples were softened in a microwave for 10 s in order to facilitate loading. Mineral oil was used to prevent drying on the edges of the caramel. Caramel samples were equilibrated for 300 s prior to beginning the test. Stress was placed on the samples for 300 s (creep) and then samples were allowed to recover for 300 s. All samples were equilibrated at 25 °C and held for the duration of the test.

Moisture

A Karl Fisher 701 Titrino (Metrohm Ltd., Herisau, Switzerland) was used to measure percent moisture. The solvent used was a 1:1 methanol (Fisher Scientific, HPLC grade, catalog number FL-07-0896) and formamide (Sigma Ultra, catalog number EC No 200-842-0) combination and Hydranal composite 5 was the reactant (Riedel-deHaen, Seelze, Germany). The Karl Fisher unit was enclosed in a plexi-glass dry box with nitrogen (pre-purified, compressed) pumped in to maintain low humidity. A re-

circulating water bath heated to 60 ºC was connected to the jacketed vessel of the titration unit in order to ensure the sample would completely dissolve. The extraction time was set at 900 s to enable the sample to dissolve. The sample size was approximately 0.25 g of caramel for each moisture determination. Each caramel replicate was tested in triplicate.

A vacuum oven (National Appliance Company, model 5831, Portland, OR, U.S.A.) was used in addition to the titration method listed above in order to confirm moisture values. Aluminum pans (Fisherbrand® catalog number 08-732) were pre-dried for 1 h at 70 °C under pressure not more than 100 mm mercury and then cooled in a desiccator for 1 h. Caramels were cut into small pieces and distributed evenly over the bottom of the tared pan. Samples were dried in the vacuum oven for 16 h at 70 °C under pressure not more than 100 mm mercury and then cooled in a desiccator for 1 h.

Water Activity

Water activity was determined using an AquaLab® (Westport, CN, U.S.A.) meter. Three replications of each caramel formulation were tested. Each replication was tested in duplicate. Each dish (2.54 cm dia) was filled to half its height with approximately 4.5 g samples. All measurements were taken at ambient temperature (23-25 ºC) in order to ensure accurate readings. Technical literature recommends calibration and sample measurements to be at 25 ºC because % equilibrium relative humidity (ERH) for solutions has been shown to be more consistent at this temperature (Marsili 1993).

Color

A Spectrogard® Color System (BYK Gardner, Silver Springs, MD, U.S.A.) was used to evaluate color using the reflection mode to measure L^* a^* b^* values based on the

Commission Internationale d'Eclariage (CIE) Lab scale. *L** is an indictor of lightness or darkness, *a** indicates hue on a green (-) to red (+) axis, and *b** indicates hue on a blue (-) to yellow (+) axis (Hunter 1942). Samples were placed in plastic RODAC plates with lids (65mm x 15 mm, with 10 mm grid, Le Pont de Claix, France) and readings were taken through the plastic plates. The machine was calibrated prior to testing samples using black and white standards.

Differential Scanning Calorimetry (DSC)

A Perkin Elmer® (Norwalk, CT, U.S.A.) 7 Series/Unix DSC 7 Differential Scanning Calorimeter with an intercooler II refrigeration unit and a dry box was used to determine glass transition temperatures of the caramels. Nitrogen gas was used at 20 ml/min to flush the sample chamber while nitrogen at 172 kPa was used to flush the dry box. The DSC unit was calibrated using dodecane and indium. Caramel samples (approximately 15 mg) were placed in aluminum pans with platinum lids. Samples were tested in the dynamic mode (isothermal for 30 s scan for 30 s) with a heating rate of 1 °C/min from -30 to 29.5 °C. The glass transition temperature was calculated using the half specific heat (C_p) extrapolated point on the storage specific heat capacity (C_p') curve. The storage specific heat is a simple linear specific heat that is the result of energy uptake during heating of the sample (DiVito and others 1995). The half specific heat extrapolated point is the midpoint of the glass transition range and averages the onset and endpoint temperatures.

Consumer Acceptability

Four caramel formulations were prepared for consumer evaluation. Samples were prepared in a food grade lab and stored at room temperature (25 ºC) in airtight containers

until analysis. The control caramel was made with sweetened condensed skim milk (SCSM) and the other 3 treatments were made with an imitation sweetened condensed skim milk (I-SCSM) containing one of three different brands of 34% whey protein concentrate (WPC). Each caramel treatment was made on a different day, with 4-600 g batches manufactured per treatment. Caramel manufacture began 4 days prior to the sensory testing due to the time intensive sample preparation.

Caramels were presented in 2 oz. soufflé cups numbered with 3-digit random codes. Caramels were cut into 2.54 x 1.27 x 0.5 cm pieces. Each cup contained 2 identical samples separated with a piece of wax paper to prevent the samples from sticking together. Samples were served at room temperature (25 ºC). Consumers were presented with de-ionized water and 2 baby carrots in order to clean their teeth between samples (Steiner and others 2003). Consumer testing was held in sensory booths located in the food science department under normal lighting conditions.

Caramel consumers (n = 106) were recruited from students, faculty, and staff from the North Carolina State University campus through the use of fliers and emails. Consumers received an informed consent form in accordance with North Carolina State University Human Subjects approval, a screener questionnaire, and a scoring ballot (Appendices A, B, C). The screener questionnaire was designed to collect basic demographic information and probe factors affecting consumer purchasing and consumption decisions regarding caramels. The ballot was designed to evaluate overall acceptance, overall appearance, overall color, overall texture, overall chewiness, overall stickiness, overall caramel flavor, overall milky/dairy flavor, and overall sweetness using

a 9-point hedonic scale. The order of caramel presentation was randomized among consumers. Following evaluation, consumers received a food treat.

Statistical Analysis

Experiments were analyzed by the Statistical Analysis System software for Windows (SAS Institute, Version 8, Cary, NC) using the mixed model (PROC MIXED) to identify significant main effects and interactions (Littell and others 1996). Least square means was used to investigate significant differences between treatments (Drake and others 2001). Significance was established at $p < 0.05$.

Results and Discussion

Experiment 1: Comparison of Caramels made with Sweetened Condensed Skim Milk (SCSM) and Caramels made with an Imitation Sweetened Condensed Skim Milk (I-SCSM) from Whey Protein Isolate (WPI) at Three Cook Temperatures

Two caramel treatments were formulated in this study: a control caramel made with sweetened condensed skim milk (SCSM) and a caramel with an imitation sweetened condensed skim milk (I-SCSM) made with whey protein isolate. The I-SCSM was formulated by matching protein levels and adding lactose, sucrose, and water to mimic the components in SCSM (Table 3). Both treatments were cooked to three different temperatures (113, 116, and 119 ºC), that fall into common cook temperature ranges for industrial caramels (Warnecke 1996; Ledger 1996). These caramels will be referred to as SCSM caramels and WPI caramels and the final cook temperature will be specified.

Creep and Recovery

Caramels made with sweetened condensed skim milk (SCSM) and whey protein isolate (WPI) varied according to final cooking temperature. Creep and recovery curves (Figures 2,3) showed that SCSM and WPI caramels with the lowest cook temperature

(113 ºC) resulted in significantly higher ($p<0.05$) maximum compliance values (Table 4), whereas caramels cooked to 116 ºC and 119 ºC were not significantly different between treatments. A higher maximum compliance value indicates a less viscous (liquid-like) material. Caramels in both treatments had the longest retardation time at 113 ºC, thus they recovered slower than caramels at other temperatures. Retardation times for SCSM and WPI caramels at 116 and 119 ºC were not significantly different (Figure 4). Retardation time reflects the time in recovery it takes for a viscoelastic material to reach full strain, (Steffe 1996). Apparent viscosity ($\eta = \sigma/\gamma$) increased significantly ($p<0.05$) in both SCSM and WPI caramels with cook temperature (Table 5). Measurements were calculated based on the point in the creep test where a linear response in strain was seen as indicated by a minimum of three identical points in succession. Apparent viscosity increased significantly ($p<0.05$) between SCSM and WPI caramels cooked to 113, 116, and 119 °C (Table 5)**.** The overall trend of viscosity increasing as cook temperature increases is expected as viscosity may be defined as the resistance to flow. Caramels made with WPI and SCSM cooked to 116 and 119 °C displayed less compliance than caramels to 113 °C, indicating they were slightly more viscous than the other caramels. Recovery (%) values (Figure 4) for caramels made with SCSM and WPI cooked to 116 ºC and caramels made with WPI cooked to 119 ºC were significantly higher ($p<0.05$) in recovery than the other formulas. This suggests these caramel treatments are slightly less viscous. Caramels made with WPI and cooked to 113 ºC displayed very little recovery, indicating they were more viscous than WPI caramels at other cook temperatures.

Cold Flow

Cold flow was measured over 24 hours and the final percentage of cold flow after 24 hours was reported, with less than 5% cold flow being seen at cook temperatures of 116 and 119 ºC for SCSM and WPI caramels (Figure 5). When caramels were cooked to 113 ºC cold flow was seen at a level of 8.0% for SCSM caramels and 36% for WPI caramels. It is well known that final cook temperature is one factor that affects cold flow, with lower cook temperatures resulting in increased cold flow (Ledger 1996). Ingredients are another factor that influence cold flow. For example, milk proteins coagulate during the cooking process and so the level of protein plays an important role in determining the final texture of caramels (Jeffrey 2001). There was not a clearly defined relationship seen between cold flow and compliance data from the creep and recovery test. Sweetened condensed skim milk (SCSM) caramels showed a slight, but insignificant increase in cold flow between caramels cooked at 116 and 119 ºC (Figure 5), but there was a clear trend in compliance values with caramels cooked to 113 ºC having the highest compliance, followed by caramels cooked to 116 and 119 ºC (Table 4). The significantly higher ($p<0.05$) cold flow seen in WPI caramels cooked to 113 ºC, indicates that SCSM created a firmer matrix than the WPI at the lowest cook temperature.

Moisture Analysis

Moisture was evaluated using a Karl Fischer titration unit as well as a vacuum oven. Data obtained from the Karl Fischer method showed the combined effect of cook temperatures between 113 and 116 ºC and 113 and 119 ºC were significant ($p<0.05$), however there were no significant differences ($p>0.05$) based on treatment alone. A

temperature dependent trend was seen in moisture content with caramels cooked to a higher temperature resulting in lower moisture content as expected based on colligative properties. Analysis of temperature-treatment interactions indicated there were no significant differences ($p>0.05$) between SCSM caramels cooked to 116 and 119 ºC (Figure 6). The boiling point elevation equation is stated below:

$$\Delta T_b = K_b m$$

where m is the molal concentration of the solute and K_b is the boiling point constant for the solvent (Walstra 20003). In a dilute system under ideal conditions, the magnitudes of these variables change in proportion to the mole fraction of the solute (Walstra 2003). The vacuum oven data showed significant differences between 113 and 116 ºC for both SCSM and WPI caramels (Figure 6). However, there were no significant differences ($p<0.05$) between 116 and 119 ºC for either treatment.

The lack of significant lowering in moisture content between all three cook temperatures does not seem to follow colligative properties presented in the boiling point elevation equation as discussed above. Possible sources of error that may occur with the Karl Fischer titration include interferences with carbonyl compounds (Bradley 1998). Carbonyl compounds react with methanol resulting in acetal formation and the release of water, which leads to an overestimation of moisture content (Bradley 1998). Aldehydes and ketones are carbonyl compounds that form during Maillard browning (Hodge, 1953). The development of these compounds in the second and third stages of the Maillard reaction may explain the moisture contents not lowering significantly between cook temperatures in the WPI caramels. Possible sources of error in the vacuum oven

method include the driving off of volatile compounds during the drying, which may result in an underestimation of moisture content (Bradley 1998).

Water Activity

Water activity values were significantly higher ($p<0.05$) for caramels at the lowest cook temperature for both SCSM and WPI formulations (Table 6). There was a reduction in water activity as the cook temperature increased to 116 ºC in both caramel formulations. There were no significant differences ($p>0.05$) between 116 and 119 ºC in either treatment. In an ideal solution water activity may be explained by the following equation:

$$a_w \text{ (ideal)} = x_w = \frac{m_w}{m_w + \Sigma m_{s,i}}$$

where m is the molar concentration of water (w) and of solutes (s), with the number concentration of solute molecules dictating the water activity (Walstra, 2003). An increase in moles of solute would result in a lower water activity while a decrease in moles of solute would increase the water activity. Therefore, slight increases in water activity or a lack of a significant decrease may be due to interferences with Maillard reaction products at higher cook temperatures. The Maillard reaction occurs rapidly around 115 ºC and progresses with increasing temperature (Jeffrey 2001). Therefore, reaction products would be more prevalent in caramels cooked to 116 and 119 ºC, hence the reduction in water activity as compared to caramels cooked to 113 °C.

Differential Scanning Calorimetry

Glass transition temperatures (Table 7) for these treatments displayed a temperature dependent trend with caramels at the lowest cook temperature resulting in the lowest glass transition temperature. This trend indicates these caramels will be more

like a rubbery viscous liquid than a glass at room temperature (Bell and others 1998) than those with higher glass transition temperatures. Glass transition is also closely related to moisture content, with an increase in water content resulting in a decrease in glass transition (Walstra, 2003).

Moisture, Water Activity, and Glass Transition Temperature

There are few linear trends observed in the caramel data relating glass transition temperature, water activity, and moisture content. There was no linear relationship seen in SCSM and WPI caramels upon comparison of vacuum oven data versus water activity (Figure 7). Sweetened condensed skim milk (SCSM) and WPI caramels cooked to 113 ºC had the highest water activity and moisture content, while caramels cooked to 116 and 119 ºC had similar water activity values and slightly varied moisture values. Sweetened condensed skim milk (SCSM) caramels cooked to 119 ºC had the lowest moisture content. The lack of a linear relationship between moisture content and water activity indicates that at higher temperatures caramel does not follow colligative properties due to its complicated nature and the variety of ingredient interactions that may occur. The relationship of water activity to glass transition temperature (Figure 8) shows that caramels cooked to 113 °C have a higher water activity and a lower glass transition temperature. However, caramels cooked to 116 and 119 ºC in both treatments have approximately the same water activity, while the glass transition continues to increase based on cook temperature (Figure 8). A linear trend is seen as expected relating moisture content to glass transition temperature (Figure 9), indicating that caramels with the highest moisture content (lowest cook temperature) have the lowest glass transition temperature (Walstra 2003).

Color Analysis

Color analysis for WPI and SCSM caramels under average daylight displayed few significant differences in L* values (black to white component or luminosity) (Table 8). Luminosity was the highest in SCSM and WPI caramels cooked to 113 ºC and WPI caramels cooked to 119 ºC and decreased at higher cook temperatures, indicating these caramels were lightest in color. However, there were no significant differences ($p<0.05$) in luminosity between SCSM caramels cooked to 113 and 116 ºC and WPI caramels cooked to 113, 116, and 119 ºC. The b* value decreased with increasing cook temperatures and therefore caramels had more of a blue component at higher cook temperatures. However, significant differences ($p >0.05$) were not seen in b* values in caramels cooked to 116 and 119 ºC. Morales and others (1998) also observed a decrease in b* with an increase in cook temperature in sugar-casein mixtures that were heated to evaluate the formation of brown components in the advanced stages of the Maillard reaction. Values for a* (+ red to – green) were not significantly different ($p>0.05$) for caramels made with SCSM cooked to 113, 116, and 119 ºC and WPI caramels cooked to 113 and 116 ºC. Caramels cooked to 119ºC made with WPI had the lowest a* value, indicating they were more green than the other caramels.

The E index was evaluated to determine perceptible differences ($\Delta E > 1$) between caramels (Morales and others 1998):

$$(L^{*2}+ a^{*2} + b^{*2})^{1/2}$$

As expected, perceptible color differences were seen based on cook temperatures within treatments. However, the only perceptible color differences for temperature-treatment interactions were between SCSM and WPI caramels cooked to 119 ºC, with SCSM caramels appearing darker than WPI caramels. Caramels in both treatments cooked to 113 ºC had the highest E values, indicating they were lightest in color. Sweetened condensed skim milk caramels at 119 ºC were significantly darker ($p<0.05$) than the other caramels. Temperature dependent changes in these SCSM and WPI caramels are most likely a result of color formation during the Maillard browning reaction. This color development is noted by the formation of unsaturated brown, nitrogenous polymers known as melanoidins (Ames 1992; Hodge 1953).

Color analysis of WPI and SCSM caramels under tungsten light displayed trends similar to those found under average daylight. Luminosity in SCSM caramels cooked to 119 ºC was lower than all other caramels, indicating it was the darkest in color (Table 9). Significant decreases ($p<0.05$) were seen in the yellow to blue component (b*) in the SCSM and WPI caramels cooked to 119 ºC, indicating an increase in the blue component at higher cook temperatures.

Conclusion

Overall, caramels made with WPI showed few significant differences compared to caramels made with SCSM. The main differences seen in this study were due to cook temperature. Based on the similarity seen in caramels made with WPI and SCSM, 34% whey protein concentrates (WPC) were explored as a more complex system containing higher levels of lipid, lactose, and minerals.

Experiment 2: Comparison of Caramels made with Sweetened Condensed Skim Milk (SCSM) and Caramels made with an Imitation Sweetened Condensed Skim Milk (I-SCSM) from Three Brands of 34% Whey Protein Concentrate (WPC)

Four caramel formulations were compared in this study: a control caramel made with sweetened condensed skim milk (SCSM) and three caramels made with an imitation sweetened condensed skim milk (I-SCSM) formulated from three brands of 34% whey protein concentrate (WPC) (Table 1). The I-SCSM was formulated by matching protein levels and adding lactose, sucrose, and water to mimic the components in SCSM (Table 2). All formulas were cooked to 116 °C. In contrast to whey protein isolate, whey protein concentrate (WPC) contains more minerals (3.30-3.85%) and lipids (4-5%).

Whey Protein Concentrate (WPC) Findings

There were no significant effects ($p>0.05$) due to brand of 34% whey protein concentrate (WPC) in compliance from the creep and recovery test (Table 10, Figure 10), viscosity (Table 11), percent recovery (Figure 11), glass transition temperature (Table 12), moisture content (Figure 12) or water activity (Table 13). Differences due to WPC brand were seen in retardation time and color.

Retardation time

Caramels made with WPC-C showed a significantly longer ($p < 0.05$) retardation time (s) than the other caramels (Figure 11). The larger retardation time indicates the material reaches full deformation more slowly (Steffe 1992) and thus caramels made with WPC-C were more viscous than caramels made with the other brands of WPC.

Cold Flow

Cold flow was more prevalent with WPC caramels than SCSM caramels. SCSM caramels showed approximately 2% cold flow after a 24-hour period (Figure 13). However, WPC-B caramels had significantly higher cold flow ($p < 0.05$) at 25%. Based on this evaluation it appears that WPC is not as effective as SCSM or WPI at forming a network in caramels.

Water Activity

Water activity values for the WPC-A, WPC-B, and WPC-C caramel formulas were not significantly different ($p>0.05$). However, SCSM caramels yielded a significantly lower water activity value ($p<0.05$) (Table 13).

Color Analysis

Color analysis under daylight conditions revealed significant differences ($p<0.05$) in the black to white component or luminosity (L*) among WPC-C, WPC-A, and SCSM caramels, with WPC-C caramels having the largest L* value and thus being the darkest caramel (Table 14). However SCSM caramels were significantly lower in L* from all other treatments, indicating it was the lightest in color. WPC-C caramels had a significantly higher ($p<0.05$) b* (+ yellow to - blue) value than the other caramels, indicating it was the most yellow in appearance, which would result from more browning. There were no significant differences among treatments ($p < 0.05$) in a* (+ red to – green).

No significant perceptible color differences (based on the "E" index) ($p<0.05$) were seen between WPC-A and WPC-B caramels under average daylight. Caramels

made with WPC-C had a significantly higher E value than the other caramels, indicating a much lighter appearance. A significantly lower ($p<0.05$) E index was seen in SCSM caramels indicating that it was perceptibly darker than the caramels made with whey protein concentrate.

Color values were also analyzed under tungsten light, with the same trends as those seen under average daylight in luminosity (L*), b* (+ yellow to - blue), and the E index (Table 15). Differences were seen in a* (+red to –green), with SCSM caramels having a significantly higher red component than caramels made with WPC-A and WPC-C.

Sensory Evaluation

Consumers were provided a survey that collected demographic information as well as probed factors that affect their purchasing decisions for caramels. The consumers tested were comprised of 61% females and 39% males with the predominant age group being 19-24 years (34%), followed by 25-29 years (25.5%). The most common consumption rate for caramels was once per month (61.3%) followed by 2 to 3 times per month (13.2%). Consumers most often used caramels individually for eating. Flavor, texture, and price were the three most important general factors influencing choice of caramel brands. The most important specific factors influencing consumer choice of caramel brands were milky/dairy flavor, chewy texture, and price.

Overall acceptance for caramels made with sweetened condensed skim milk (SCSM) and WPC-A were not significantly different ($p < 0.05$) (Table 16). All caramel formulations had similar scores for color liking. Therefore, analytical differences in color did not seem to affect the consumer liking scores of the caramels during sensory

evaluation. Texture liking was not significantly different among caramels made with WPC-A, WPC-B, and SCSM. Consumers liked caramels made with WPC-A as much as SCSM caramels, with the exception of the stickiness that WPC-A caramels possessed. Caramels made with WPC-B were also similar in liking scores to SCSM caramels with the exception of lower scores in appearance, chewiness, and stickiness. Appearance was the only attribute that WPC-C caramels had comparable hedonic scores to SCSM caramels. The WPC-A caramel received the highest liking scores for the flavor attributes: caramel flavor, milky/dairy flavor, and sweetness. These results indicate that the flavor of some 34% WPC may be desirable, but there are specific texture properties provided by the SCSM, such as chewiness and stickiness, that the 34% WPC caramels are lacking.

Conclusions

Overall, few differences were seen among WPC brands used in caramels compared to each other and compared to caramels made with SCSM from an analytical standpoint. However, one WPC was consistently scored lower in consumer acceptance than the others indicating that differences in functionality and taste do exist among WPC brands. Consumers scored one of the caramels made with WPC highest in all flavor attributes, but texture characteristics were scored lower than the SCSM caramels. Therefore, the total replacement of SCSM with an imitation SCSM made with WPC may be somewhat undesirable based on stickiness.

Evaluation of Commercial Caramels

Three commercial caramels ("A", "B", and "C") were characterized by evaluating moisture, water activity, glass transition temperatures, color, and rheological properties

including maximum compliance, retardation time, and creep and recovery. These caramels were purchased at the grocery store and two replications were performed for glass transition, moisture, water activity, and color analysis. Three replications of rheological data were collected. Commercial caramels were tested in order to validate that the data from analytical testing was similar to that found in experimental caramels.

Rheological Properties

Commercial caramels yielded maximum compliance values similar to caramels cooked to 116 °C made with sweetened condensed skim milk (SCSM), whey protein isolate (WPI), and whey protein concentrate (WPC) (Table 17, Figure 14). Apparent viscosity values for commercial caramels "A" and "C" were in the range of viscosities seen in SCSM and WPI caramels cooked to 116 °C as well as caramels formulated with WPC. However, commercial caramel "B" had a much higher viscosity value than all other caramels (Table 18). Commercial caramels "A" and "C" also fall within the range of caramels made with WPI and SCSM and cooked to 113, 116, and 119 °C and WPC formulas for retardation time, but showed slightly more recovery (Figure 15). Commercial caramel "B" displayed a shorter retardation time than the experimental formulations indicating it was more slightly more elastic (Figure 15).

Moisture

Moisture values for commercial caramels were determined using a Karl Fischer titration unit and a vacuum oven. As seen in the other caramels, moisture values collected using the Karl Fischer titration method yielded consistently higher values than those collected from the vacuum oven method. Caramels ranged from 8.1 to 9.5% moisture using a Karl Fischer titration unit, however there were no significant differences

($p>0.05$) among commercial caramels A, B, and C using this method (Figure 16). Values collected using the Karl Fischer titration method were within the typical range of experimental caramels made with SCSM, WPI, and WPC. Moisture values were between 5.4 and 7.3 % using the vacuum oven method. Unlike the experimental caramels, a case hardening effect was seen in the commercial caramels. Commercial caramel "A" was much lower in moisture using the vacuum oven method than the Karl Fischer titration method. Maillard browning appeared to have taken place in this sample during the course of the drying. However, the Karl Fischer titration method has been known to result in overestimation of moisture values when foods that contain carbonyl compounds, such as aldehydes and ketones are tested (Bradley 1998).

Water Activity

Water activity values for the commercial caramels were not significantly different ($p>0.05$) (Table 19). All values were in the 0.5 range. Recommended water activity values for caramels is less than 0.65 for a shelf life of 6 to 9 months (Jeffrey 2001a). The water activity values for commercial caramels were most similar to caramels cooked to 113 °C made with SCSM and WPI and those made with WPC (cooked to 116 °C).

Glass Transition

Glass transition temperatures for commercial caramels followed the temperature dependent trend of SCSM and WPI caramels. Commercial caramel "A" had a glass transition temperature similar to SCSM and WPI caramels cooked to 113 °C. Commercial caramel "A" had the lowest T_g, indicating that at room temperature this caramel will be more like a rubbery viscous liquid than a glass (Bell and others 1998) compared to those with higher glass transition temperatures. The glass transition

temperature of commercial caramel "B" was slightly higher than caramel "A" and in the range of SCSM, WPI, and WPC caramels cooked to 116 °C. Commercial caramel "C" the highest glass transition temperature, similar to SCSM and WPI caramels cooked to 119 °C (Table 20).

Moisture, Water Activity, and Glass Transition Temperature

Few linear relationships are seen upon comparison of moisture content, water activity, and glass transition temperature in the commercial caramels tested. However, there appears to be a linear relationship between moisture content and water activity (Figure 17) with higher moisture resulting in lower water activity values. There is no clear trend looking at water activity versus glass transition temperature (Figure 18). Commercial caramel "A" has the lowest water activity and the lowest glass transition temperature, but caramels "B" and "C" have similar water activity values and very different glass transition temperatures (Figure 18). A comparison of moisture content with glass transition shows no linear relationship for the commercial caramels (Figure 19).

Color Analysis

Caramels were analyzed under average daylight and tungsten light sources. Luminosity (L*) values were also significantly higher ($p<0.05$) in caramel "B" compared to caramels "A" and "C," again illustrating that caramel "B" is the lightest of the three commercial products (Table 21). Caramel "B" had the highest b* (+ yellow to – blue) value, demonstrating that it was the most yellow in appearance among caramels. There were no significant differences ($p>0.05$) in the a* (red to green component) among

caramels. There were no significant differences ($p>0.05$) in a* (red to green component) among caramels.

The E index was calculated as a parameter to indicate perceptible color differences among caramels (Morales and others 1998). Under average daylight caramel "B" had a significantly higher ($p<0.05$) E index than caramels "A" and "C," indicating that it was the lightest in color. Caramels "A" and "C" were not significantly different ($p>0.05$) from each other in the E index.

Color values under tungsten light revealed the same trends with the exception of the red to green component (a*) (Table 22). Caramel "B" was significantly higher ($p<0.05$) than the other caramel "A", indicating more of a red element. However, caramels "B" and "C" were not significantly different ($p>0.05$) from each other in this component.

In comparison to experimental caramels, the color values for commercial caramels were in the range of SCSM, WPI, and WPC caramels under both average daylight and tungsten light sources.

Conclusion

Overall, only slight differences were seen in rheological properties amongst commercial caramels and between commercial caramels and experimental caramels. Differences were mostly seen in color, which may be attributed to by final cook temperature (unknown) or ingredient formulations. Color values did fall within the range of experimental caramel formulations using SCSM, WPI, and WPC. Based on these three popular commercial brands, it may be concluded that caramels containing a variety of textures and appearances may find acceptance among consumers.

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Table 1. Protein and mineral analysis of whey protein concentrates (WPC) and isolate (WPI)*

Protein Source	*% Protein*	*% P*	*% K*	*% Ca*	*% Mg*	*Na, ppm*	*% S*
WPI	90.9	0.040	0.090	0.100	0.020	6911	1.60
WPC-A	35.6	0.760	1.89	0.500	0.110	8763	0.510
WPC-B	33.8	0.610	2.06	0.590	0.110	6212	0.480
WPC-C	34.5	0.550	1.63	0.500	0.110	4605	0.500

*Values are on a wet basis.

Table 2. Caramel Formulations.

Ingredient	*NCA* (%)*	*SCSM** Formulation (%)*	*WPI*** Formulation (%)*	*WPC**** Formulation (%)*
Water	11.3	14.8	14.8	14.8
Sugar, Granulated	30.2	13.0	13.0	13.0
Corn Syrup, 42DE	24.5	42.0	42.0	42.0
Sweetened Condensed Skim Milk	20.7	20.0	0.00	0.00
Imitation Sweetened Condensed Skim Milk	0.00	0.00	20.0	20.0
Partially Hydrogenated Vegetable Fat	12.2	10.0	10.0	10.0
Salt	0.94	0.00	0.00	0.00
Soya Lecithin	0.16	0.20	0.20	0.20
Total	100.0	100.0	100.0	100.0

NCA* : National Confectioner's Associaton
SCSM**: Sweetened Condensed Skim Milk
WPI***: Whey Protein Isolate
WPC****: Whey Protein Concentrate

Table 3. Components of Sweetened Condensed Skim Milk (SCSM), Imitation Sweetened Condensed Skim Milk (I-SCSM) with Whey Protein Isolate (WPI), and Imitation Sweetened Condensed Skim Milk (I-SCSM) with Whey Protein Concentrate (WPC)

*Components**	*SCSM (%)*	*I-SCSM with WPC (%)*	*I-SCSM with WPI (%)*
Protein	10.0	10.0	10.0
Fat*	**0.05**	**0.40**	**0.03**
Minerals*		**0.70**	**0.18**
Sucrose	42.0	42.0	42.0
Lactose	18.0	18.0	18.0
Moisture	30.0	30.0	30.0
Total	100.00	100.00	100.00

*Based on specifications provided by manufacturers.
Numbers in bold are a component of the protein source.

Table 4. Maximum compliance (Jmax) (1/Pa) values for sweetened condensed skim milk (SCSM) and whey protein isolate (WPI) caramels at three cook temperatures

Treatment	*Jmax (1/Pa)*
113 ºC SCSM	1.71E-02 ^{B*}
116 ºC SCSM	2.17E-03 ^{C}
119 ºC SCSM	5.70E-04 ^{C}
113 ºC WPI	4.00E-02 ^{A}
116 ºC WPI	2.28E-03 ^{BC}
119 ºC WPI	1.77E-03 ^{BC}

*Means in the same column with different letters represent significant differences ($p<0.05$). Standard error for all data was approximately 0.007.

Table 5. Apparent viscosity measurements (Pa-s) and onset strain for linear region for sweetened condensed skim milk (SCSM) and 34% whey protein concentrate (WPC) caramels cooked to 116 ºC

Treatment	*Onset Strain for Linear Region*	*Apparent Viscosity (Pa-s)*
113 ºC SCSM	1.05E+00 ^{A} *	22,000 ^{C}
116 ºC SCSM	1.43E-01 ^{AB}	210,000 ^{B}
119 ºC SCSM	3.92E-02 ^{B}	393,000 ^{A}
113 ºC WPI	3.15E+00 ^{B}	13,000 ^{C}
116 ºC WPI	1.14E-01 ^{B}	197,000 ^{B}
119 ºC WPI	4.14E-03 ^{B}	511,000 ^{A}

*Means in the same column with different letters represent significant differences ($p<0.05$).

Table 6. Water activity (a_w) values at ambient temperature for sweetened condensed skim milk (SCSM) and whey protein isolate (WPI) caramels at three cook temperatures

Treatment	a_w
113 ºC SCSM	0.505^{A*}
116 ºC SCSM	0.449^{B}
119 ºC SCSM	0.445^{B}
113 ºC WPI	0.550^{A}
116 ºC WPI	0.451^{B}
119 ºC WPI	0.466^{B}

*Means in the same column with different letters represent significant differences ($p<0.05$). Standard error for all data was approximately 0.02.

Table 7. Glass transition temperatures (T_g) (ºC) for sweetened condensed skim milk (SCSM) and whey protein isolate (WPI) caramels at three cook temperatures

Treatment	*T_g (ºC)*
113 ºC SCSM	-10.0 [B*]
116 ºC SCSM	-5.00 [A]
119 ºC SCSM	0.48 [A]
113 ºC WPI	-12.5 [B]
116 ºC WPI	-3.10 [A]
119 ºC WPI	3.90 [A]

*Means in the same column with different letters represent significant differences ($p<0.05$). Standard error for all data was approximately 2.56.

Table 8. Average daylight color values (L*, a*, b*, and E index) for sweetened condensed skim milk (SCSM) and whey protein isolate (WPI) caramels at three cook temperatures.

Treatment	*L**	*a**	*b**	*E index*
113 ºC SCSM	52.6 ^{A}	10.1 ^{AB}	23.0 ^{A}	58.3 ^{A}
116 ºC SCSM	50.3 ^{AB}	10.3 ^{AB}	19.8 ^{B}	55.0 ^{B}
119 ºC SCSM	48.6 ^{B}	10.0 ^{AB}	17.0 ^{C}	52.5 ^{C}
113 ºC WPI	52.2 ^{A}	11.0 ^{A}	24.3 ^{A}	58.6 ^{A}
116 ºC WPI	51.0 ^{AB}	11.0 ^{A}	20.0 ^{B}	56.0 ^{B}
119 ºC WPI	52.4 ^{A}	9.82 ^{B}	17.2 ^{BC}	56.1 ^{B}

Means in the same column with different letters represent significant differences ($p<0.05$). Standard error for L data was approximately 0.77; standard error for a* data was approximately 0.26; standard error for b* data was approximately 0.63; and standard error for E index data was approximately 0.53.

Table 9. Tungsten color values (L*, a*, b*, and E index) for sweetened condensed skim milk (SCSM) and whey protein isolate (WPI) caramels at three cook temperatures.

Treatment	*L**	*a**	*b**	*E index*
113 ºC SCSM	56.0^{A}	13.8^{A}	22.6^{A}	62.5^{A}
116 ºC SCSM	52.7^{B}	13.9^{A}	23.3^{A}	59.3^{B}
119 ºC SCSM	50.8^{B}	13.4^{A}	20.3^{B}	56.4^{C}
113 ºC WPI	54.8^{AB}	15.0^{A}	28.0^{A}	63.4^{A}
116 ºC WPI	53.4^{AB}	13.4^{A}	23.4^{A}	60.0^{B}
119 ºC WPI	54.5^{AB}	13.3^{A}	20.4^{B}	59.7^{B}

Means in the same column with different letters represent significant differences ($p<0.05$). Standard error for L data was approximately 0.76; standard error for a* data was approximately 0.53; standard error for b* data was approximately 1.14; and standard error for E index data was approximately 0.47.

Table 10. Maximum compliance (Jmax) (1/Pa) values for sweetened condensed skim milk (SCSM) and 34% whey protein concentrate (WPC) caramels cooked to 116 ºC

Treatment	*Jmax (1/Pa)*
WPC-B	3.26E-03*[A]
WPC-C	7.77E-03[A]
WPC-A	2.27E-03 [A]
SCSM	2.16E-03 [A]

*Means in the same column with different letters represent significant differences ($p<0.05$). Standard error for all data was approximately 0.002.

Table 11. Apparent viscosity measurements (Pa-s) and onset strain for linear region for sweetened condensed skim milk (SCSM) and 34% whey protein concentrate (WPC) caramels cooked to 116 ºC

Treatment	*Onset Strain for Linear Region*	*Apparent Viscosity (Pa-s)*
WPC-B	1.82E-01 [A]*	299,000 [A]
WPC-C	8.57E-02 [A]	215,000 [A]
WPC-A	1.15E-01 [A]	192,000 [A]
SCSM	1.43E-01 [A]	210,000 [A]

*Means in the same column with different letters represent significant differences ($p<0.05$).

Table 12. Glass transition temperatures (T_g) (ºC) values for sweetened condensed skim milk (SCSM) and 34% whey protein concentrate (WPC) caramels cooked to116 ºC

Treatment	T_g *(ºC)*
WPC-B	-4.84 ^{A*}
WPC-C	-3.40 ^{A}
WPC-A	-5.00 ^{A}
SCSM	-5.04 ^{A}

*Means in the same column with different letters represent significant differences ($p<0.05$). Standard error for all data was approximately 1.46.

Table 13 . Water activity (a_w) values at ambient temperature for sweetened condensed skim milk (SCSM) and 34% whey protein concentrate (WPC) caramels cooked to 116 ºC

Treatment	a_w
WPC-B	0.522 ^{A*}
WPC-C	0.512 ^{A}
WPC-A	0.525 ^{A}
SCSM	0.449 ^{B}

***** Means in the same column with different letters represent significant differences ($p<0.05$). Standard error for all data was 0.02.

Table 14. Average daylight color values (L*, a*, b*, and E index) for sweetened condensed skim milk (SCSM) and 34% whey protein concentrate (WPC) caramels cooked to 116 ºC.

Treatment	*L**	*a**	*b**	*E index*
WPC-B	54.5 ^{A}	10.8^{A}	22.1 ^{B}	60.0 ^{B}
WPC-C	56.3 ^{A}	10.9^{A}	28.5 ^{A}	64.0 ^{A}
WPC-A	53.1 ^{A}	11.3^{A}	25.3 ^{A}	60.0 ^{B}
SCSM	50.3 ^{B}	10.3 ^{A}	19.8 ^{B}	55.0 ^{C}

Means in the same column with different letters represent significant differences ($p<0.05$). Standard error for L WPC data was approximately 0.76 and 0.66 for SCSM; standard error for a* WPC data was approximately 0.41 and 0.35 for SCSM; standard error for b* WPC data was approximately 1.33 and 1.15 for SCSM; and standard error for E index data was approximately 0.60 and 0.51 for SCSM.

Table 15. Tungsten color values (L*, a*, b*, and E index) for sweetened condensed skim milk (SCSM) and 34% whey protein concentrate (WPC) caramels cooked to 116 ºC.

Treatment	*L**	*a**	*b**	*E index*
WPC-B	57.1 ^{AB}	14.6^{A}	25.7 ^{B}	64.5 ^{B}
WPC-C	59.1 ^{A}	15.5^{A}	32.2 ^{A}	69.1 ^{A}
WPC-A	55.8 ^{B}	15.4^{A}	29.0 ^{A}	64.8 ^{B}
SCSM	52.7 ^{C}	14.0 ^{A}	23.3 ^{B}	59.3 ^{C}

Means in the same column with different letters represent significant differences ($p<0.05$). Standard error for L data was approximately 0.90; standard error for a* data was approximately 0.30; standard error for b* data was approximately 0.66; and standard error for E index data was approximately 0.64.

Table 16. Consumer acceptability of caramels made with or without sweetened condensed skim milk (SCSM) substitution.

Attribute	*WPC-A*	*WPC-B*	*WPC-C*	*SCSM*
Acceptance	6.33^{AB}*	6.14^{B}	4.94^{C}	6.55^{A}
Appearance	7.01^{A}	6.68^{B}	6.94^{AB}	7.13^{A}
Color	7.07^{A}	6.95^{A}	6.97^{A}	7.24^{A}
Texture	6.36^{A}	6.35^{A}	5.37^{B}	6.63^{A}
Chewiness	6.33^{AB}	6.05^{B}	5.11^{C}	6.77^{A}
Stickiness	5.51^{B}	5.42^{BC}	5.02^{C}	6.57^{A}
Caramel Flavor	6.38^{A}	6.24^{A}	4.96^{B}	6.06^{A}
Milky/Dairy Flavor	6.24^{A}	6.15^{A}	5.03^{B}	6.00^{A}
Sweetness	6.50^{A}	6.42^{A}	5.56^{B}	6.25^{A}

*Means in the same row with different letters represent significant differences ($p<0.05$). Each attribute was scored on a 9 point hedonic scale where 1 = dislike extremely and 9 = like extremely.

Table 17. Maximum compliance values of three commercial caramels.

Commercial Caramel	*Jmax (1/Pa)*
A	4.81E-03[A]
B	3.21E-03 [A]
C	2.13E-03 [A]

No significant differences were seen in mean values ($p>0.05$). Standard error for data set was approximately 0.001.

Table 18. Apparent viscosity (Pa-s) measurements and onset strain for linear region of three commercial caramels.

Treatment	*Onset Strain for Linear Region*	*Apparent Viscosity (Pa-s)*
Caramel-A	3.78E-01 [A]*	101,000 [B]
Caramel-B	2.77E-02 [A]	941,000 [A]
Caramel-C	1.48E-01 [A]	224,000 [B]

*Means in the same column with different letters represent significant differences ($p<0.05$).

Table 19. Water activity values at ambient temperature of three commercial caramels.

Commercial Caramel	*Water Activity (a_w) at 25 ºC*
A	0.520 [A]
B	0.580 [A]
C	0.550 [A]

No significant differences were seen in mean values ($p>0.05$). Standard error for all data was 0.02.

Table 20. Glass transition temperatures of three commercial caramels

Commercial Caramel	T_g
A	-8.70 ± 0.70^{A}
B	-2.40 ± 1.4^{A}
C	4.80 ± 0.98^{A}

No significant differences were seen in mean values ($p>0.05$).

Table 21. Average daylight color values (L*, a*, b*, and E index) for three brands of commercial caramels.

Commercial Caramel	*L**	*a**	*b**	*E index*
A	48.1[B]	11.6[A]	23.5[C]	54.8[B]
B	54.7[A]	12.5[A]	29.4[A]	63.1[A]
C	48.8[B]	12.5[A]	25.1[B]	56.4[B]

Means in the same column with different letters represent significant differences ($p<0.05$). Standard error for L data was approximately 0.45; standard error for a* data was approximately 0.25; standard error for b* data was approximately 0.23; and standard error for E index data was approximately 0.53.

Table 22. Tungsten color values (L*, a*, b*, and E index) for three brands of commercial caramels.

Commercial Caramel	*L**	*a**	*b**	*E index*
A	50.8 ^{B}	15.6^{B}	27.3 ^{C}	59.7 ^{B}
B	57.7 ^{A}	17.2^{A}	33.5 ^{A}	69.0 ^{A}
C	51.6 ^{B}	16.7 ^{AB}	29.1 ^{B}	61.7 ^{B}

Means in the same column with different letters represent significant differences ($p<0.05$). Standard error for L data was approximately 0.42; standard error for a* data was approximately 0.22; standard error for b* data was approximately 0.30; and standard error for E index data was approximately 0.41.

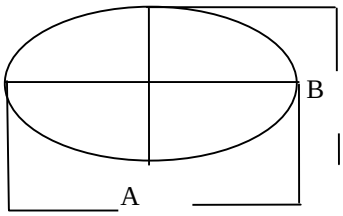

FIGURE 1- Elliptical area diagram used to calculate cold flow: A = long axis, B = short axis of ellipse equation: $A*B/4 *\pi$

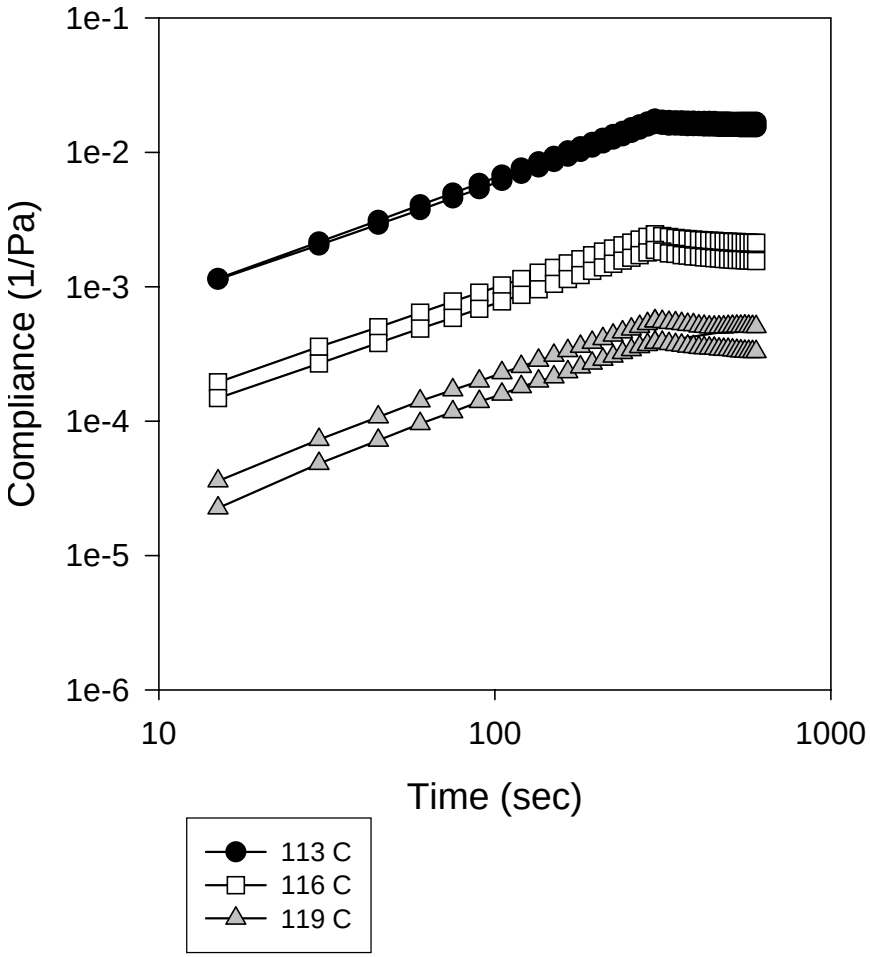

FIGURE 2- Creep and recovery of caramels made with sweetened condensed skim milk (SCSM) cooked to three temperatures.

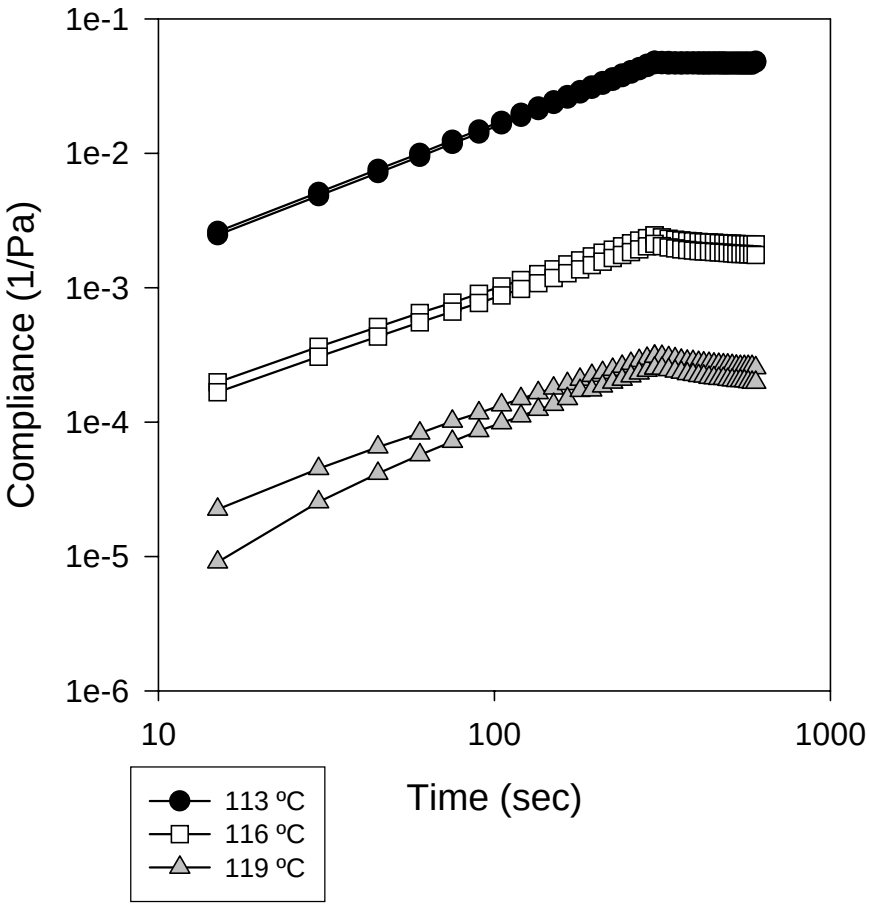

FIGURE 3- Creep and recovery of caramels made with whey protein isolate (WPI) cooked to three temperatures.

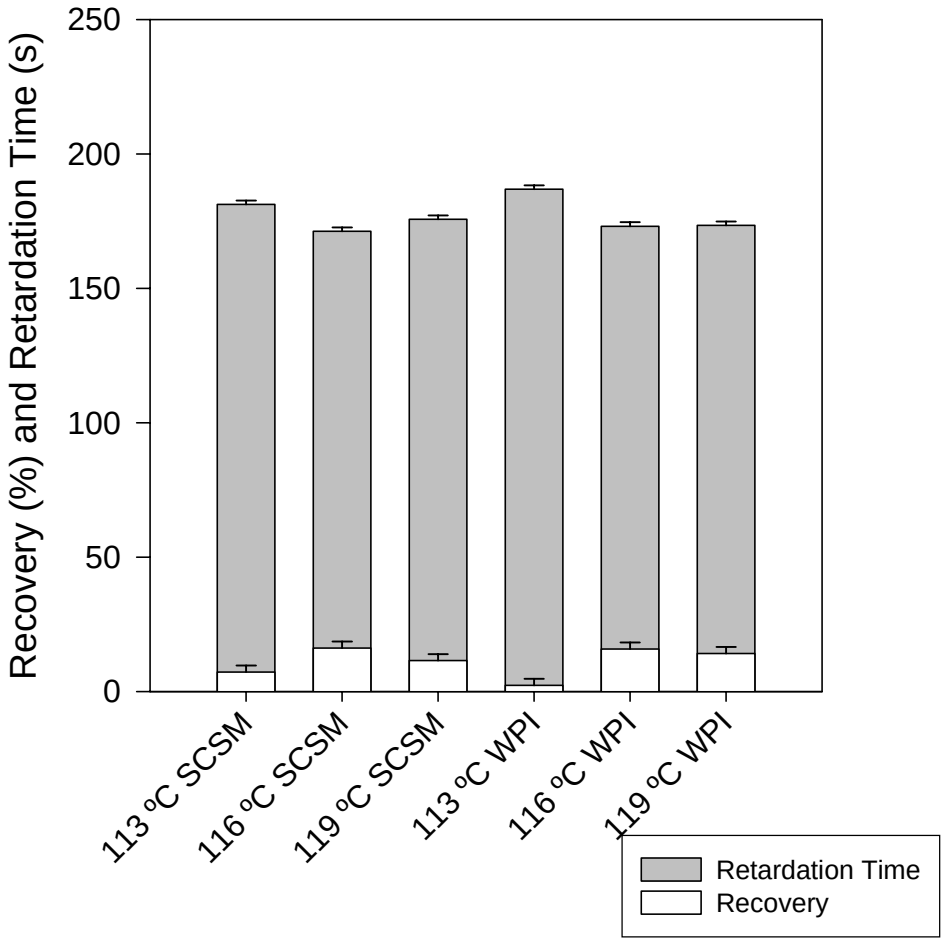

FIGURE 4- Retardation time and recovery for caramels made with sweetened condensed skim milk (SCSM) and whey protein isolate (WPI) cooked to three temperatures.

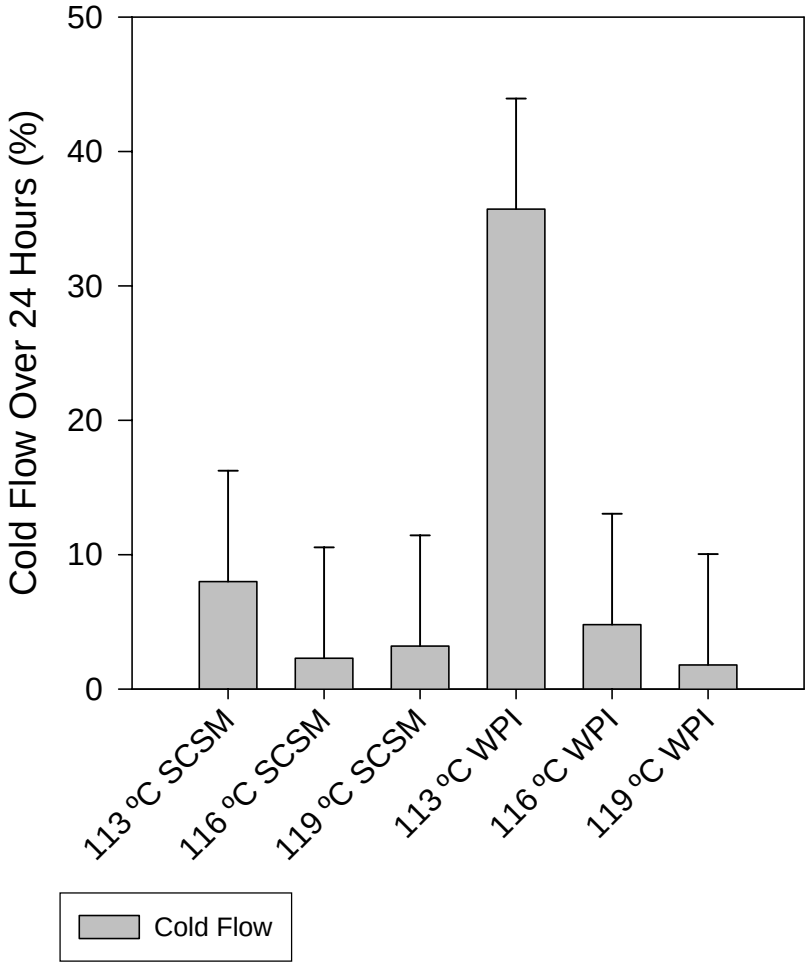

FIGURE 5- Cold flow of caramels made with sweetened condensed skim milk (SCSM) and whey protein isolate (WPI) cooked to 113, 116, and 119 ºC after 24 hours.

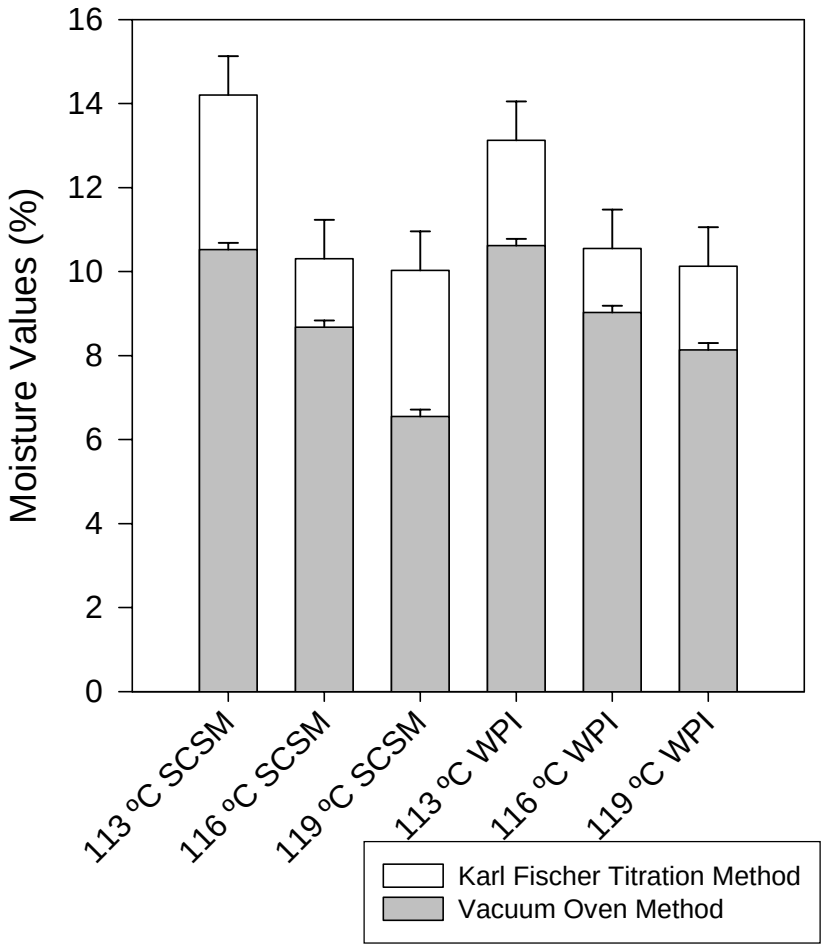

FIGURE 6- Comparison of moisture methods for caramels made with sweetened condensed skim milk (SCSM) and whey protein isolate (WPI) cooked to three temperatures.

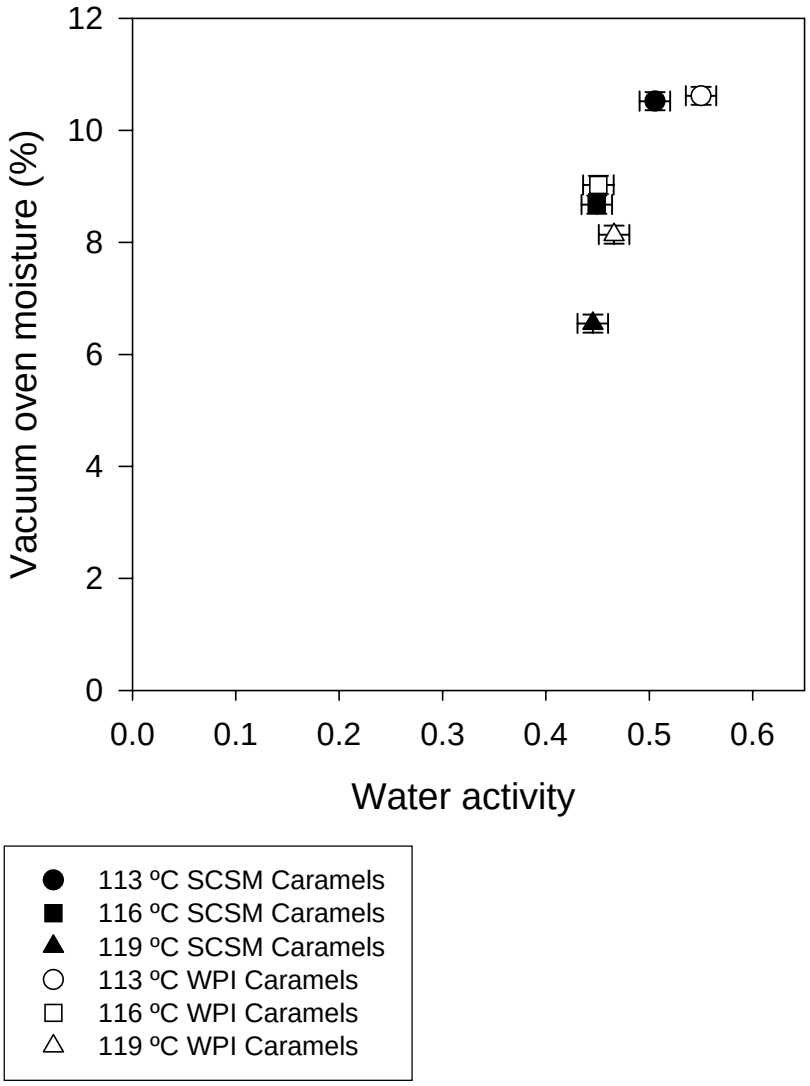

FIGURE 7- Vacuum oven moisture versus water activity in caramels made with sweetened condensed skim milk (SCSM) and whey protein isolate (WPI) cooked to three different temperatures.

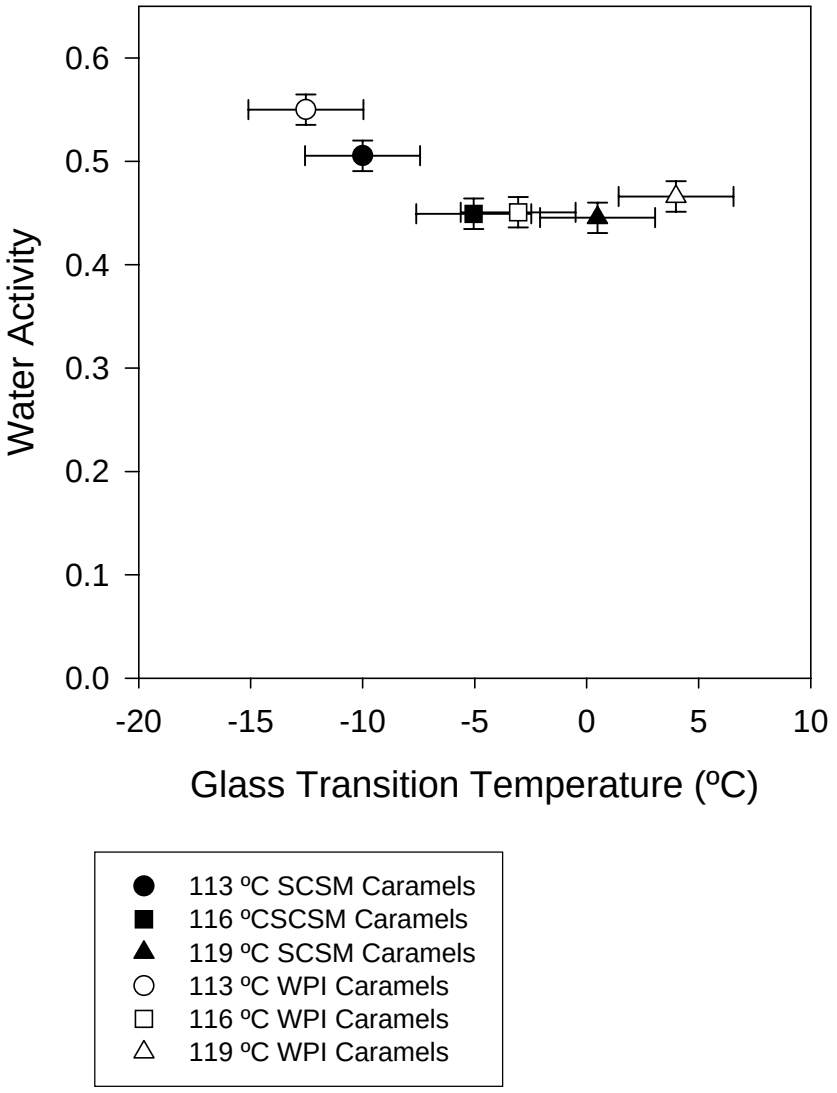

FIGURE 8 -Water activity versus glass transition temperatures for caramels made with sweetened condensed skim milk (SCSM) and whey protein isolate (WPI) cooked to three different temperatures.

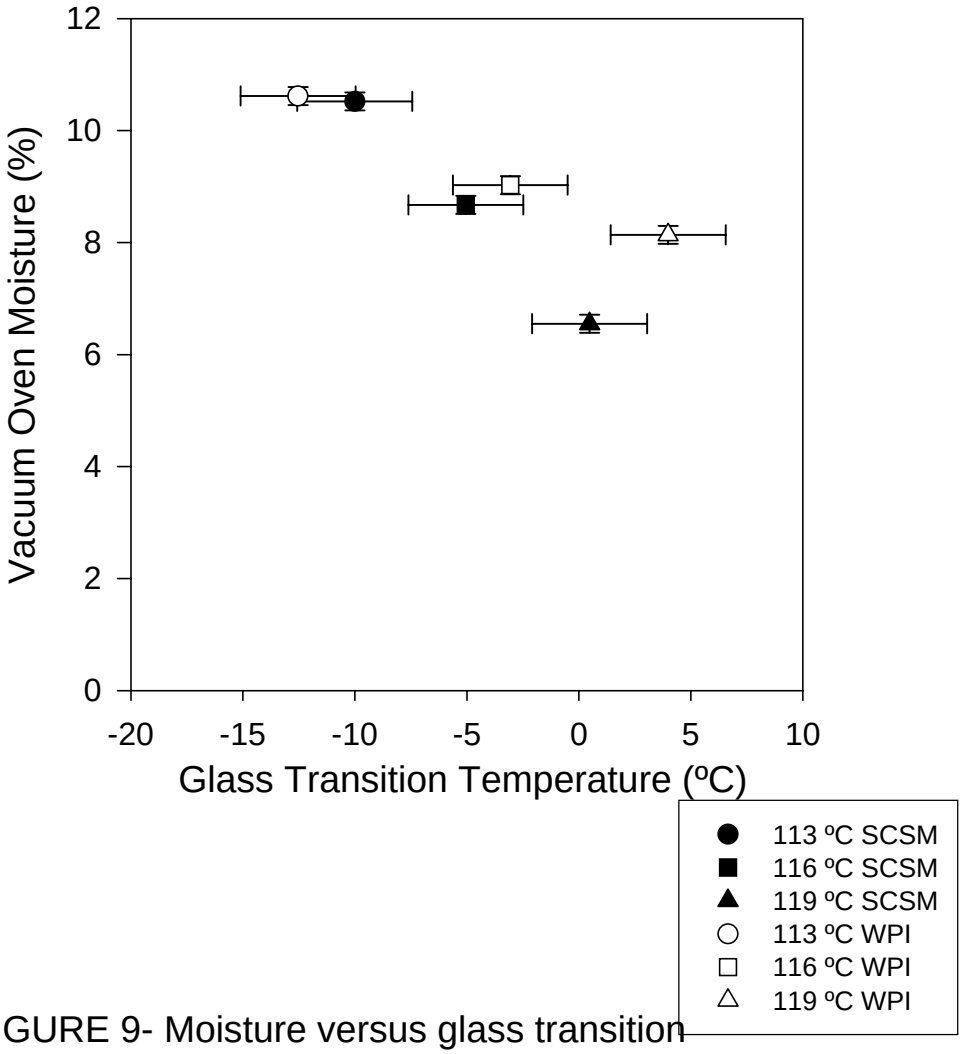

FIGURE 9- Moisture versus glass transition temperature for caramels with sweetened condensed skim milk (SCSM) and whey protein isolate (WPI) cooked to three temperatures.

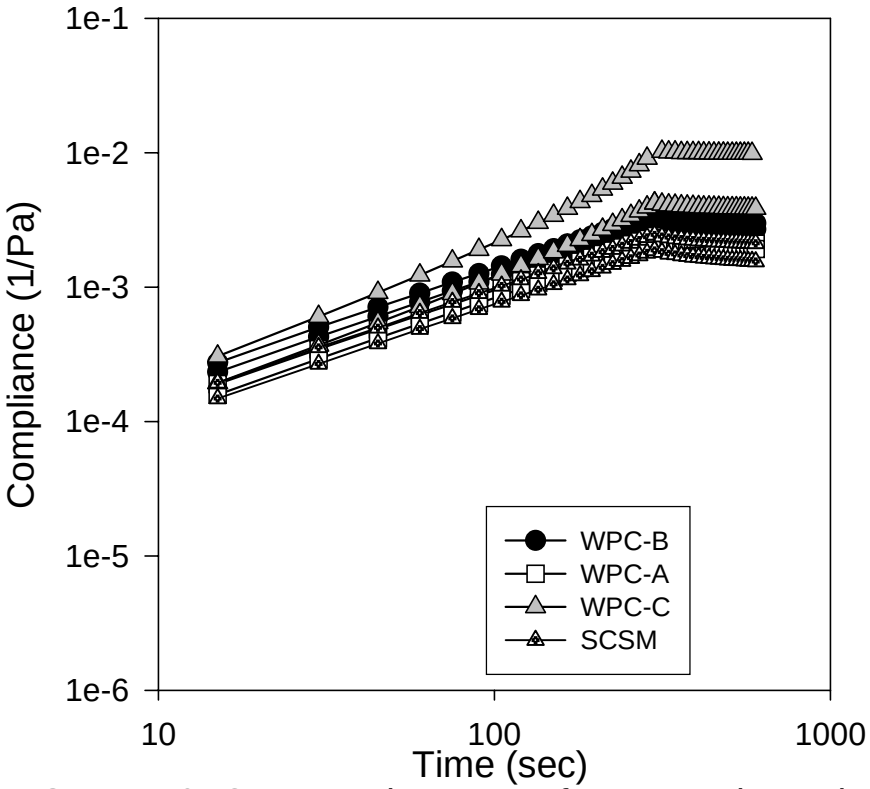

FIGURE 10- Creep and recovery for caramels made with 34% whey protein concentrate (WPC) and sweetened condensed skim milk (SCSM).

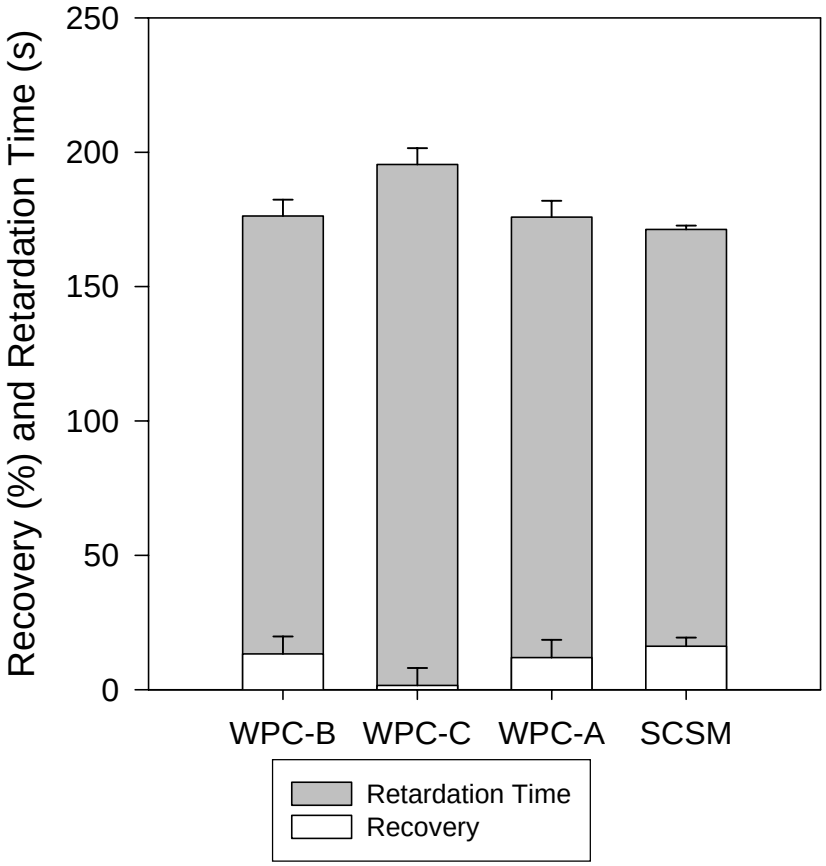

FIGURE 11- Retardation time and recovery of caramels made with 34% whey protein concentrate (WPC) and sweetened condensed skim milk (SCSM).

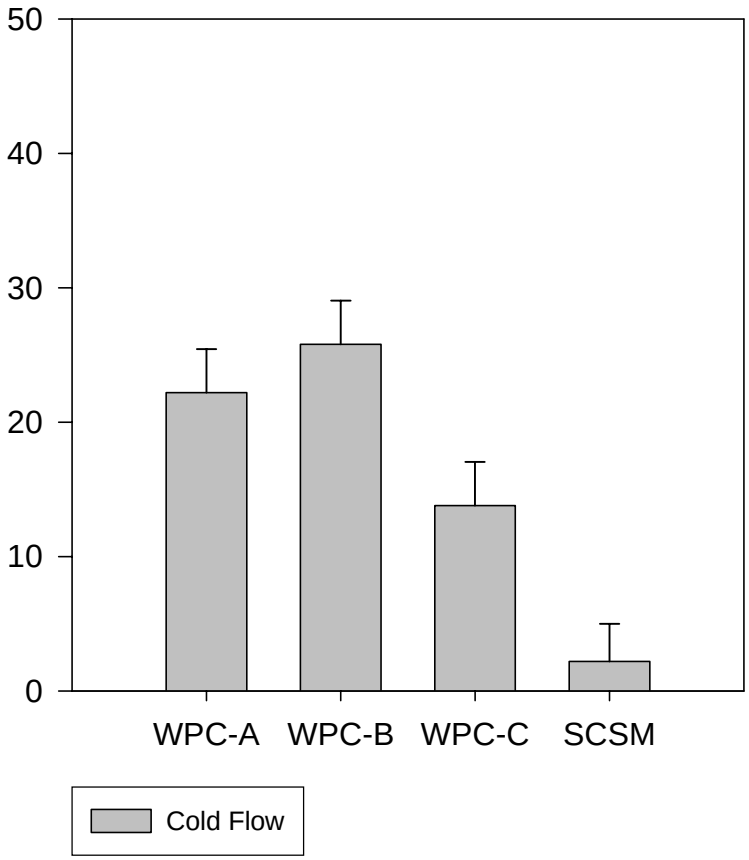

FIGURE 12- Cold flow of caramels made with 34% whey protein concentrate (WPC) and sweetened condensed skim milk (SCSM) after 24 hours.

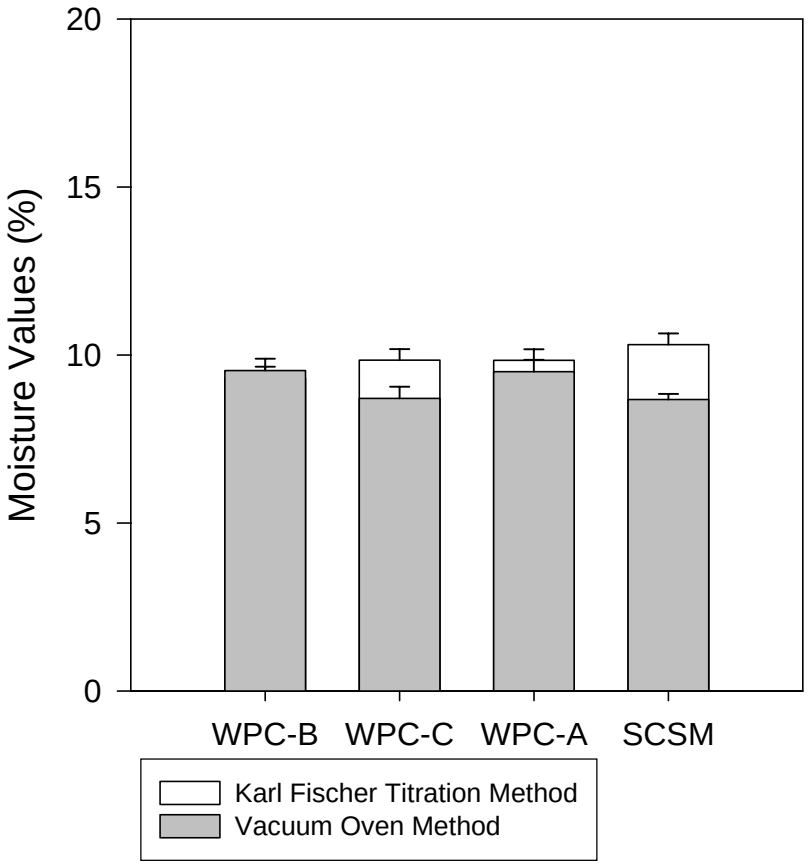

FIGURE 13- Comparison of moisture methods for caramels made with 34% whey protein concentrate (WPC) and sweetened condensed skim milk (SCSM).

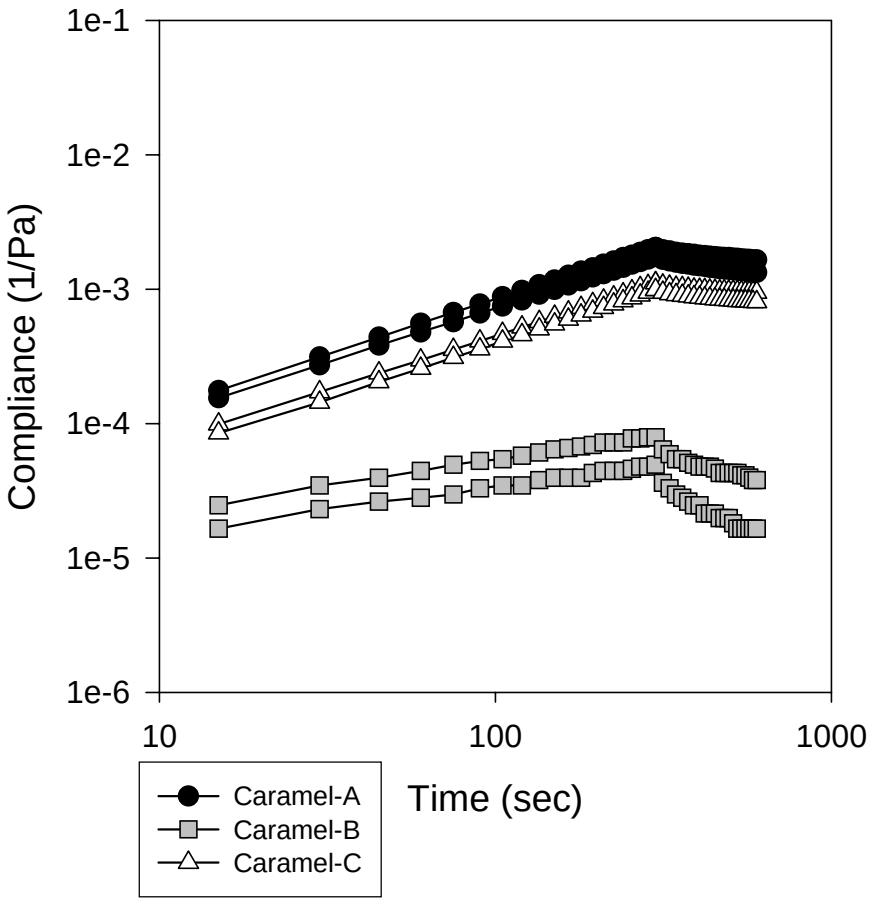

FIGURE 14- Creep and recovery of three commercial caramels.

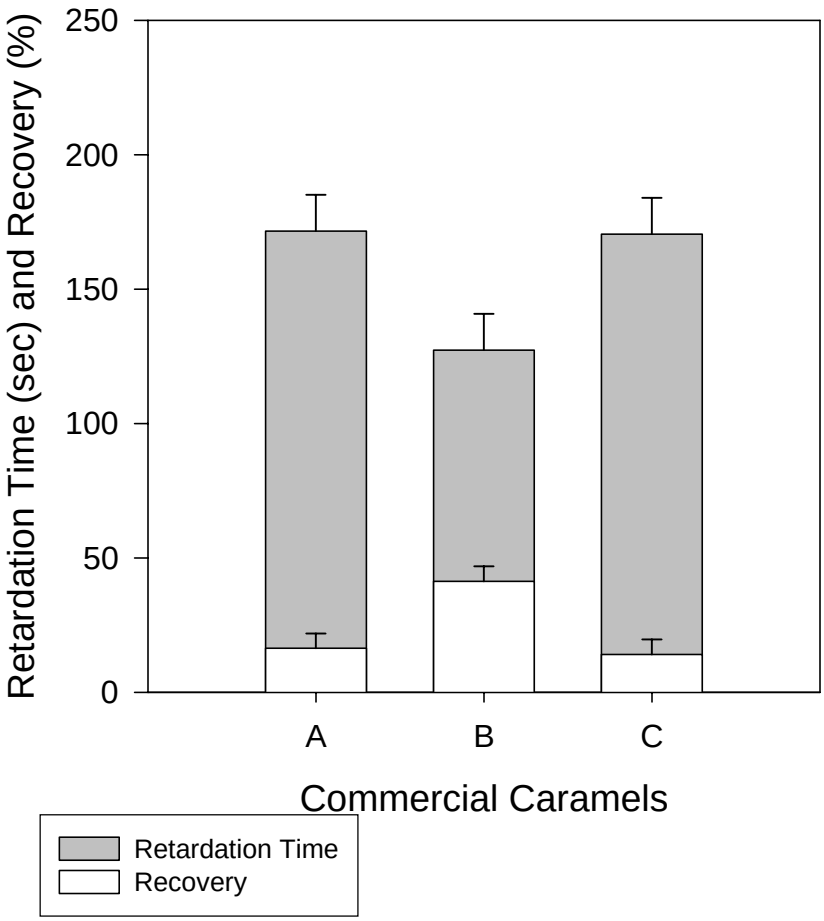

FIGURE 15- Retardation time and recovery of three commercial caramels.

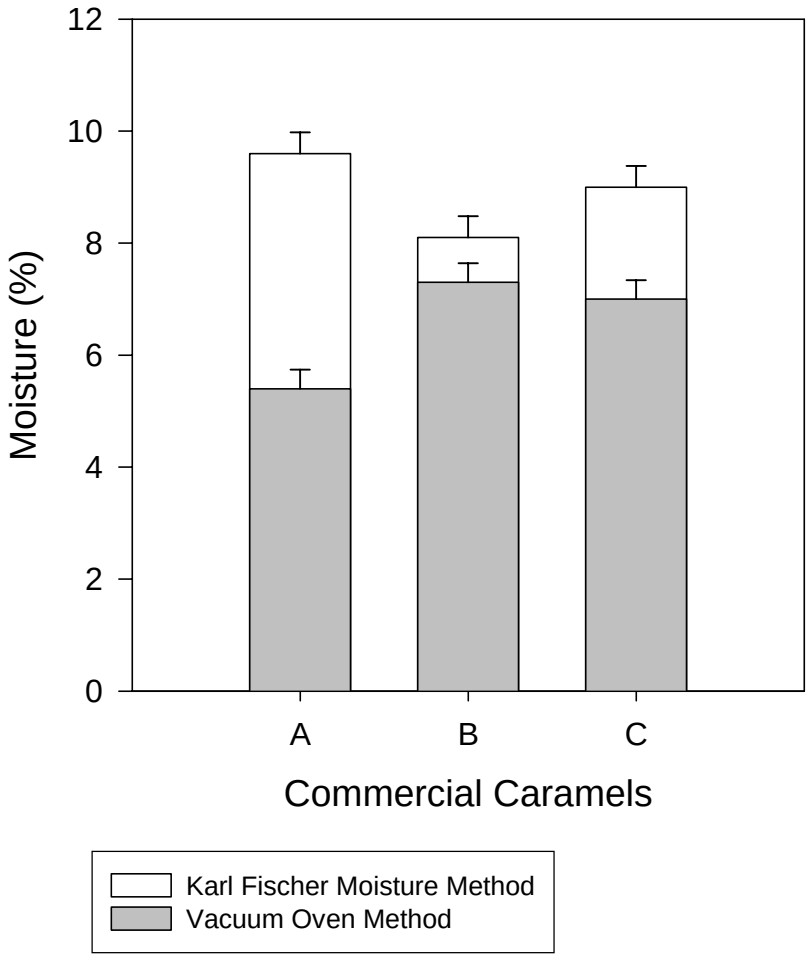

Figure 16. Comparison of moisture methods for commercial caramels.

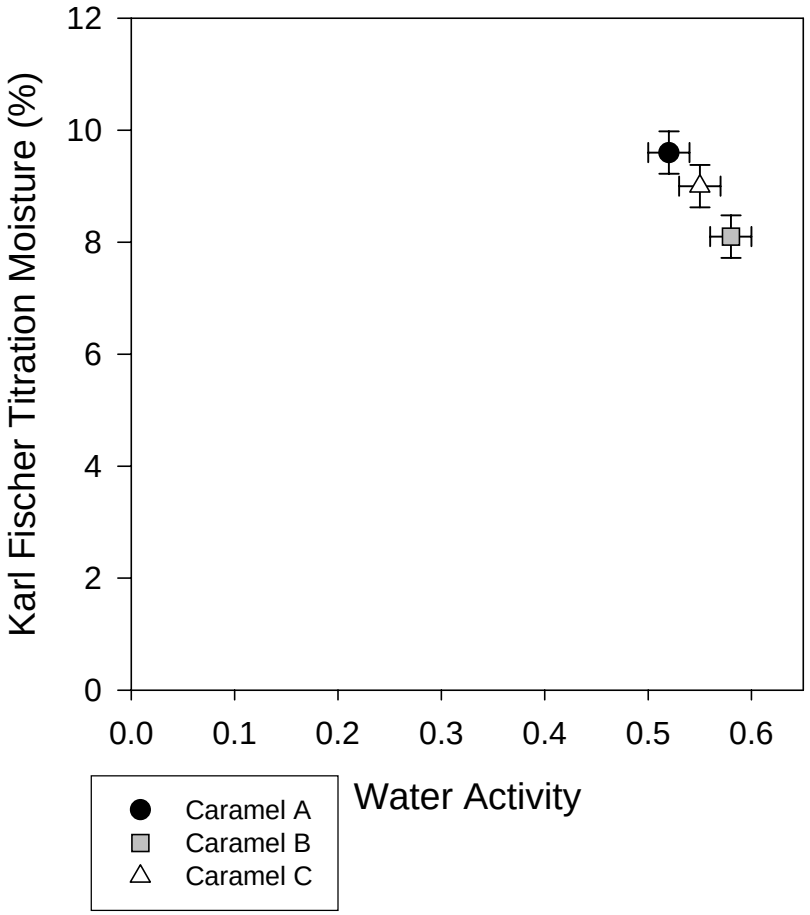

FIGURE 17- Moisture content versus water activity for three commercial caramels.

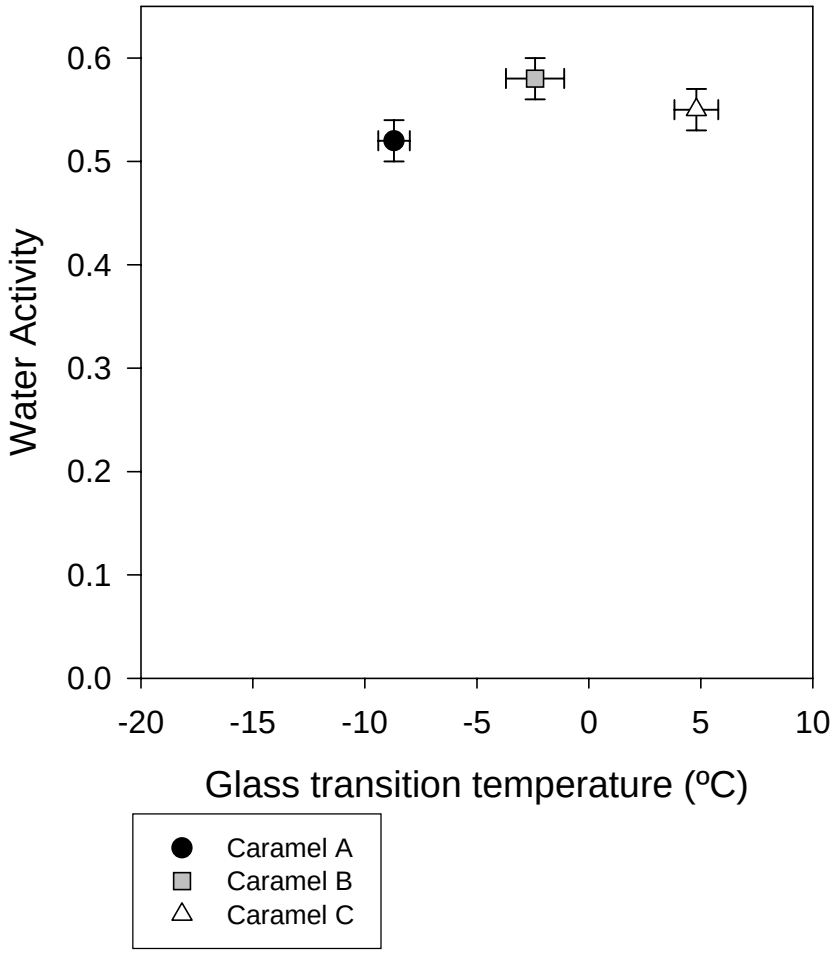

FIGURE 18- Water activity versus glass transition temperature for three brands of commercial caramels.

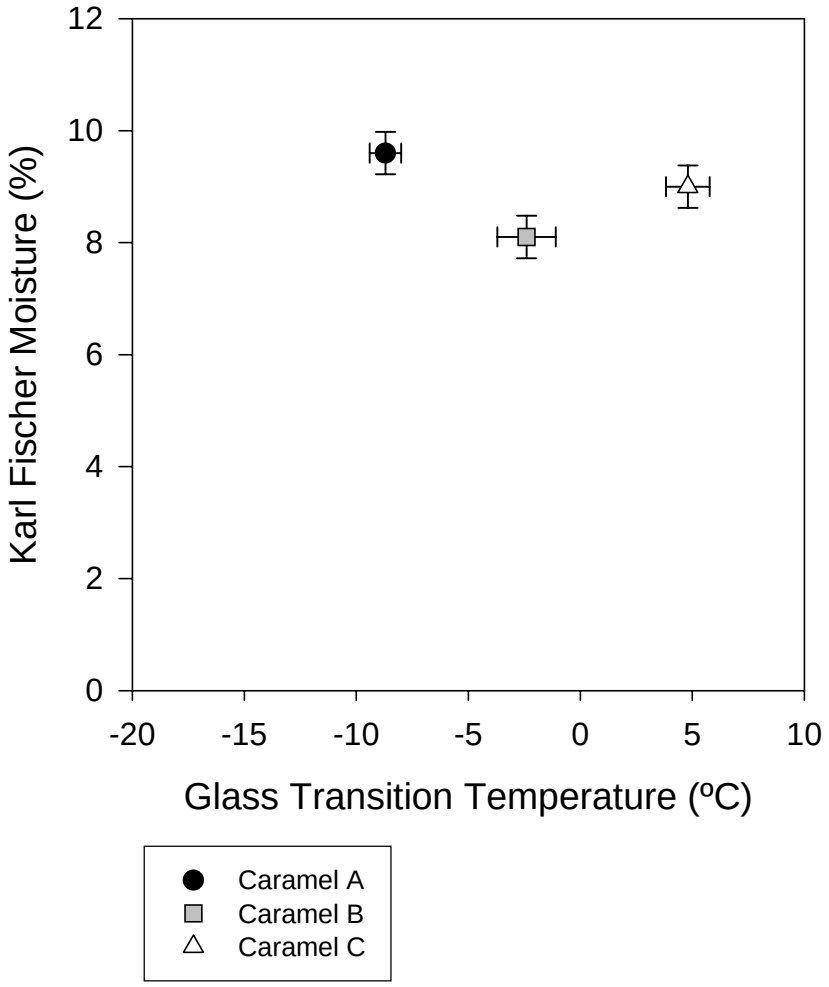

FIGURE 19- Moisture versus glass transition temperature for three commercial caramels.

Appendix 5.1

Subject Consent to Sensory Evaluation

Date:

I agree to participate in the sensory evaluation of caramel candies for the Department of Food Science at North Carolina State University. I am aware of possible allergen issues associated with dairy ingredients, and I have no pre-existing allergies to dairy ingredients. I understand that participation in this panel is voluntary and that I may terminate my participation at any time. I also understand that information I provide is confidential and that results will not be portrayed with my name.

The caramels may contain one or more of the following ingredients:

corn syrup
lactose powder
lecithin
sugar
sweetened condensed skim milk
vegetable fat
whey protein concentrate

Appendix 5.2

Consumer Caramel Questionnaire

Please take a few moments to answer the following questions. Your answers will provide helpful information about your choices as a consumer of caramel. Following completion of this questionnaire, please return it to the turntable and you will receive your caramel samples for evaluation.

Gender: ☐ female ☐ male

Age:
☐ 18 or younger
☐ 19 – 24
☐ 25 – 29
☐ 30 – 39
☐ 40 – 49
☐ 50 – 59
☐ 60 or over

How often do you consume caramels?
☐ never
☐ at least once per month
☐ at least 2-3 times per month
☐ at least once per week
☐ two to three times per week
☐ four or more times per week

What brands of caramels do you consume? (check all that apply)
☐ Hershey's
☐ Kraft
☐ Werther's
☐ Milk maid
☐ Brach's
☐ Other (please specify):_____

How do you most often use/consume caramels?
☐ individually for eating
☐ as an ingredient in a recipe
☐ as a dessert topping

What general factors influence your choice of caramel brands? (check all that apply)
☐ color
☐ flavor
☐ texture
☐ price
☐ sweetness
☐ mouthfeel

What specific factors influence your choice of caramel brands? (check all that apply)
☐ dark color
☐ chewy texture
☐ milky/dairy flavor
☐ price
☐ light color dark color
☐ firm texture
☐ high sweetness
☐ availability

Appendix 5.3

Please take a bite of carrot and a sip of water between samples. The carrot helps to clean your teeth. Taste the caramel samples in the order indicated by the numerical codes below. After you have tasted the product, please circle your response for each of the questions below. PLEASE ANSWER ALL QUESTIONS. Thank you for your participation. Sample _____

Overall Acceptance

1	2	3	4	5	6	7	8	9
Dislike Extremely				Neither like nor dislike				Like Extremely

Overall Appearance

1	2	3	4	5	6	7	8	9
Dislike Extremely				Neither like nor dislike				Like Extremely

Overall Color

1	2	3	4	5	6	7	8	9
Dislike Extremely				Neither like nor dislike				Like Extremely

Overall Texture

1	2	3	4	5	6	7	8	9
Dislike Extremely				Neither like nor dislike				Like Extremely

Overall Chewiness

1	2	3	4	5	6	7	8	9
Dislike Extremely				Neither like nor dislike				Like Extremely

Overall Stickiness

1	2	3	4	5	6	7	8	9
Dislike Extremely				Neither like nor dislike				Like Extremely

Overall Caramel Flavor

1	2	3	4	5	6	7	8	9
Dislike Extremely				Neither like nor dislike				Like Extremely

Overall Milky/Dairy Flavor

1	2	3	4	5	6	7	8	9
Dislike Extremely				Neither like nor dislike				Like Extremely

Overall Sweetness

1	2	3	4	5	6	7	8	9
Dislike Extremely				Neither like nor dislike				Like Extremely

Comments:
Likes:_____
Dislikes:_____

Appendix 5.4

Table showing significant differences for retardation time and recovery in caramels made with sweetened condensed skim milk (SCSM) and whey protein isolate (WPI) cooked to three temperatures.

Treatment	*Retardation Time (sec)*	*Recovery (%)*
113 ºC SCSM	181 ^{A}	7.25 ^{B}
116 ºC SCSM	171 ^{B}	16.2 ^{A}
119 ºC SCSM	175 ^{B}	11.5 ^{B}
113 ºC WPI	187 ^{A}	2.34 ^{C}
116 ºC WPI	173 ^{B}	15.8 ^{A}
119 ºC WPI	173 ^{B}	14.2 ^{AB}

*Means in the same column with different letters represent significant differences ($p<0.05$). Standard error for all retardation data was approximately 1.36. Standard error for all recovery data was approximately 2.38.

Appendix 5.5

Table showing significant differences in cold flow for caramels made with sweetened condensed skim milk (SCSM) and whey protein isolate (WPI) cooked to three temperatures.

Treatment	*Cold Flow (%)*
113 ºC SCSM	8.04 ^{AB}
116 ºC SCSM	2.30 ^{B}
119 ºC SCSM	3.20 ^{B}
113 ºC WPI	35.7 ^{A}
116 ºC WPI	4.77 ^{B}
119 ºC WPI	1.81 ^{B}

*Means in the same column with different letters represent significant differences ($p<0.05$). Standard error for all data was approximately 2.13.

Appendix 5.6

Table showing significant differences in moisture content using two methods for caramels made with sweetened condensed skim milk (SCSM) and whey protein isolate (WPI) cooked to three temperatures.

Treatment	*Moisture Content using a Karl Fischer Titration Unit (%)*	*Moisture Content using a Vacuum Oven (%)*
113 ºC SCSM	14.2 ^{A}	10.5^{A}
116 ºC SCSM	10.3 ^{B}	8.67^{B}
119 ºC SCSM	10.0 ^{B}	7.55^{B}
113 ºC WPI	13.1 ^{A}	10.6^{A}
116 ºC WPI	10.5 ^{B}	9.02^{B}
119 ºC WPI	10.1 ^{B}	8.13^{B}

*Means in the same column with different letters represent significant differences ($p<0.05$). Standard error for all Karl Fischer titration data was approximately 0.93. Standard error for all vacuum oven data was approximately 0.16.

Appendix 5.7

Table showing significant differences for retardation time and recovery in caramels made with three brands of 34% whey protein concentrate (WPC) compared to caramels made with sweetened condensed skim milk (SCSM).

Treatment	*Retardation Time (sec)*	*Recovery (%)*
WPC-B	176 ^{B}	13.3 ^{A}
WPC-C	195 ^{A}	1.57 ^{A}
WPC-A	176 ^{B}	12.0 ^{A}
SCSM	171 ^{B}	16.2 ^{A}

*Means in the same column with different letters represent significant differences ($p<0.05$). The standard error for all WPC data was approximately 5.03. The standard error for all SCSM data was approximately 4.35.

Appendix 5.8

Table showing significant differences in cold flow in caramels made with three brands of 34% whey protein concentrate (WPC) compared to caramels made with sweetened condensed skim milk (SCSM).

Treatment	*Cold Flow (%)*
WPC-B	25.8 ^{A}
WPC-C	13.8 ^{B}
WPC-A	22.2 ^{A}
SCSM	2.23 ^{C}

*Means in the same column with different letters represent significant differences ($p<0.05$). Standard error for all WPC data was approximately 3.23. Standard error for all SCSM data was approximately 2.80.

Appendix 5.9 Table showing significant differences in moisture content using two method in caramels made with three brands of 34% whey protein concentrate (WPC) compared to caramels made with sweetened condensed skim milk (SCSM).

Treatment	*Karl Fischer Titration Method Moisture Content (%)*	*Vacuum Oven Method Moisture Content (%)*
WPC-B	9.32[A]	9.53 [A]
WPC-C	9.88 [A]	8.70 [A]
WPC-A	9.83 [A]	9.50 [A]
SCSM	10.3 [A]	8.67 [A]

*Means in the same column with different letters represent significant differences ($p<0.05$). Standard error for all Karl Fischer WPC data was approximately 0.33. Standard error for all Karl Fischer SCSM data was approximately 0.28. Standard error for all vacuum oven data was 0.32.

Appendix 6.0 Table showing significant differences for retardation time and recovery in three brands of commercial caramels.

Commercial Caramels	*Retardation Time (sec)*	*Recovery (%)*
A	172 ^{A}	16.4 ^{B}
B	127 ^{A}	41.3 ^{A}
C	170 ^{A}	14.1 ^{B}

*Means in the same column with different letters represent significant differences ($p<0.05$). Standard error for all retardation time data was approximately 13.5. Standard error for all recovery data was approximately 5.60.

Appendix 6.1

Table showing moisture content using two methods for three commercial caramel brands.

Treatment	*Moisture Content using a Karl Fischer Titration Unit (%)*	*Moisture Content using a Vacuum Oven (%)*
A	9.57 [A]	5.40 [A]
B	8.07 [A]	7.27 [A]
C	9.01 [A]	7.04 [A]

*Means in the same column with different letters represent significant differences ($p<0.05$). Standard error for all Karl Fischer titration data was approximately 0.39. Standard error for all vacuum oven data was approximately 0.34.