EFFECTS OF STARCH-BASED ANTI-CAKING AGENTS ON THE BROWNING OF SHREDDED MOZZARELLA CHEESE

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ABSTRACT

The effects of starch-based anti-caking agents on the browning of Mozzarella cheese were evaluated in this experiment. Six commercially available anti-caking agent treatments were examined and color measurements indicated that the starch-based anti-caking agents produced a baked cheese with a greater degree of browning than the samples treated with cellulose based anti-caking agents or no treatment (control). The cellulose-based treatments and the control also had a significantly greater moisture loss than the potato starch-based treatments. A negative correlation between percent moisture loss and the amount of browning was found (R^2=0.51). The average surface temperature was at least 16°C higher for the treatments containing potato starch than for the cellulose-based treatments. A significant relationship between average surface temperature and browning was also found (R^2=0.67). These relationships suggest that the starch-based treatments impeded moisture loss, which decreased the amount of evaporative cooling. An increase in surface temperature resulted from the decrease in the amount of evaporative cooling and thus the Maillard reaction was accelerated leading to increased browning.

The effects of the starch source were examined using starches from corn, rice and wheat. These starches were compared to commercially available potato starch and cellulose anti-caking agents. All starch sources were found to produce a greater degree of browning on the cheese sample compared to the cellulose treatment and control.

Four adjuncts treatments, including dimethypolysiloxane, lactic acid, partially hydrogenated sunflower oil, and a combination of the dimethylpolysiloxane and sunflower oil were added to cheese treated with potato starch to determine if a reduction in the degree of browning could be achieved. No differences in browning between the potato starch treatment and those with added adjuncts were found.

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CHAPTER 1

INTRODUCTION

More than 2 billion lbs. of Mozzarella and Mozzarella-like cheese were produced in the U.S. in 1999 (IDFA, 2000). The large demand for Mozzarella and Mozzarella-like cheese can be attributed to the continued popularity of pizza and other Italian specialty foods. Over 70% of the Mozzarella cheese produced in the U.S. is used for pizza (Matzdorf et al., 1994). Low moisture, part skim Mozzarella is the preferred form of cheese used as an ingredient for pizza (Kindstedt, 1993). Browning is an attribute that is desirable at low levels on pizza, but can be considered a defect when extreme scorching occurs. One report showed that 50% of pizza restaurants reported having occasional to frequent problems with the blistering or browning of Mozzarella cheese (Pilcher and Kindstedt, 1990).

Maillard browning is the result of a reaction between reducing sugars and amino acids, which through a series of reactions produce melanoidins, a group of compounds that exhibit a brown coloration. The brown coloration of Mozzarella cheese as a result of baking is due to the Maillard reaction. The rate of browning is influenced by many properties of the cheese including amount of reducing sugars, salt content, fat content, proteolytic activity, aging, and the moisture-to-protein ratio. The physical change during baking that has been associated with increased browning of Mozzarella cheese baking is the formation of a skin-like layer due to dehydration. Prevention of excessive browning can be achieved by the addition of a hydrophobic coating, vegetable oil, on the surface of the shreds of low fat and fat-free Mozzarella cheeses (Rudan and Barbano, 1998).

Maillard browning kinetics are dependent on a number of factors including temperature and heating duration. An increase in either of these factors will increase the rate of the Maillard reaction. Water activity, pH, diffusion resistance of reaction medium, and the presence of certain metal and chemical compounds can also alter the kinetics of the Maillard reaction.

Due to the high moisture content of Mozzarella cheese, caking is a common problem in shredded cheese. Anti-caking agents are commonly added to inhibit the caking of shreds and achieve a better flow profile (McGinley and Thomas, 1975). One anti-caking agent commonly used in the industry to prevent lumping is cellulose. Commercial forms of cellulose used as anti-caking agents include common-type cellulose, microcrystalline cellulose, and cellulose impregnated with glucose sugar and glucose oxidase enzyme. Cellulose has been shown to not only decrease clumping, but to also decrease the amount of moisture migration between cheese and the environment at many relative humidities (McGinley and Thomas, 1975). The major drawbacks for using these anti-caking agents are: 1) They are relatively expensive; 2) The product efficiency is questionable depending on the chemical specification of the cheese; 3) Products exhibit too much dusting in the packaging room providing a health hazard to workers; and 4) These products intrinsically have excessive, unwanted bacteria, yeast and mold contamination (Reddy, 1997). Starch based anti-caking agents are an option for use on shredded Mozzarella cheese and may provide the industry with a superior and cost-effective alternative to anti-caking agents being used today.

Although there has been research conducted on the browning of shredded Mozzarella cheese for use on pizza, none of this research has taken into account the anti-caking agents used within the industry on cheese. When anti-caking agents are applied to cheese, changes in browning are of particular interest because of physical characteristics of the anti-caking agents and their influence on the surface of the cheese. The degree of browning on Mozzarella cheese treated with anti-caking agents may possibly controlled once a model identifying causes for browning is found.

CHAPTER II

REVIEW OF THE LITERATURE

Shredded Mozzarella Cheese

Since 1980, production of Mozzarella cheese in the US has increased over 200% (IDFA, 2000). Over 70% of this Mozzarella produced is used as an ingredient for pizza (Matzdorf et al., 1994).

Low-moisture part-skim (LMPS) Mozzarella cheese is the preferred type of Mozzarella used as an ingredient on pizza because of the low water content, longer shelf life, and good shredding properties (Kindstedt, 1993). The standards of identity for LMPS Mozzarella cheese are defined on a basis of moisture and fat-in-dry-matter (FDM). The legal range for moisture is greater than 45% but less than or equal to 52%, and the range for FDM is greater or equal to 30% but less than 45% (USDA, 2001). A survey conducted on the chemical composition of commercial LMPS Mozzarella cheese found the following mean percentages: 48.5% moisture, 37.9% FDM, 1.65% salt, 26.1% protein. The ranges for moisture, salt and FDM reported were very large due to variability between producers. The typical pH of Mozzarella cheese is around 5.2, which is the pH at which the cheddaring process is stopped and the cheese is milled and stretched (Kindstedt, 1993).

When Mozzarella is used as an ingredient in pizza and most other applications, the cheese is first shredded, diced or cut. Thus, it is imperative that the cheese has good shredability and is resistant to clumping (Kindstedt, 1993). Due to the high moisture content of Mozzarella cheese, caking is a common problem in shredded cheese. Anti-caking agents are commonly added to inhibit the caking of shreds and achieve a better flow profile (McGinley and Thomas, 1975).

Baking is the final step before consumption of Mozzarella cheese used on pizza, and therefore properties of baked cheese are very important. The physical properties of melted Mozzarella cheese are highly complex, but they yield at least five important functional characteristics: meltability, strechability, elasticity, free oil formation, and browning (Kindstedt, 1993). On pizza, browning is an attribute that is desirable at low levels, but can be considered a defect when extreme scorching occurs. One study reported that 50% of pizza restaurants reported that they have occasional to frequent problems with the blistering or browning of Mozzarella cheese (Pilcher and Kindstedt, 1990). For one major pizza chain, the physical specifications associated with browning include color/appearance, blister size, blister coverage, and blister color (Alvarez, 1986).

Browning

Browning Reactions

There are three major non-enzymatic browning reactions that occur in food. The most common is the Maillard browning reaction. The substrates for Maillard browning are reducing sugars and free amino acids or free amino groups of amino acids that are part of protein chains (BeMiller and Whistler, 1996). Through a variety of reactions the reducing sugar and amino acid are converted to melanoidins. Melaniodins are a group of nitrogenous polymers and copolymers that exhibit a brown coloration (Eskin, 1990). The other two non-enzymatic browning reactions are carmelization and ascorbic acid browning. Carmelization occurs with simple sugars in the absence of nitrogenous compounds, such as protein, under high heat conditions (deMan, 1999). The browning reaction of ascorbic acid oxidation requires the presence of ascorbic acid as a substrate (Eskin, 1990). Browning of cheese occurs due to the Maillard reaction.

The first reaction in the Maillard browning sequence is the condensation of reducing sugars with amino groups to form glycosylamino acids. These unstable compounds undergo a series of rearrangements to form 1-amino-1-deoxy-2-ketose. From this point the pathway spits depending on number of factors including the pH of the system. Normally under acidic conditions, the pathway taken leads to the formation of furfurals and the eventual products of melanoidins, which impart a brown color (Eskin, 1990).

Ashoor and Zent (1984) found that the intensity of Maillard browning is associated with the type of sugar and amino acid utilized in the reaction. All twenty-two amino acids were heated with the sugars: D-glucose, D-fructose, D-ribose and α-lactose. Alpha-lactose yielded the highest browning with the majority of amino acids. The individual amino acids that produced the highest browning intensity with α-lactose were glycine, tryptophan and lysine.

Browning of Cheese

In Mozzarella cheese, Maillard browning is a result of the reaction between the sugars and proteins (Olson et al., 1983). The browning of Mozzarella cheese during high temperature baking occurs through the formation of a skin-like layer which contains colored areas that can range from light or golden brown to black (Kindstedt, 1993). The skin formation of Mozzarella cheese is a result of dehydration on the surface of the cheese during baking. The increase of melting, flowing and fusion of shreds decreased the amount of severe browning and scorching of Mozzarella cheese during baking. Mozzarella cheese that was prepared with homogenized milk or homogenized cream exhibited less melting and fusion of shred, and thus more browning, than a control cheese prepared with non-homogenized cream (Rudan et al., 1998a).

The ability to manipulate the degree of browning on baked Mozzarella cheese with an additive has been explored in a few studies. Prevention of excessive browning can be achieved by the addition of a hydrophobic coating on the surface of the shreds of low fat and fat-free Mozzarella cheeses. The hydrophobic coating does not prevent moisture loss, but prevents the cheese surface from forming a skin allowing the cheese to flow. In full fat Mozzarella cheese, the free oil released during baking is the major factor in preventing the skin formation that leads to excess browning (Rudan and Barbano, 1998). Metzger et al. (2001) evaluated the browning of Mozzarella cheese produced with preacidified milk with and without a hydrophobic surface coating. The cheese coated with the hydrophobic coating of vegetable oil produced excellent melt and normal browning characteristics. Poor shred melt and excessive burning were reported on the cheese when no hydrophobic surface coating was used.

Numerous studies have been conducted on the links between the composition of Mozzarella cheese and the degree of browning associated with these constituents. Browning may be controlled by the amount of reducing sugars contained in the cheese. Incomplete fermentation of lactose by the starter culture will result in the accumulation of galactose causing increased browning (Johnson and Olson, 1985). Mozzarella cheese made using *Lactobacillus helviticus* and *Streptococcus* ssp., galactose fermenting cultures that also do not release free galactose into the curd, were compared to cheese made with typical Mozzarella cultures. Upon baking, the galactose fermenting, galactose non-releasing strains browned much less than the control cheese under high temperatures (Matzdorf et al., 1994; Mukherjee and Hutkins, 1994). A positive correlation between galactose content and brown color intensity was found in studies comparing galactose fermenting and galactose non-fermenting culture strains. The galactose non-fermenting cultures produced a Mozzarella cheese that had a higher content of galacose in the finished cheese than cheeses made with galactose fermenting organisms (Johnson and Olson, 1985). Differences in browning due to culture strain also were noted by Hong et al. (1998). The culture strain with the highest proteolytic activity and lowest peptidase activity showed more browning intensity and smaller blisters on pizza and maintained these characteristics over storage time.

Functional properties, including browning, of lower fat cheese can be improved by increasing the moisture content sufficiently to provide a moisture-to-protein ratio that is equal or higher to full-fat Mozzarella cheese. Usually the moisture on a fat-free basis in reduced fat Mozzarella cheese is slightly less than that of LMPS Mozzarella cheeses. Increased levels of water available to hydrate the proteins in the surrounding matrix allow for better flowability of the proteins during baking. Increased meltablity of cheese has been associated with a lower degree of browning (McMahon and Oberg, 1998). Browning was also increased by the addition of the fat replacer, Salatrim®, in reduced fat Mozzarella (Rudan et al., 1998b).

The salt content and specifically the salt to moisture (S/M) ratio of cheese impact the color development of natural cheese. Higher S/M ratios retarded sugar fermentation whereas low S/M ratios allowed faster and more complete metabolism. The higher S/M ratios thus resulted in more intense color development, due to an increase in sugar available for the Maillard reaction (Olson et al., 1983).

Browning of Mozzarella cheese may also be affected by the fat content. Fife et al. (1996) reported that low fat cheese had a lower b* value (a greenish tint) compared to the part skim control cheese. Nonfat Mozzarella cheese typically exhibits poor meltability and increased dehydration that can result in excessive browning and charring of the surface (McMahon and Oberg, 1998). An increase in the proteolytic activity (production of amino acids and small peptides) of Mozzarella cheese will increase the amount of browning. Differences in the casein: fat ratio of Mozzarella cheese did not have a significant effect on the browning (Merrill et al., 1994).

Reduction in calcium content by preacidifaction had little influence on the melting and browning characteristics of low fat Mozzarella cheese during pizza baking (Metzger et al., 2001). Other factors that do not have an effect on the browning of cheese include freezing temperature, thawing temperature, and shredding of Mozzarella cheese (Oberg et al., 1992).

Other reported factors affecting the color development of Mozzarella cheese during baking include length of storage and interaction of cheese with other food constituents. Fife et al. (1996) found that overall storage does not affect the browning of Mozzarella cheese, although cook color would be expected to decrease over storage to due residual sugars being utilized by bacteria. Storage after two weeks led to an increase in browning due to microbial breakdown and spoilage. Scorching has been noted in cheese that is baked shortly after being produced. Thus, aging of one to three weeks is typical to develop optimal functional characteristics desired in Mozzarella cheese (Kindstedt and Guo, 1997). Pizza cheese is often in contact with pizza sauce during a time of storage due to in increase in the frozen and fresh, refrigerated market. The composition and meltability of Mozzarella cheese is influenced by contact with pizza sauce, although the effect on browning was not determined in this study. Increased time of contact between cheese and pizza sauce caused a larger decrease in the meltability compared to the control cheese that was not in contact with pizza sauce (Wang et al., 1998).

Kinetics of the Maillard Reaction

An increase in the temperature or time of a heat treatment will accelerate the rate of Maillard browning. Therefore, a decrease in the processing temperature can lengthen the period needed for the formation of brown colored products (Eskin, 1990). When varying temperature treatments were applied to milk powder, it was found that the L* value decreased (increased darkness) with increasing temperature (Mohammed et al., 2000). A high correlation was noted between toasting time of bread and browning when color formation was measured by: 1-L*-value, absorbance of hydroxymethylfurfural (HMF) at 420 and 284nm, and by ΔE (Ramirez-Jimenez et al., 2001).

Water activity can also have an effect on the rate of the browning reaction. Maximum browning has been observed at water activities (A_w) of 0.3 to 0.7. In a casein-glucose model, the disappearance of amino nitrogen was measured and the maximum reaction was determined to be between A_w of 0.65 and 0.7. This reaction maximum was found at similar A_w in a dried milk system where lysine loss was measured. The maximum rate of the browning reaction at high water activities is influenced by the concentration of the reactants (Eichner, 1975). Decreases in A_w from 0.90 to 0.60 at 45°C in a model system of taurine and glucose resulted in an increased browning rate of 4.1 times (Tsai et al., 1991). Changes in browning between A_w 0.90 and 0.95 in a model system of lysine and glucose were minimal (Petriella et al., 1985). The A_w of unbaked LMPS Mozzarella cheese is typically in the range of 0.91 to 0.95 (Fennema, 1996) and would be expected to decrease as the cheese is baked. From the studies conducted on the influence of water activity on the kinetics of the Maillard browning reaction, the reaction rate should increase as the baking decreases the A_w below 0.90.

The rate of Maillard browning may be affected by the pH of system. Although the carboxylamino reaction can develop in acidic or alkaline conditions, the Maillard reaction rate increases in basic media because a higher ratio of the amine groups of the amino acids and proteins are in the basic form. A study of color intensity as a function of pH demonstrates an increasing color (420 nm) with increasing pH. At temperatures of 100°C and 110°C, the function is parabolic with the break points a pH 5 and 6, respectively (Eskin, 1990). In model systems using various amino acids and sugars, the development of brown color was measured with the pH range of 6.0 to 12.0, with the optimum pH observed at 10.0 (Ashoor and Zent, 1984). The color development in a glucose-lysine model at pH values of 7.0, 6.0, and 5.0 decreased with decreasing pH (Petriella et al., 1985). The moderately acidic nature (pH~5.2) of Mozzarella cheese suggests that the rate of Maillard browning would be lowered in comparison with foods of at a more neutral pH.

Alteration of the diffusion resistance of the reaction medium by action of additives can affect the browning rate and position of browning maximum. In a solution of glucose and lysine, the addition of Avicel (microcrystalline cellulose), a water-insoluble polymer did not change the browning reaction rate or A_w at which the browning maximum occured. The addition of gum arabic, a water soluble polymer, to the glucose lysine solution decreases the browning rate and the browning maximum is shifted to a higher A_w. This effect can be attributed to the higher viscosity and increased diffusion resistance of the medium containing the substrates (Eichner, 1975).

The rate of the Maillard reaction can be influenced by the presence of certain metal compounds. Copper and iron catalyze the reaction, while manganese and tin were inhibitors to the reaction. Other chemical inhibitors of the Maillard reaction include sulfur dioxide and sulfites, and aspartic and glutamic acids (Eskin, 1990).

Common Browning Determination Methods

A colorimeter can be used to quantitatively measure the cook color of Mozzarella cheese by yielding L*, a*, and b* values. These values can then be converted into a single numerical descriptor (ΔE) to determine differences between the sample and the control. The equation used for this calculation is $((\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2)^{1/2}$ = color difference (ΔE) (Johnson and Olson, 1985). This method is nondestructive, but can only take pinpoint measurements on the surface of the sample.

Papadakis et al. (2000) employed the use of a digital camera and graphics software to determine the color of the bottom of pizza crusts. The method allowed for the analysis of the entire sample or selected regions and is nondestructive. Histograms of L, a, and b-values allowed for analysis of mean coloration, as well as dark spots on the samples as determined by the percentage of area below an L-value of 150.

Color formation may also be measured by extracting the Maillard reaction intermediate, hydroxymethylfurfural (HMF). Extraction of HMF can be achieved by shaking and centrifugation of the sample with deionized water. The supernatants are then clarified with Carrez solution. The aqueous extracts of HMF can be quantified through measurement at 284 and 420nm in a UV/VIS spectrophotometer (Ramirez-Jimenez et al., 2001). Because an intermediate of the Maillard reaction is measured, the possibility exists to have variation due to progress of the reaction.

Reduction in the amount of free amino acids or specific amino acids in a protein can be measured with an amino acid analyzer to follow the progression of the Maillard reaction. Measurement of decreasing amounts of reducing sugars has also been utilized to determine the degree to which the Maillard reaction has occurred (Tsai et al., 1991). Both of these measurements look at the decrease in substrates of the Maillard reaction.

Sensory analysis of the sample can also be used to determine color differences and acceptability. Maztdorf et al. (1994) utilized a consumer panel to evaluate the appearance of cheese on the surface of a baked pizza. Panelists were asked to state their opinions on the appearance of the color (very light to very dark), appearance other than color (very undesirable to very desirable), and overall acceptability.

Structural and functional differences between cellulose and starch

Cellulose

Cellulose is a fibrous material found in the cell walls of plants. The polymeric structure of cellulose consists of repeating β-D-glucopyranosyl units joined by β-1→4 linkages. Cellulose molecules are fairly rigid and contain approximately 3000 β-D-glucopyranosyl units that associate easily with one another (BeMiller and Whistler, 1996). Although insoluble, powdered cellulose has the ability to bind relatively large amounts of water due to a large surface area:weight ratio (Ang, 2001). Microcrystalline cellulose (MCC) is a physically modified form of cellulose that is comprised of fine crystalline pieces that are less reactive than cellulose in the native state (Coffey et al., 1995).

Starch

Starch is one of the most abundant food sources in the world and is produced from number of different plant sources including corn, wheat, rice, and potato. Commercial sources of starch contain two structurally different molecules, amylose and amylopectin, in a ratio of one to three, respectively. Amylose is a linear polymer of glucose molecules that have α(1→4) linkages. Amylopectin is a multiply branched molecule consisting of glucose molecules linked together by α(1→4) linkages with branching points consisting of α(1→6) linkages (Zobel and Stephen, 1995). The unbranched structure of amylose leads to one reducing end and one non-reducing end. In amylopectin, branching causes the molecule to have one reducing end and many non-reducing ends (Boyer, 1999). The reducing end of both amylose and amylopectin are substrates of the Maillard reaction (BeMiller and Whistler, 1996).

Starch granules are insoluble in cold water, but have the ability to reversibly imbibe water. Gelatinization occurs when starch granules are heated in water and causes the irreversible granule swelling due to imbibed water. Birefringence and crystallinity are both lost as a result of gelatinization of the starch granule (BeMiller and Whistler, 1996). The Kofler gelatinization temperature is determined by examining the starch granules under polarized light and determining the temperature at which the loss of birefringence occurs. Although each individual granule will gelatinize quite sharply, the starch sample will gelatinize over a temperature range due to differences in internal bonding and forces within the granules. Thus, the Kofler gelatinization temperature is usually reported over a range of 8°-10°C (Snyder, 1984). In the presence of excess water and additional heating, the starch granules will swell further and leach soluble components, eventually leading to the disruption of the starch granule. The result of the disruption is the formation of a starch paste (BeMiller and Whistler, 1996). Gelatinization temperatures may be lowered in alkaline conditions and raised by some salts and sugars (Zobel and Stephen, 1995). Surfactants can also decrease the degree of gelatinization of starches (Kim and Walker, 1992; Keetels et al., 1996). Water binding capacity and amylose leaching of starch during heating is reduced in the presence of free fatty acids, monoglycerides, surfactants, alcohols and iodine. Conformational changes of the amlyose molecule due to the inclusion of low molecular weight organic compounds causes the inhibition of starch granule swelling (Wasserman and Meste, 2000).

Changes in the viscosity of the starch solution are brought about by the gelatinization and pasting of the starch granule. Brabender curves plot the changes in viscosity of a starch solution during a process of heating to 95°C, then holding for 1hr, cooling to 50°C and holding for 1hr. Useful information from the Brabender curves include the peak viscosity, the viscosity when 95°C has been reached, and the viscosity after cooking for 1hr at 95°C which indicates the stability or breakdown of the paste (Zobel, 1984).

Swelling power refers to the increase in the size of the starch granule due to the imbibing of water when heated. Measurement of swelling power can be accomplished by sedimentation methods. A known weight of dried starch is added to a large excess of water and heated at a given temperature. The solution is then centrifuged, and the swollen granules are collected. The loss in weight of a known volume of sediment is dried allows for the swelling power to be determined. Swelling power for various starches can be graphed over a range of temperatures to demonstrate how water is imbibed (Collison, 1968).

Many properties of starch, including granule size and shape, gelatinization temperature, gel viscosity, and swelling power vary depending on the source of the starch. The potato starch granule is much larger and has a number of distinct properties when compared to starches from other common sources. The oval or spherical granules have an average diameter of 33µm (Swinkels, 1985). The gelatinization temperature of potato starch is relatively low at 58° to 66°C (Moore et al., 1984). Potato starch has the highest peak viscosity and undergoes very rapid and extremely high swelling at relatively low temperatures. The swelling power of starch at 95°C is 1153, which means that for every one gram of dry starch, 1153 grams of swollen starch granules are collected after 30 min in a thermostated bath (Swinkels, 1985). The viscosity of gelatinized potato starch is decreased in the presence of calcium salts. "Thin boiling" potato starch can also be achieve through acid treatments of the native starch (Mitch, 1984).

Corn starch is the most commonly used starch in the US. The corn starch granule is typically 15µm in diameter and has a round or polygonal shape (Swinkels, 1985). Corn starch has a gelatinization temperature range of 62° to 70°C (Moore et al., 1984). The paste of corn starch has an intermediate viscosity and a swelling power of 24 at 95°C (Swinkels, 1985).

The wheat starch granule is round and has an average diameter of 15µm (Swinkels, 1985). The gelatinization temperature for wheat starch is 59.5° to 64°C (Moore et al., 1984). Wheat starch produces a paste with a medium-low viscosity and has a swelling power at 95°C of 21 (Swinkels, 1985).

The rice starch granule is the smallest of all commercial starches, with an average diameter of 5µm. The granules typically have a polygonal, angular shape and tend to aggregate in clusters (Swinkels, 1985). The gelatinization temperature for rice starch is relatively high at 68° to 78°C (Moore et al., 1984). Rice starch produces a medium-low viscosity paste and has a low swelling power of 19 (Swinkels, 1985).

Anti-caking Agents

Anti-caking agents are finely divided solids that are added to a food product to prevent individual food particles from agglomerating (Peleg and Hollenbach, 1984). The most common anti-caking agent currently used by industry to prevent lumping of shredded, diced or chunked cheese is cellulose. Commercial forms of cellulose used as anti-caking agents include, common-type cellulose, microcrystalline cellulose, and cellulose impregnated with glucose sugar and glucose oxidase enzyme.

Cellulose has an affinity for moisture and free fat contained on the surface of the cheese shreds. Anti-caking is achieved by decreasing the cheese to cheese contact between shreds by allowing cellulose to cellulose contact on the surface of the shred. Even when pressure is applied to the shredded cheese during blending and storage resulting in cheese to cheese contact, the surface area involved is small enough and the contact weak enough that gentle agitation will result in the breaking apart of the agglomerated shreds (McGinley and Thomas, 1975).

McGinley and Thomas (1975) conducted a study to determine the moisture change of a Mozzarella, Cheddar, and Romano cheese blends coated with MCC versus a control with no anti-caking agent. The moisture changes of the blend coated with MCC were –25%, -4.5% and 1.1% compared to the control blend changes in moisture of –23%, -3.2% and 0.45% at the relative humidities of 15%, 33%, and 97%, respectively. Thus, the addition of MCC aided in reducing the migration of moisture between the cheese and the environment.

Potato starch is another commonly used anti-caking agent for shredded Mozzarella cheese. Although starches are often modified to enhance physical and chemical properties needed for food processing application, unmodified starch is useful as an anti-caking agent. The granular composition of native starch is beneficial for anti-caking and is due to a modest degree of structural order (Zobel and Stephen, 1995). Akins (2002) found no differences in the strechability or meltability of Mozzarella cheese with potato starch added as an anti-caking agent when compared to cellulose and a control with no anti-caking agent. Potato starch did decrease the amount of free oil of melted shredded Mozzarella cheese when compared to a control with no anti-caking agent applied. There was no difference in the amount of free oil produced with the cheese treated with potato starch and the cellulose treatment.

Adjuncts and Effects on Browning

One patented formulation, submitted by Reddy (1997), for a cheese anti-caking agent includes fine mesh vegetable flour, bentonite, cellulose, and antimycotic agents or bacterial cultures. In this patent, the addition of a defoaming agent, polydimethyl siloxane, to the anti-caking agent improves the functional properties of cheese during pizza baking. Although no traditional foams are present on the cheese surface, an oil/water emulsion exists. The addition of a defoaming agent such as polydimethyl siloxane may act as a surfactant or emulsifying agent (Heertje, 1993). Bentonite is a mineral material with a defined crystalline clay-like structure. Barbanti et al. (1997) found that bentonite exhibits hygroscopic properties and could be used in food applications as a moisture regulating system. The structure of bentonite causes water to be adsorbed at a higher rate that water is desorbed, therefore causing systems incorporating bentonite to be more hygrostatic.

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CHAPTER III

EFFECTS OF STARCH-BASED ANTI-CAKING AGENTS ON THE BROWNING OF MOZZARELLA CHEESE

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ABSTRACT

Mozzarella cheese treated with the starch-based anti-caking agents were examined to determine if differences in browning and physical changes would occur. Six commercial anti-caking agent that contained either cellulose or potato starch were applied to cheese and compared to a control. Color measurements indicated that the starch-based anti-caking agents produced a baked cheese with a greater degree of browning than the samples treated with cellulose-based anti-caking agents or no treatment (control). The cellulose-based treatments and the control also had a significantly greater moisture loss than the potato starch-based treatments. This shows that there is a negative correlation between the amount of moisture lost in a sample and the amount of browning that occurred. This correlation was significant with an R^2 of 0.51. The average surface temperature was at least 16°C higher for the treatments containing potato starch than for the cellulose-based treatments. A significant relationship between average surface temperature and browning was also found (R^2=0.67). These relationships suggest that the starch-based treatments impeded moisture loss, which decreased the amount of evaporative cooling. An increased surface temperature resulted from the decrease in the amount of evaporative cooling and thus the Maillard reaction was accelerated leading to increased browning.

A study examining the effects of the starch source was also conducted using starches from corn, rice and wheat. These starches were compared to commercially available potato starch and cellulose anti-caking agents. None of the starch sources were found to produce degree of browning on the cheese sample that was comparable to that of the cellulose or control sample. Similar relationships between browning and the moisture loss were found.

Key words: Mozzarella, anti-caking agents, browning, starch

INTRODUCTION

The growth of the Mozzarella cheese industry over the past decade has been dramatic and is due, in large part, to the increasing popularity of pizza. The annual production of Mozzarella cheese in 1999 was over three billion pounds (IDFA, 2000). The increasing demand for Mozzarella cheese as an ingredient on pizza has produced a need to better understand and be able to control the functional properties of the cheese during baking. Browning is one of the most important factors affecting pizza cheese because low levels are desired, but extreme scorching is considered a quality defect (Pilcher and Kindstedt, 1990).

The browning of cheese is due to the Maillard reaction where reducing sugars and proteins go through a series of reactions that produce melanoidins, which impart a brown color. Increasing the time and temperature are the major factors in acceleration of the Maillard reaction, although other factors such as pH, water activity, and the presence of certain metallic compounds can also change the rate of the reaction (Eskin, 1990). Rudan and Barbano (1998) describe one model of the melting and browning of Mozzarella cheese. In this model browning occurs after the formation of a skin-like layer which prevents the escape of steam generated during the baking process. Browning is caused due to the trapped steam that raises blisters on the cheese bringing the surface of the cheese closer to the heat source.

Anti-caking agents are commonly used to prevent the clumping of shredded Mozzarella cheese. Both cellulose-based and starch-based anti-caking agents are currently being used in the shredded cheese industry. Anti-caking is achieved by decreasing the cheese to cheese contact due to the coating of potato starch or cellulose on the surface of the individual shreds (McGinley and Thomas, 1975). The use of starch as an anti-caking agent has many benefits including some superior properties and economical benefits. Potato starch has a bland flavor and excellent binding power that are essential in anti-caking agent formulations (Mitch, 1984). Starches from other sources including wheat, rice, and corn contain many of the same anti-caking functional properties as potato starch while having a number of different physical properties that can affect the browning of Mozzarella cheese due to anti-caking agents. Although starch and cellulose both contain reducing sugars that are substrates in the Maillard reaction, other physical properties of starch and cellulose may contribute more the rate of browning on cheese treated with these anti-caking agents.

The results of a study on the effects of cellulose and starch-based anti-caking on the browning of shredded Mozzarella cheese will prove useful for the both the cheese and pizza industries. Since little data is currently available on the impact of these anti-caking agents on browning, it is important not only to determine the ultimate browning effects but also the cause of any differences in the browning. This research focused on determining the browning differences between commercially available anti-caking agents and pinpointing factors that may lead to any changes in the degree of browning.

MATERIALS AND METHODS

Sample Preparation

Low moisture, part skim (LMPS) Mozzarella cheese was commercially produced (Alto Dairy Cooperative, Waupun, WI) in 20-lb blocks. Cheese was aged for 7 d ± 2 at 4°C then shredded using a Hallde Shredder, type RG-7 (AB Hallde Makiner, Kista, Sweden). Shredded cheese was commingled before the addition of anti-caking agents to ensure uniformity. Seven treatments were used in the first study. Six anti-caking agents supplied by Mississippi Blending Co., Inc. (Keokuk, IA) were applied to the shredded cheese (Table 3-1). Cheese with no anti-caking agent was used as the control. Anti-caking agents were added at 2% (wt/wt) to the shredded cheese and placed in a tumbler. The cheese were tumbled with the anti-caking agent treatments in a 27.9 cm diameter container for 5 min at 7 rpm to produce complete and even coverage of cheese shreds. Cheese was packaged under modified atmospheres using a gas mixture of 75% CO_2 and 25% N_2 (Eliot et al., 1998) using a proportional gas blender (Smith Equip, Model 299-037F, Watertown, SD) and vacuum packager (Koch, Model X-200, Kansas City, MO). Oxygen and carbon dioxide levels in the package were verified using a Model 6600 Headspace Oxygen/Carbon Dioxide Analyzer (Illinois Instruments, Inc., Ingleside, IL). Packed cheese was stored in a walk-in refrigerator (W.H. Porter, Inc, Model 120, Holland, MI) at 4°C. Cheese samples were aged for a total of 25 d ± 4 before analysis was completed.

A study also was conducted to examine the effects that various starch-based anti-caking agents had on the browning of Mozzarella cheese. Five anti-caking agents were separately applied to shredded cheese. The anti-caking agents used were cellulose, potato starch, corn starch, wheat starch (Mississippi Blending Co., Inc., Keokuk, IA), and rice starch (National Starch and Chemical Co., Bridgewater, NJ) and were applied to the cheese at 2% (wt/wt). Sample preparation procedures were identical to that used to compare browning and physical changes of the commercial anti-caking agents.

Table 3-1. Composition of anti-caking agents including powdered cellulose or unmodified potato starch with and without anhydrous dextrose applied at 2% (w/w) to shredded low moisture part skim Mozzarella cheese.

Treatment	% Anti-caking Agent		
	Cellulose	Potato Starch	Dextrose
Control	0	0	0
Cellulose	100	0	0
Cellulose/ Dextrose	80	0	20
Potato	0	100	0
Potato/ Dextrose	0	80	20
Blend A[1]	12	68	20
Blend B[1]	12	88	0

[1] Blends A and B are proprietary blends developed by Allied Starch and Chemical, Keokuk, IA

Proximate analyses conducted on each lot of cheese included butterfat, protein, moisture, sugar, salt, and pH. All proximate analyses were conducted in triplicate and conducted before anti-caking agents were applied. The fat content of the cheese was determined by the Babcock test for fat in cheese (Van Slyke and Price, 1979). Moisture content was determined by drying shredded cheese samples in a force draft oven according to AOAC Official Method 948.12 (AOAC, 1998). Total protein content was determined by quantifying the nitrogen present in the cheese samples by AOAC Official Method 991.20 for Kjeldahl (AOAC, 1998). The pH of the cheese was measured by the quinhydrone electrode method (Van Slyke and Price, 1979). The amount of chloride as a quantification of salt in each cheese sample was determined using Hach Quantab® titrators for chloride as described by AOAC Official Method 971.19 (AOAC, 1998). Lactose and galactose concentrations were measured by enzymatic procedures using assay kits from R-Biopharm Enzymatic Bioanalysis and Food Analysis (R-Biopharm, Inc., Marshall, MI).

Prior to baking, samples of shredded cheese weighing 100 g $\pm$ 0.01 were evenly spread on the bottom of aluminum pans (Pactive Corp., Lake Forest, IL) with a diameter of 21.6 cm. Samples were held at 4°C $\pm$ 2 prior to being baked. An insulating mat (Flame Protector, Oatey, Inc., Cleveland, OH) was placed under the pans going through the oven to decrease the degree of heat transfer from the bottom of the oven. The pans of cheese were placed through a belt type commercial food service convection pizza oven (Impinger® model 1302; Lincoln Food Service Products, Inc., Fort Wayne, IN) for 5 min at 232°C. Baked samples of cheese were allowed to cool to a temperature of 25°C $\pm$ 2 prior to chemical and physical analysis, unless noted otherwise.

Browning Determination

Cheese samples were analyzed using three color indices, L*-values (white to black), a*-values (red to green), and b*-values (yellow to blue) by a Minolta 200CR Color Difference Meter (Minolta Corp., Ramsey, NJ). The measurement was taken 20min $\pm$ 3 after the sample was removed from the oven. Color indices were measured at five locations on the surface of the baked cheese. Four of the color measurements were taken 4cm from the edge of the pan at angle increments of 90 degrees. The fifth color measurement was taken in the center of the pan. Color differences (ΔE) between samples were calculated by the following equation (Johnson and Olson, 1985):

$$\Delta E = [(\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2]^{1/2}$$

Spectrophotometric determination of browning also was used. Baked cheese was minced with a food processor and a commingled sample weighing 2.00 g ± 0.01 was taken. The sample was homogenized in a Waring Blender 7010 (Waring Products Div., New Hartford, CT) with 20 mL of 10% w/v trichloroacetic acid for 60 s. The sample then was filtered with No. 42 Whatman filter paper (Whatman Int., Ltd., Maidstone, England). A Spectronic 1001 spectrophotometer (Milton Roy, Co., Rochester, NY) was used to measure absorbance of supernatants at 420nm (Ramirez-Jimenez et al., 2001).

Digital photographs of the cheese surface were taken to document visual appearance. An Olympus D-600L digital camera (Olympus America, Inc., Melville, NY) was mounted on a tripod with the lens facing down, 30.5 cm from the surface of the food sample. The lighting system consisted of two D_{65} lamps (Daylight Ultra 6500, General Electric, Co., Cleveland, OH) mounted 30.5 cm and at a 45° angle from the surface of the sample. Analysis of color from digital photographs was conducted using PhotoShop (Adobe Systems, Inc., San Jose, CA). Sample photographs were cropped using the elliptical marquee tool to produce a circular area that included only the surface of the cheese. The color histogram function was then used on the cropped picture to analyze mean L-, a-, and b-values. The histogram function also was used to determine the percentage of darkspots on the surface of the sample. The percentage of surface with an L*-value less than 60 was defined as "darkspots" (Papadakis et al., 2000).

Analysis of Physical Changes

Water activity (A_w) was measured for unbaked and baked samples of cheese using an Aqua Lab CX-2 water activity meter (Decagon Devices, Inc., Pullman, WA). Change in water activity (ΔA_w) was determined by subtracting the A_w for the baked sample from the A_w from the unbaked sample. Water activity for the unbaked cheese also was taken at day 0, 1, and 7 after shredding to monitor any differences over time in the water equilibrium due to the anti-caking agent treatments.

Mozzarella cheese was weighed prior to and after baking to determine the amount of moisture lost. The weight of moisture loss then was divided by the total initial weight of the cheese, multiplied by 100, to express the moisture loss per 100 g of cheese.

A Radiance 1T infrared (IR) camera (Raytheon Commercial Infrared, Dallas, TX) with a 25 mm lens attachment was utilized to determine the heat distribution on the surface of the cheese during baking. When baking samples to be used for IR analysis, the belt speed to the oven was reduced to allow the cheese to remain in the oven for the entire 5min to prevent any cooling of the sample from occurring. Samples were removed from the oven and the IR photographs were taken immediately following the five-minute baking time.

IR images were cropped using the elliptical marquee tool to produce a circular area that included only the surface of the cheese. Average, maximum, and minimum temperature of the surface of the cheese was calculated using Image Desk II, Version 2.1 (Raytheon Systems Co., Goleta, CA).

Analysis of Data

A completely randomized design was used for both experiments. Three replications were performed and data was analyzed using one-way ANOVA in SAS® version 8.2 (SAS, 2001). Fisher's least significant difference was used to determine mean comparisons when significant differences ($p<0.05$) were observed. Simple linear regression was used to calculate the coefficient of determination (R^2)

RESULTS AND DISCUSSION

Proximate Analysis

The percentage of fat, total solids, protein, galactose, lactose, and salt, as well as pH were analyzed to ensure a standard cheese was used for the experiment (Table 3-2). Results of the compositional analysis were consistent with previously published values for low moisture part skim Mozzarella cheese (Kindstedt, 1993; Mukherjee and Hutkins, 1994).

Table 3-2. Mean[1] composition of low moisture part skim Mozzarella cheese used in browning experiments for various anti-caking agents and starches.

Component	Mean	SD
Fat %	20.8	0.30
Total Solids %	51.5	0.34
Protein %	25.9	0.11
Galactose %	0.4	0.11
Lactose %	nd[2]	-
NaCl %	2.0	0.10
PH	5.4	0.02

[1]n=6
[2]nd – none detected

Browning Development

L*a*b* values were used to quantitatively determine the color of the baked cheese surface. The L*-value represents the degree of luminance or lightness on a scale from 0 to 100, with higher values representing samples with a lighter coloration. The red to green spectrum is based on the a*-value, with a scale of –120 to 120, respectively. The b*-value represents the blue to yellow scale and is also based on a scale of –120 to 120, respectively (Papadakis et al., 2000). The overall color difference, ΔE, is a calculated value based on all the color components. An increase in the ΔE indicates a greater degree of browning.

The degree of coloration for the baked samples treated with various anti-caking agents is shown in Table 3-3. The readings from the Minolta colorimeter for the control, cellulose and cellulose/dextrose treatments indicated L*-values in the range of 75 to 76. The L*-values for the potato starch, potato/dextrose, blend A, and blend B treatments were in the range of 64 to 68. This data indicates a whiter when cellulose or no treatment was applied compared to the starch-based treatments. The digital image data showed similar trends in the L*-value data with the control, cellulose, and cellulose/dextrose treatments having higher L*-values than treatments containing potato starch. Visual confirmation of these differences can be seen in Figure 3-1. Comparison of the L*-value measurements between the colorimeter and digital image methods show that the colorimeter method found greater differences between treatments. The L*-values were always higher using the colorimeter than when the digital images were used.

The digital a*-values were significantly lower for the control and treatments containing cellulose than the starch-based anti-caking agent treatments. A lower a*-value means that the surface of the sample had a red tint while the higher a*-values indicate a green tint. The colorimeter determination of a*-values showed less differences between treatments compared to the digital image method, but blend A had higher a*-values than did the control, cellulose, and cellulose/dextrose treatments. Overall, there were more differences in a*-values with the digital image data. This may be due to the intensity of environmental light used to take the digital images.

The ΔE values from the colorimeter analysis were highest for the potato starch (28), potato/dextrose blend (26), and blend A (30) which indicates a greater color change. The control and cellulose treatment had ΔE values of 18 and 19, respectively. The potato-starch based anti-caking agent that had a ΔE similar to cellulose (20) was blend B (26). The ΔE values from the digital image analysis did not show any significant differences in coloration although the values were the lowest for the cellulose-based treatments and the highest for the potato starch treatment. The trends for ΔE are comparable for the two methods, but the values are higher with the digital image method and were not significant between treatments. This indicates that there was a greater degree of variability in ΔE with the digital method compared to the colorimeter measurements.

The percentage of darkspots on the surface of the sample was calculated by the digital image software as the area which had an L*-value of less than 60. This measurement can give an indication of the amount of blistering on the cheese surface. The percentage of darkspots was highest for the potato starch treatment (54%) and lowest for the cellulose treatment (27%)(Table 3-3).

A comparison of color determination methods used show that although are many similarities in the results there are also some differences in the mean values, separation of means by least significant difference, and in the variability when using L*a*b* values and ΔE. Both methods were able to show the differences in coloration between the cellulose-based anti-caking agents and the starch-based anti-caking agents. Also, the digital image method is more versatile by allowing for the quantification of the number of darkspots on the surface of the sample.

Table 3-3. Coloration determination by mean[1] L*-, a*-, and b*-values, color difference (ΔE), and percentage of darkspots of baked Mozzarella cheese with various anti-caking agents.

Treatment[2]	Minolta Colorimeter				Digital Images[3]				
	L*[4] Value	a*[4] Value	b*[4] Value	ΔE[5]	L* Value	a* Value	b* Value	ΔE	% Dark-spots[6]
Control[7]	76^{a}	-1^{b}	35	18^{c}	$63^{a,b}$	-6^{b}	54^{a}	41	$31^{b,c}$
100% Cellulose	76^{a}	-2^{b}	38	$20^{b,c}$	64^{a}	-7^{b}	$50^{a,b}$	37	27^{c}
80% Cellulose/ 20% Dextrose	75^{a}	-3^{b}	35	19^{c}	$61^{a,b}$	-3^{b}	$48^{a,b}$	38	$37^{b,c}$
100% Potato Starch	65^{b}	$4^{a,b}$	36	28^{a}	56^{b}	7^{a}	47^{b}	42	54^{a}
80% Potato Starch/ 20% Dextrose	68^{b}	$3^{a,b}$	37	26^{a}	$60^{a,b}$	6^{a}	48^{b}	39	$41^{a,b}$
Blend A[8]	64^{b}	7^{a}	36	30^{a}	$59^{a,b}$	7^{a}	46^{b}	39	$44^{a,b}$
Blend B[9]	68^{b}	$3^{a,b}$	37	$26^{a,b}$	$59^{a,b}$	6^{a}	47^{b}	40	$44^{a,b}$
SE	1.1	0.9	0.4	1.0	0.7	1.3	0.6	0.6	4.4

[1]n=3
[2]Applied to cheese at 2% wt/wt
[3]Digital photographs analyzed with the histogram function in PhotoShop graphical software
[4]L*a*b* values are based on scales of 0 to 100, -120 to 120, and –120 to 120, respectively with color endpoint of dark to light, red to green, and blue to yellow, respectively.
[5]Color difference (ΔE) is based on the calculation of $((\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2)^{1/2}$ with darkest sample having highest values
[6]Percentage of sample surface with L*-value <60
[7]Control – no anti-caking agent
[8]Blend A – 68% potato starch/ 20% dextrose/ 12% cellulose
[9]Blend B – 88% potato starch/ 12% cellulose
[abc]Means with different superscripts in columns are significantly different at $p<0.05$

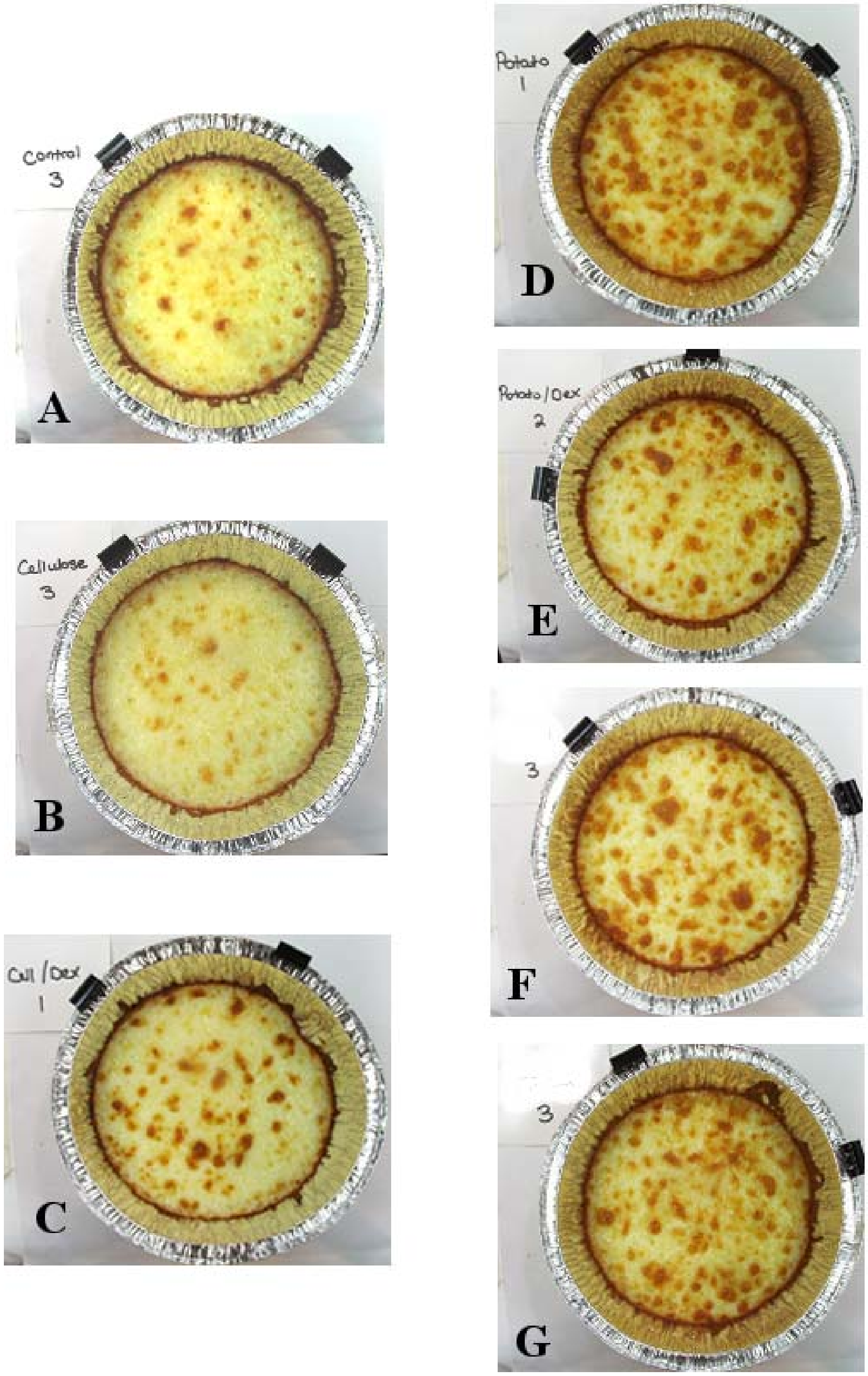

Figure 3-1. Appearance at room temperature of low fat part skim Mozzarella cheese after baking (232°C for 5 min) with no treatment (A), 2% (wt/wt) cellulose anti-caking agent (B), 1.6% cellulose anti-caking agent + 0.4% dextrose (C), 2% potato starch anti-caking agent (D), 1.6% potato starch anti-caking agent + 0.4% dextrose (E), 2.0% Blend A anti-caking agent (12% cellulose, 68% potato starch, 20% dextrose)(F), 2.0% Blend B anti-caking agent (12% cellulose, 88% potato starch)(G).

The values in Table 3-4 show the color of the baked cheese surface when treated with cellulose and starches from various sources. The control and cellulose treatments produced similar values and varies from the coloration produced by the starch-based anti-caking agents. L*-values were higher for the control (68) and cellulose (73) than for the potato, wheat, corn, and rice starches which had L*-values of 64, 65, 60, and 64, respectively. The digital image L*-values were also higher for the control and cellulose than the starch-based treatments.

Negative a*-values were found in the control, cellulose and wheat starch treatments, while the potato, corn and rice starches had positive a*-values using both the colorimeter and digital images. Negative a*-values are associated with a more red coloration while the positive a*-values indicate a green tint. No differences were noted with the b*-values measured by the colorimeter method. The digital image reading indicated that rice starch produced the highest b*-value which corresponds with the most yellow sample while the control had the lowest b*-value.

Overall color differences (ΔE) from the colorimeter were highest for the corn starch, 29, and lowest for the control, 19. The digital images found overall color changes, as measured by ΔE, to be highest in the rice starch (42) and corn starch (40), and were lowest in the control (27). The ΔE was 30 for the cellulose treatment, 40 for the potato starch, and 35 for the corn starch.

The percentage of darkspots was 15% for the control, which was the lowest amount of darkspots found. The cellulose treatment had the second lowest amount of darkspots, followed by wheat starch and corn starch. The greatest percentage of darkspots was found on the potato and rice starch treatments with 53% and 56% darkspots, respectively.

Table 3-4. Coloration determination by mean[1] L*-, a*-, and b*-values, color difference (ΔE), and percentage of darkspots of baked Mozzarella cheese with various anti-caking agents and starches.

Treatment[2]	Minolta Colorimeter				Digital Images[3]				
	L*[4] Value	a*[4] Value	b*[4] Value	ΔE[5]	L* Value	a* Value	b* Value	ΔE	% Dark-spots[6]
Control[7]	73^{a}	-5^{d}	34	19^{c}	68^{a}	-6^{d}	40^{b}	27^{d}	15^{d}
Cellulose[8]	73^{a}	$-3^{c,d}$	36	$20^{b,c}$	$65^{a,b}$	$-3^{c,d}$	$42^{a,b}$	$30^{c,d}$	27^{c}
Potato Starch	64^{b}	$1^{a,b,c}$	33	$26^{a,b,c}$	58^{c}	4^{b}	$47^{a,b}$	$40^{a,b}$	53^{a}
Wheat Starch	65^{b}	$-2^{b,c,d}$	33	$24^{a,b,c}$	$60^{b,c}$	-1^{c}	$43^{a,b}$	$35^{b,c}$	41^{b}
Corn Starch	60^{b}	4^{a}	31	29^{a}	$60^{b,c}$	4^{b}	49^{a}	40^{a}	$48^{a,b}$
Rice Starch	64^{b}	$2^{a,b}$	34	$27^{a,b}$	57^{c}	9^{a}	$47^{a,b}$	42^{a}	56^{a}
SE	1.3	0.8	0.6	1.0	1.0	1.2	1.0	1.4	3.9

[1]n=3

[2]Applied to cheese at 2% wt/wt

[3]Digital photographs analyzed with the histogram function in PhotoShop graphical software

[4]L*a*b* values are based on scales of 0 to 100, -120 to 120, and –120 to 120, respectively with color endpoint of dark to light, red to green, and blue to yellow, respectively.

[5]Color difference (ΔE) is based on the calculation of $((\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2)^{1/2}$ with darkest sample having highest values

[6]Percentage of sample surface with L*-value < 60.

[7]Control – no anti-caking agent

[8]Cellulose – powdered cellulose

[abcd]Means in columns with different superscripts are significantly different at $p<0.05$

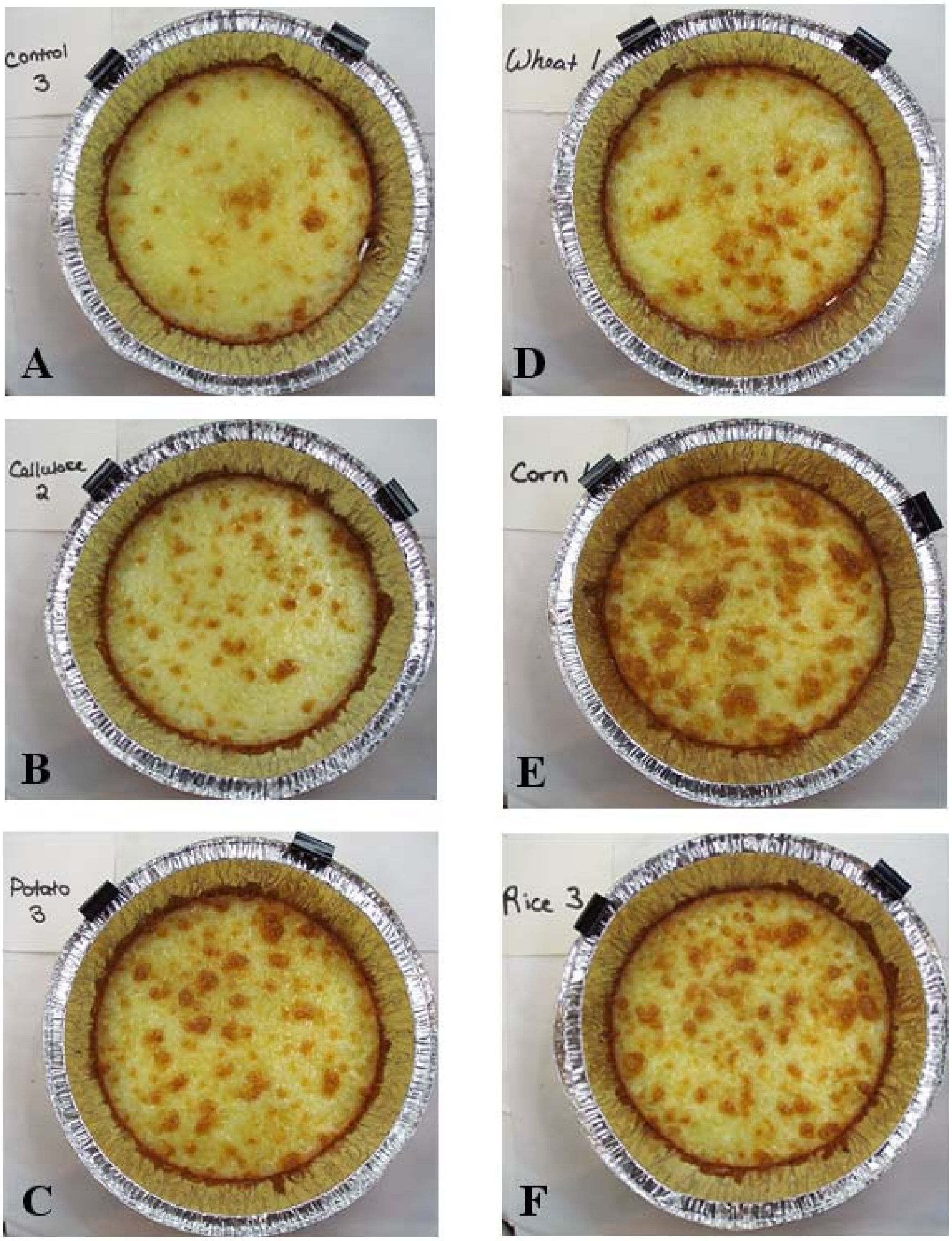

Figure 3-2. Appearance at room temperature of low fat part skim Mozzarella cheese after baking (232°C for 5 min) with no treatment (A), 2% (wt/wt) cellulose anti-caking agent (B), 2% potato starch anti-caking agent (C), 2% wheat starch (D), 2% corn starch (E), 2% rice starch (F).

Spectrophotometric analysis of filtrate prepared from the treatments was analyzed at 420 nm to detect the amount of Maillard browning reaction products, thus indicating color change. In both experiments, the spectrophotometer method of color determination was determined to be unacceptable in this study for two reasons. Baked cheese proved to be very difficult to homogenize for the purpose of extracting the browning pigments. Also the baked cheese treated with anti-caking agents produced large variations in the turbidity of the filtrate for some of the treatments. The turbidity was apparently the effect of the starch and cellulose-based anti-caking agents.

Digital photographs of the baked samples (Figure 3-1 and 3-2) demonstrate the degree of browning on the surface of each treatment. In Figure 3-1 a higher degree of browning can be observed on the samples containing potato starch in the anti-caking agent when compared to the cellulose treatment and the control. Dextrose appears to alter the degree of browning, but not in a consistent manner. When combined with cellulose, dextrose increases the number of visible darkspots on the surface of the cheese. When combined with potato starch, dextrose decreases number of visible darkspots. These visual differences closely follow the amount of darkspots on the sample, while the overall browning may not have been affected as greatly. Further visual examination does show that the surface within darkspots on the samples with added dextrose are darker in color than the corresponding samples with no dextrose added to the anti-caking agent. Figure 3-2 shows the browning on the surface of the cheese treated with starches from various sources as well as a control and a cellulose treatment. Again, the degree of browning appears to be greater in the starch-based samples, while the control and cellulose treatment had less browning. Of the starches, the wheat treatment appears to have the lowest degree of browning. The corn starch produced the highest degree of browning and the potato and rice starch caused an intermediate degree of browning. These observations agree with the ΔE data generated by both the colorimeter and digital imaging methods.

Analysis of Physical Changes

Moisture loss of the cheese during baking was measured to determine the degree to which the anti-caking agent treatment would hinder the evaporation of water from the cheese surface. The formation of skin-like layer on the surface of the cheese during baking has been associated with moisture loss. This skin causes the entrapment of steam causing blisters that will brown faster than the rest of the surface (Rudan and Barbano, 1998). The percent moisture lost during baking of samples with various anti-caking agents (Table 3-5) shows that the use of a starch-based anti-caking agent significantly decreases the amount of water lost during baking. The potato starch containing samples lost between 15.0% and 15.6% during baking while the control, cellulose and cellulose/dextrose treatments had moisture losses of 16.7% to 17.7%. Lower moisture loss due to the potato starch may be associated with the amount of water imbibed by the starch granules upon baking. An increase in the viscosity on the cheese surface due to gelatinization of the starch may also increase the degree of skin formation. The skin formation also may occur earlier in the baking process due to the starch gelatinization. The overall losses of moisture were much lower in this study than values reported by Rudan and Barbano (1998) where 27.9% moisture was lost during baking of a LMPS Mozzarella cheese under similar time and temperatures. The differences between the two studies may be due to the use of the insulating mat in this study used to better simulate the conditions of cheese baked on a pizza. Also, no anti-caking agents were used in the study by Rudan and Barbano. The results from this study indicated that the moisture loss was at the surface of the cheese shred and not moisture loss as a whole that led to skin formation on the cheese and subsequent cheese formation.

Moisture loss of baked cheese treated with anti-caking agents from a variety of starch sources (Table 3-6) was lowest for the rice starch (15.5%). The control lost 17.8% moisture, which was the highest of the treatments. The cellulose, potato starch, wheat starch and corn starch lost 16.8%, 15.8%, 16.7%, and 16.0% moisture, respectively. Since moisture loss differences were noted between cellulose and potato starch in the previous experiment where different starch sources were used to determine if there were any physical attributes of the starch that affected evaporation from the surface of the cheese. No corresponding trends were noted between moisture loss and published values for the size of the starch granule, swelling power, paste viscosity, or gelatinization temperature (Swinkels, 1985; Moore et al., 1984). No single attribute appears to influence the moisture loss of the cheese during baking, but it is likely that a number of these factors may play a role in moisture loss and corresponding browning of the cheese.

An IR camera was used to determine the surface temperature of the cheese (Table 3-5) and differences were noted between the treatments with potato starch as the main component and the treatments with cellulose as the main component. The average temperatures for the cellulose and cellulose/dextrose treatment were 106°C and 105°C, respectively. The average temperature of the potato starch, potato starch/dextrose, and blends A and B ranged between 118°C and 120°C. The minimum temperatures of the cellulose and cellulose/dextrose treatments were 82°C and 82°C. The minimum temperature ranged from 101°C to 103°C for the treatments containing potato starch. No significant differences for the maximum temperature of the treatments were noted. Figure 3-3 shows the IR images of samples treated with cellulose and potato starch anti-caking agents and the corresponding digital photographs of the samples. The increased temperature where the darkspots have been produced is also evident in Figure 3-3. The correlation between the moisture loss and the average temperature was R^2=0.82. Since this correlation is negative, meaning that an increase in moisture loss is correlated with a decrease in the surface temperature of the sample, evaporative cooling is the likely cause of this trend. Evaporative cooling occurs when the rate of heat transfer exceeds the transfer needed to supply the heat of vaporization causing a decrease in the material temperature (Toledo, 1991). The 10°C difference in the average temperature and 20°C difference in minimum temperature between the cellulose-based anti-caking agents and the starch-based anti-caking agents suggests that the 1% change in moisture loss can greatly alter the temperature of the cheese surface.

Water activity is defined as the ratio between the water vapor pressure exerted by the food and the water vapor pressure of pure water (Fox and McSweeney, 1998).

Measurement of the water activity of the unbaked cheese taken at 0, 1, and 7 days after application of the anti-caking agents showed no differences between treatments on any of the days (Appendix Table 1 & 2). Water activity changes between the baked cheese and the unbaked cheese (ΔAw) were also measured and no significant differences were noted between treatments (Table 3-5).

Table 3-5. Mean values[1] for moisture loss, surface temperature as measured by infrared (IR) analysis, and water activity change (ΔA_w) after baking of low moisture part skim Mozzarella cheese with varying anti-caking agents.

Treatment[2]	% Moisture Loss	IR Average Temperature (°C)	IR Minimum Temperature (°C)	IR Maximum Temperature (°C)	ΔA_w
Control[3]	16.7^a	109^b	85^b	143	-0.06
Cellulose	16.9^a	106^b	82^b	144	-0.06
Cellulose/Dex[4]	17.7^a	105^b	82^b	146	-0.06
Potato Starch	15.6^b	118^a	101^a	155	-0.06
Potato/Dex[5]	15.4^b	119^a	101^a	156	-0.06
Blend A[6]	15.5^b	118^a	101^a	153	-0.07
Blend B[7]	15.0^b	120^a	103^a	157	-0.06
SE	0.21	1.4	2.1	1.7	0.01

[1]n=3
[2]Applied to cheese at 2% wt/wt
[3]Control – no anti-caking agent
[4]80% Cellulose/ 20% Dextrose
[5]80% Potato starch / 20% Dextrose
[6]Blend A – 68% potato starch/ 20% dextrose/ 12% cellulose
[7]Blend B – 88% potato starch/ 12% cellulose
[ab]Means in columns with different superscripts are significantly different at $p<0.05$

Table 3-6. Mean values[1] for moisture loss and water activity change (ΔA_w) after baking of low moisture part skim Mozzarella cheese with anti-caking agents from various starch sources.

Treatment[2]	% Moisture Loss	ΔA_w [4]
Control[3]	17.8^{a}	-0.08
Cellulose	16.8^{a,b}	-0.07
Potato Starch	15.8^{b,c}	-0.07
Wheat Starch	16.7^{a,b,c}	-0.05
Corn Starch	16.0^{b,c}	-0.07
Rice Starch	15.5^{c}	-0.05
SE	0.21	0.01

[1]n=3
[2]Applied to cheese at 2% wt/wt
[3]Control – no anti-caking agent
[4]Change in water activity between unbaked cheese and baked cheese
[ab]Means in columns with different superscripts are significantly different at $p<0.05$

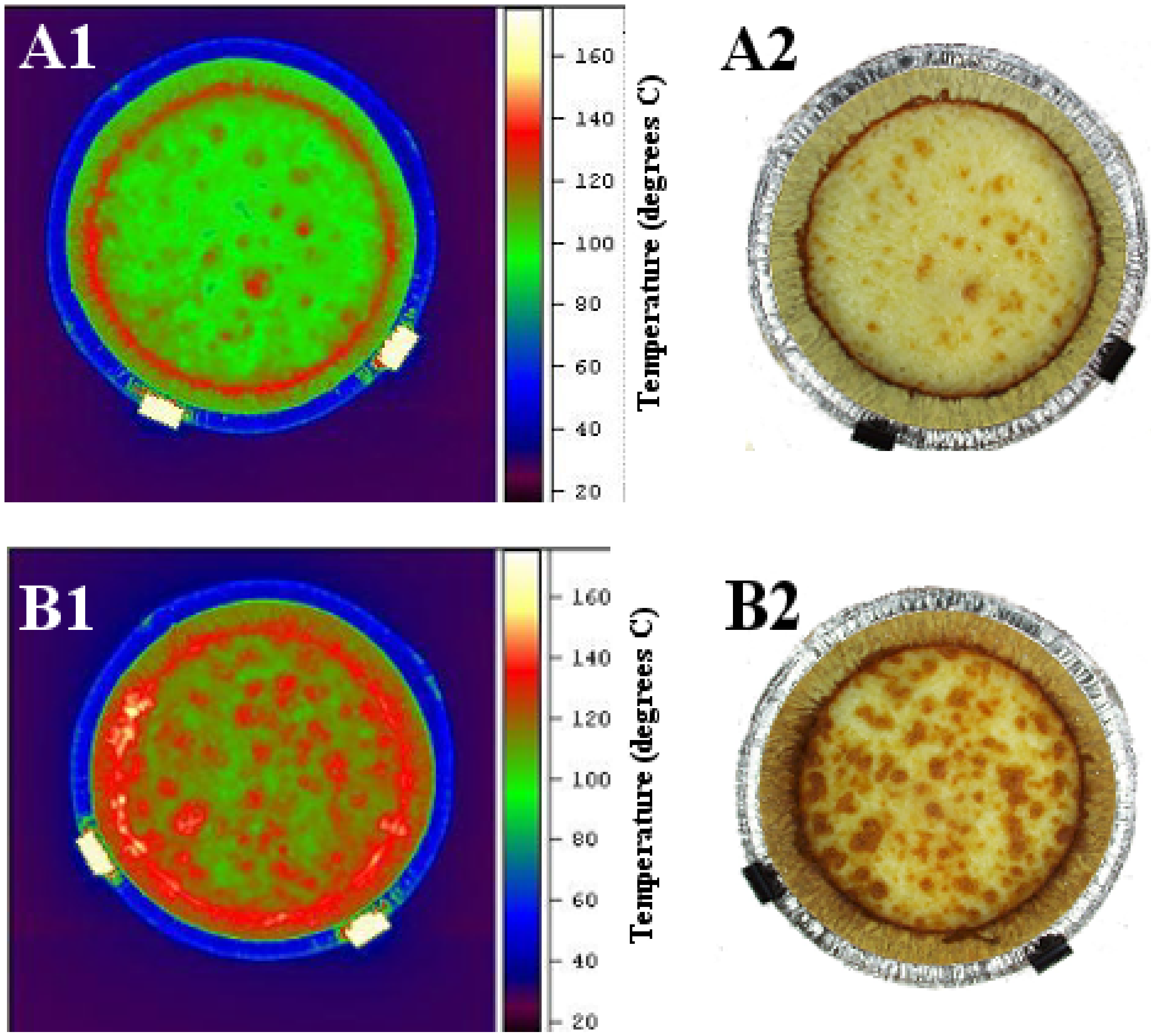

Figure 3-3. Comparison of infrared (IR) photographs and digital photographs of cheese surface after baking (232°C for 5 min). Pictures of samples treated with 2% (wt/wt) cellulose using IR camera (A1) and digital camera (A2). Pictures of sample treated with 2% potato starch using IR camera (B1) and digital camera (B2).

Correlation between Physical Parameters of Baked Cheese and Browning

Correlation between color formation and physical changes of the treatments was analyzed by regression analysis. A significant correlation was found between moisture loss and many of the measurements of color determination. Both the moisture loss and the average surface temperature measured by the IR camera also had a significant correlation ($p=0.05$) to the color measurements that had significant differences between treatments. The colorimeter L*-values were correlated to the moisture loss and average surface temperature with R^2 values of 0.50 and 0.71, respectively. The colorimeter ΔE also was correlated to the percent moisture loss and average temperature of the cheese surface with R^2 values of 0.51 and 0.67, respectively. The color change was positively correlated to the surface temperature of the sample and negatively correlated to the moisture loss. This again would point to evaporative cooling decreasing the amount of browning by lowering the surface temperature of the cheese and thus decreasing the rate of browning. The rate of the Maillard browning reaction is increased with an increase in the temperature of the treatment (Eskin, 1990).

The experiment investigating the impact of varying starch sources on the browning of baked Mozzarella cheese showed similar results in the correlation between moisture loss and the degree of browning. Moisture loss was negatively correlated to the degree of browning with an R^2 of 0.43 when compared to the colorimeter L*-value. An R^2 of 0.58 resulted from the comparison of moisture loss to the percentage of darkspots on the surface of the cheese.

CONCLUSIONS

Starch based anti-caking agents cause Mozzarella cheese to brown to a greater degree than cheese with no anti-caking agents and cheese with cellulose and cellulose/dextrose anti-caking agents. Cheese with cellulose produced a similar degree of browning to that of the control cheese that had no anti-caking agent applied. The addition of dextrose to anti-caking agent blends produced no change in overall browning. This would suggest that the amount of reducing sugars as substrates for the Maillard browning reaction is not a limiting factor.

The degree of browning on Mozzarella cheese treated with starch from various sources showed an increase in browning over the cellulose treatment and similar to that of cheese with commercially available potato starch anti-caking agent. The starch sources analyzed included corn, wheat, rice and potato. No physical or chemical characteristics of the various starches were found that could explain the differences in the degree of browning. Also, there were no significant differences in the moisture loss of the samples treated with the starches from different sources.

Moisture loss during baking is an important factor in the amount of browning on Mozzarella cheese. Increased moisture loss may be associated with evaporative cooling that would lower a surface temperature of the baking cheese. A decreased temperature will lead to less browning because the rate of the Maillard browning reaction will be slowed. This hypothesis is further confirmed by the correlation of the temperature of the baked cheese, as measured by the infrared camera, to degree of browning. Whether the differences in moisture loss is due to the anti-caking agents ability to imbibe water that would otherwise leave the surface of the cheese, or if the anti-caking agents when heated form a viscous barrier that does not allow steam to leave the cheese surface is unknown. Further research on the physical and chemical properties of the anti-caking agents that may affect browning rates and pinpointing methods for altering these properties is proposed.

Methods employed to measure the degree of browning of the samples and the physical changes that are associated with this color change were evaluated. Both the Minolta colorimeter and the digital image method provided useful information on the differences between the treatments. Although some differences were noted in the two methods, both are recommended for their ease of use and effectiveness. Some of the differences could be due to the fact the colorimeter measures a set number of pinpoint readings, while the digital image method can analyze the entire sample surface. The IR camera effectively measured the temperature of the sample surface. A visual image of the surface temperature of the sample also could be generated and compared with color photographs to examine the relationship between hotter areas and darkspots.

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CHAPTER IV

EFFECTS OF ANTI-CAKING AGENTS AND ADJUNCTS ON THE BROWNING OF MOZZARELLA CHEESE

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ABSTRACT

Studies have demonstrated that starch-based anti-caking agents lead to increased browning of baked Mozzarella cheese when compared to cheese treated with cellulose-based anti-caking agents. Four adjuncts treatments were added to cheese treated with 2% (wt/wt) potato starch to determine if a reduction in the degree of browning could be achieved. The four adjunct treatments, 0.050% (wt/wt) dimethylpolysiloxane, 0.050% lactic acid, 0.025% spray dried partially hydrogenated sunflower oil, and a combination of 0.025% spray dried partially hydrogenated sunflower oil and 0.050% dimethylpolysiloxane, were compared to baked cheese treated with 2% cellulose, 2% potato starch and no anti-caking agent. Adjuncts were selected based on properties that may control the degree of browning on cheese treated with starch-based anti-caking agents. Color determination and physical changes of the samples during baking were conducted. No differences in browning between the potato starch treatment and those with added adjuncts were found. The cellulose treatment and the control did have significantly lighter surfaces, as measured by L*-values than treatments containing potato starch as the anti-caking agent. A negative correlation between moisture loss and the degree of browning also was noted. The relationship between the Minolta colorimeter L*-, a*-, and b*-values and moisture loss produced R^2 values of 0.60, 0.63, and 0.63,

respectively. The digital image data showed a high correlation between moisture loss and ΔE (R^2=0.61).

The adjuncts showed no reduction in the degree browning on the surface of the baked sample when compared to a sample with only potato starch as an anti-caking agent. Therefore these adjuncts would not be recommended additions to starch-based anti-caking agents for the reduction of browning on baked Mozzarella cheese.

Key words: Mozzarella, anti-caking agents, browning, starch

INTRODUCTION

The production and consumption of Mozzarella and Mozzarella-like cheese has increased dramatically over the past decade. Much of this growth can be attributed to the expanding popularity and demand for pizza and other Italian specialty foods. These foods often require baking, and therefore understanding the functional properties of baked Mozzarella cheese is imperative. The physical properties of melted Mozzarella cheese are highly complex, but they yield at least five important functional characteristics: meltability, strechability, elasticity, free oil formation, and browning (Kindstedt, 1993). Browning of the cheese surface during baking is especially important in production of pizza where low levels of browning are considered desirable attributes, but extreme scorching is detrimental to the quality of the product (Pilcher and Kindstedt, 1990).

Rudan and Barbano (1998) described a model for the melting and browning of Mozzarella cheese during baking. This model attributed browning to the formation of a shell or skin-like layer on the surface of the cheese during baking which resulted in the inability of steam to escape from the baking cheese. The subsequent excessive browning was due to blister formation when steam raised the surface of the cheese.

Anti-caking agents are common additions to shredded cheese for prevention of clumping during packaging, transport, and storage. The shredded cheese industry currently uses two types of anti-caking agents: potato starch-based and cellulose-based. Previous studies have demonstrated increases in browning of baked cheese when treated with starch-based anti-caking agents compared to a cheese treated with a cellulose anti-caking agent and a control with no anti-caking agent treatment. This study also demonstrated a negative correlation between moisture loss and the degree of browning (Chapter 3). The addition of adjuncts to starch-based anti-caking agents that affect the interaction between moisture escaping the cheese during baking and the anti-caking agent may lower the degree of browning on the cheese surface.

The addition of bentonite and dimethylpolysiloxane were reported to decrease the degree of browning of shredded cheese during baking (Reddy, 1997). Dimethlypolysiloxane may act as an as a surfactant or emulsifying agent (Heertje, 1993). Spray dried partially hydrogenated sunflower oil is a hydrophobic material similar to that used by Rudan and Barbano (1998). Lactic acid may also be used to denature the proteins on the surface of the cheese (Damodaran, 1996) that can affect the apparent viscosity of the molten cheese (Rudan and Barbano, 1998).

The economic benefits of potato starch as an anti-caking agent for use on shredded Mozzarella cheese will increase as the Mozzarella market continues to expand. Changes in browning of Mozzarella cheese due to different properties of cellulose and starch-based anti-caking agents increases the need for a system to control and manipulate the degree of browning. The focus of this research was to identify food-grade adjuncts to control the degree of browning of Mozzarella cheese treated with starch-based anti-caking. Achieving a decrease in browning with the adjunct so that the starch-based treatment browning similar to a cellulose-based treatment was targeted.

MATERIALS AND METHODS

Sample Preparation

Low moisture, part skim (LMPS) Mozzarella cheese was commercially produced (Alto Dairy Cooperative, Waupun, WI) in 20-lb blocks. Cheese was aged for 7 d ± 2 at 4°C then shredded using a Hallde Shredder, type RG-7 (AB Hallde Makiner, Kista, Sweden). Shredded cheese was commingled before the addition of anti-caking agents to ensure uniformity. Seven treatments were used in this study. Two anti-caking agents supplied by Mississippi Blending Co., Inc. (Keokuk, IA) and adjunts were applied to shredded cheese (Table 4-1), and a control with no anti-caking agent also was used. Anti-caking agents and adjuncts were added to shredded cheese at levels stated in Table 4-1 with adjuncts being added on a wt/wt basis of the active ingredient. Antifoaming agent was applied as a powder containing 20% wt/wt dimethylpolysiloxane, the active ingredient. Lactic acid was added as calcium lactate powder with an acidity of 45%. Shortening was applied as a spray-dried powder consisting of 73% partially hydrogenated sunflower oil (Kerry Ingredients, Inc., Beloit, WI). The cheese and treatments were placed in a 29.7 cm diameter container and tumbled for 5min at 7rpm to produce a complete and even coverage. Cheese was packaged under modified atmospheres using a gas mixture of 75% CO_2 and 25% N_2 (Eliot et al., 1998) using a proportional gas blender (Smith Equip, Model 299-037F, Watertown, SD) and vacuum packager (Koch, Model X-200, Kansas City, MO). Oxygen and carbon dioxide levels in the package were verified using a Model 6600 Headspace Oxygen/Carbon Dioxide Analyzer (Illinois Instruments, Inc., Ingleside, IL). Packed cheese was stored in a walk-in refrigerator (W.H. Porter, Inc, Model 120, Holland, MI) at 4°C. Cheese samples were aged for a total of 25 d ± 4 before analysis was completed.

Table 4-1. Application rates of anti-caking agents and adjuncts to shredded Mozzarella cheese.

	% Anti-caking Agent and Adjunct (wt/wt) on Shredded Mozzarella Cheese				
Treatment	Powdered Cellulose	Unmodified Potato Starch	Lactic Acid[1]	Shortening[2]	Antifoaming Agent[3]
Control					
Cellulose	2.000				
Potato		2.000			
Potato + Lactic Acid		2.000	0.050		
Potato + Shortening		2.000		0.025	
Potato + Antifoam		2.000			0.050
Potato + Shortening/Antifoam		2.000		0.025	0.050

[1]Antifoam – antifoaming agent, dimethylpolysiloxane
[2]Lactic acid – as calcium lactate
[3]Shortening – spray dried partially hydrogenated sunflower oil

Proximate analyses conducted on the cheese included butterfat, protein, moisture, sugar, salt, and pH. All proximate analysis was conducted in triplicate and conducted on cheese with no treatment applied. Fat content of cheese was determined by the Babcock test for fat in cheese (Van Slyke and Price, 1979). Moisture content was determined by drying shredded cheese samples in a forced draft oven according to AOAC Official Method 948.12 (AOAC, 1998). Total protein content was determined by quantifying the nitrogen present in the cheese samples by AOAC Official Method 991.20 for Kjeldahl (AOAC, 1998). The pH of the cheese was measured by the quinhydrone electrode method (Van Slyke and Price, 1979). The amount of chloride as a quantification of salt in each cheese sample was determined using Hach Quantab® titrators for chloride as described by AOAC Official Method 971.19 (AOAC, 1998). Lactose and galactose concentration was measured by enzymatic procedures using assay kits from R-Biopharm Enzymatic Bioanalysis and Food Analysis (R-Biopharm, Inc., Marshall, MI).

Prior to baking, samples of shredded cheese weighing 100 g $\pm$ 0.01 were evenly spread on the bottom of aluminum pans (Pactive Corp., Lake Forest, IL) with a diameter of 21.6 cm. Samples were held at 4°C $\pm$ 2 prior to being baked. An insulating mat (Flame Protector, Oatey, Inc., Cleveland, OH) was placed under the pans going through the oven to decrease the degree of heat transfer from the bottom of the oven. The pans of cheese were placed through a belt type commercial food service convection pizza oven (Impinger® model 1302; Lincoln Food Service Products, Inc., Fort Wayne, IN) for 5 min at 232°C. Baked samples of cheese were allowed to cool to a temperature of 25°C $\pm$ 2 prior to chemical and physical analysis, unless noted otherwise.

Browning Determination

Cheese samples were analyzed using three color indices, L*- (white to black), a*- (red to green), and b*- (yellow to blue) by a Minolta 200CR Color Difference Meter (Minolta Corp., Ramsey, NJ). The measurement was taken 20 min $\pm$ 3 after the sample was removed from the oven. Color indices were measured at five locations on the surface of the baked cheese. Four of the color measurements were taken 4 cm from the edge of the pan at angle increments of 90 degrees. The fifth color measurement was taken in the center of the pan. Color differences (ΔE) between samples were calculated by the following equation (Johnson and Olson, 1985):

$$\Delta E = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2}$$

Spectrophotometric determination of browning also was used. Baked cheese was minced with a food processor and a commingled sample weighing 2.00 g ± 0.01 was taken. The sample was homogenized in a Waring Blender 7010 (Waring Products Div., New Hartford, CT) with 20 mL of trichloroacetic acid for 60 s. The sample then was filtered with No42 Whatman filter paper (Whatman Int., Ltd., Maidstone, England). A Spectronic 1001 spectrophotometer (Milton Roy, Co., Rochester, NY) was used to measure the absorbance of the supernatants at 420 nm (Ramirez-Jimenez et al., 2001).

Digital photographs of the cheese surface were taken to document visual appearance. An Olympus D-600L digital camera (Olympus America, Inc., Melville, NY) was mounted on a tripod with the lens facing down, 30.5 cm from the surface of the food sample. The lighting system consisted of two D_{65} lamps (Daylight Ultra 6500, General Electric, Co., Cleveland, OH) mounted 30.5 cm and at a 45° angle from the surface of the sample. Analysis of color from digital photographs was conducted using PhotoShop (Adobe Systems, Inc., San Jose, CA) (Papadakis et al., 2000). Sample photographs were cropped using the elliptical marquee tool to produce a circular area that included only the surface of the cheese. The color histogram function then was used on the cropped picture to analyze mean L-, a-, and b-values. The histogram function also was used to determine the percentage of darkspots on the surface of the sample. The percentage of surface with an L*-value less than 60 was defined as “darkspots” (Papadakis et al., 2000).

Analysis of Physical Changes

Water activity (A_w) was measured for unbaked and baked samples of cheese using an Aqua Lab CX-2 water activity meter (Decagon Devices, Inc., Pullman, WA). Change in water activity (ΔA_w) was determined by subtracting the A_w for the baked sample from the A_w from the unbaked sample. Water activity for the unbaked cheese was also taken at day 0, 1, and 7 after shredding to monitor any differences over time in the water equilibrium due to the anti-caking agent treatments.

Mozzarella cheese was weighed prior to and after baking to determine the amount of moisture lost. The weight of moisture loss was then divided by the total initial weight of the cheese, multiplied by 100, to express the moisture loss per 100 g of cheese.

Analysis of Data

A completely randomized design was used for the experiment. Analysis was performed in triplicate and data was analyzed using one-way ANOVA in SAS® version 8.2 (SAS, 2001). Fisher's least significant difference was used to determine mean comparisons when significant differences ($p<0.05$) were observed. Simple linear regression was used to calculate the coefficient of determination (R^2).

RESULTS AND DISCUSSION

Proximate Analysis

The percentage of fat, total solids, protein, galactose, lactose, and salt, as well as pH were analyzed to ensure a standard cheese was used for the experiment (Table 4-2). Compositional content of the cheese sampled was consistent with previously published values for LMPS Mozzarella cheese (Kindstedt, 1993; Mukherjee and Hutkins, 1994).

Table 4-2. Mean[1] composition of low moisture part skim Mozzarella cheese used in browning experiments for various anti-caking agents and adjuncts.

Component	Mean	SD
Fat %	21.2	0.76
Total Solids %	51	1.1
Protein %	25.4	0.23
Galactose %	0.51	0.01
Lactose %	nd	-
NaCl %	1.9	0.18
ph	5.4	0.02

[1]n=3

Browning Determination

A number of color determination methods, including a Minolta colorimeter, spectrophotometer, and digital photographs were employed to analyze the color differences between treatments. L*a*b* values of the cheese were taken to quantitatively analyze the color of the cheese surface. The L*-value represents the degree of sample luminance or lightness on a scale of 0 to 100, with higher values representing lighter samples and lower values representing samples with a darker coloration. The a*-values represent the red to green spectrum and the b*-values represent the blue to yellow spectrum. Both a* and b* chromatic components are based on a scale of –120 to 120 (Papadakis et al., 2000). Overall color difference is determined using the calculated value, ΔE. The higher the ΔE, the greater the overall color change between the unbaked cheese and the baked cheese, therefore indicating a greater degree of browning.

The coloration differences between treatments (Table 4-3) demonstrate that there is typically a similarity in coloration between the control and cellulose treatments, which is different than the treatments that include potato starch with and without adjuncts. The colorimeter readings of L*-values for the control and cellulose treatments were 74 and 73, respectively, while the L*-values for the treatments containing potato starch treatments ranged from 64 to 68 indicating a darker surface. The digital image method produced lower L*-values readings than the colorimeter, but the cellulose and control treatments still had higher L*-values. The a*-values were lower in the control and cellulose treatment, indicating a more red surface than the remaining treatments.

The digital image data showed an overall color difference (ΔE) that was lower in the control and cellulose treatment, 29 and 26, respectively, than in the treatments with potato starch where the ΔE values ranged from 38 to 40. No conclusive differences were found between the treatments containing potato starch and adjunct compared to the potato starch treatment. One notable difference between the two methods is in the analysis of the ΔE values. The ΔE for the colorimeter method showed no statistical significance between treatments, while the ΔE for treatments from the digital image method had a lower variation and showed statistical difference.

The percentage of darkspots on the surface of the samples was calculated by the digital image software as the area which had an L*-value of less than 60. This measurement can give an indication of the amount of blistering on the cheese surface. The percentage of darkspots was highest for the treatment containing potato starch (45%) and the treatment of potato starch with the lactic acid adjunct (52%). Some of the adjunct treatments were not significantly different than the cellulose treatment as measured by percentage of darkspots. The adjunct that had the greatest effect on the reduction of darkspot formation was the shortening, which produced a sample with 37% darkspots. Still, the control contained only 17% darkspots and the cellulose treatment contained 28% darkspots, which is much lower than treatments with adjuncts. Since the percentage of darkspots was related to the distribution of the L*-value instead of the mean L*-value, slightly different statistical results were noted between the L*-value and ΔE measurement.

Spectrophotometric analysis of filtrate prepared from the treatments was analyzed at 420 nm to detect the amount of Maillard browning reaction products, thus indicating color change. The spectrophotometer method of color determination was determined to be unacceptable in this study for two reasons. Baked cheese proved to be very difficult to homogenize for the purpose of extracting the browning pigments. Also the baked cheese treated with anti-caking agents produced large variations in the turbidity of the filtrate for some of the treatments. The turbidity was apparently the effect of the starch and cellulose-based anti-caking agents.

Digital photographs the baked samples (Figure 4-1) demonstrate the degree of browning on the surface of each treatment. A higher degree of browning can be observed on the samples containing potato starch anti-caking agents when compared to the cellulose treatment and the control. Therefore, the quantification of browning as represented by ΔE closely mirrors the amount of browning found by visual observation. Other differences in the degree and pattern of browning also can be noted though visual observation of the surface of the treatments. The antifoaming agent adjunct appeared to increase the coloration of the blisters while decreasing the color of the surface where blisters did not form. This trend can be noted in both the potato starch samples with antifoaming agent and the combination of antifoaming agent and shortening added.

Table 4-3. Coloration determination by mean[1] L*-, a*-, and b*-values, color difference (ΔE), and percentage darkspots of baked Mozzarella cheese with various anti-caking agents and adjuncts for browning control.

Treatment[2]	Minolta Colorimeter				Digital Images[3]				
	L*[4] Value	a*[4] Value	b*[4] Value	ΔE[5]	L* Value	a* Value	b* Value	ΔE	% Dark-spots[6]
Control[7]	74^{a}	-5^{a}	39^{a}	22	67^{a}	-4^{b}	43^{b}	29^{b}	17^{c}
Cellulose[8]	73^{a}	-3^{a}	37^{a}	21	$64^{a.b}$	-3^{b}	31^{a}	26^{b}	$28^{b,c}$
Potato[9]	64^{c}	2^{a}	31^{b}	25	$60^{b.c}$	3^{a}	50^{b}	40^{a}	45^{a}
Potato + 0.05% Antifoam[10]	$66^{b,c}$	2^{a}	30^{b}	23	$62^{b,c}$	3^{a}	50^{b}	39^{a}	$37^{a,b}$
Potato + 0.05% Lactic Acid[11]	$65^{b,c}$	1^{a}	31^{b}	24	58^{c}	3^{a}	46^{b}	39^{a}	52^{a}
Potato + 0.025% Shortening[12]	$65^{b,c}$	0^{a}	29^{b}	23	$61^{b.c}$	2^{a}	478^{b}	38^{a}	$43^{a,b}$
Potato + 0.05% Antifoam/ 0.025% Shortening	68^{b}	0^{a}	30^{b}	21	$60^{b,c}$	3^{a}	46^{b}	38^{a}	$43^{a,b}$
SE	1.2	1.0	1.7	2.0	1.5	0.7	2.7	1.4	5.2

[1]n=3

[2]Adjunct(s) applied to cheese on a wt/wt basis of active ingredient

[3]Digital photographs analyzed with the histogram function in PhotoShop graphical software

[4]L*a*b* values are based on scales of 0 to 100, -120 to 120, and –120 to 120, respectively with color endpoint of dark to light, red to green, and blue to yellow, respectively.

[5]Color difference (ΔE) is based on the calculation of $((\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2)^{1/2}$ with darkest sample having highest values

[6]Percentage of sample surface with L*-value < 60.

[7]Control – no anti-caking agent

[8]Cellulose – powdered cellulose applied to cheese at 2% wt/wt

[9]Potato – Unmodified potato starch applied to cheese at 2% wt/wt

[10]Antifoam – antifoaming agent, dimethylpolysiloxane

[11]Lactic acid – as calcium lactate

[12]Shortening – spray dried partially hydrogenated sunflower oil

[abc]Means in columns with different superscripts are significantly different at $p<0.05$

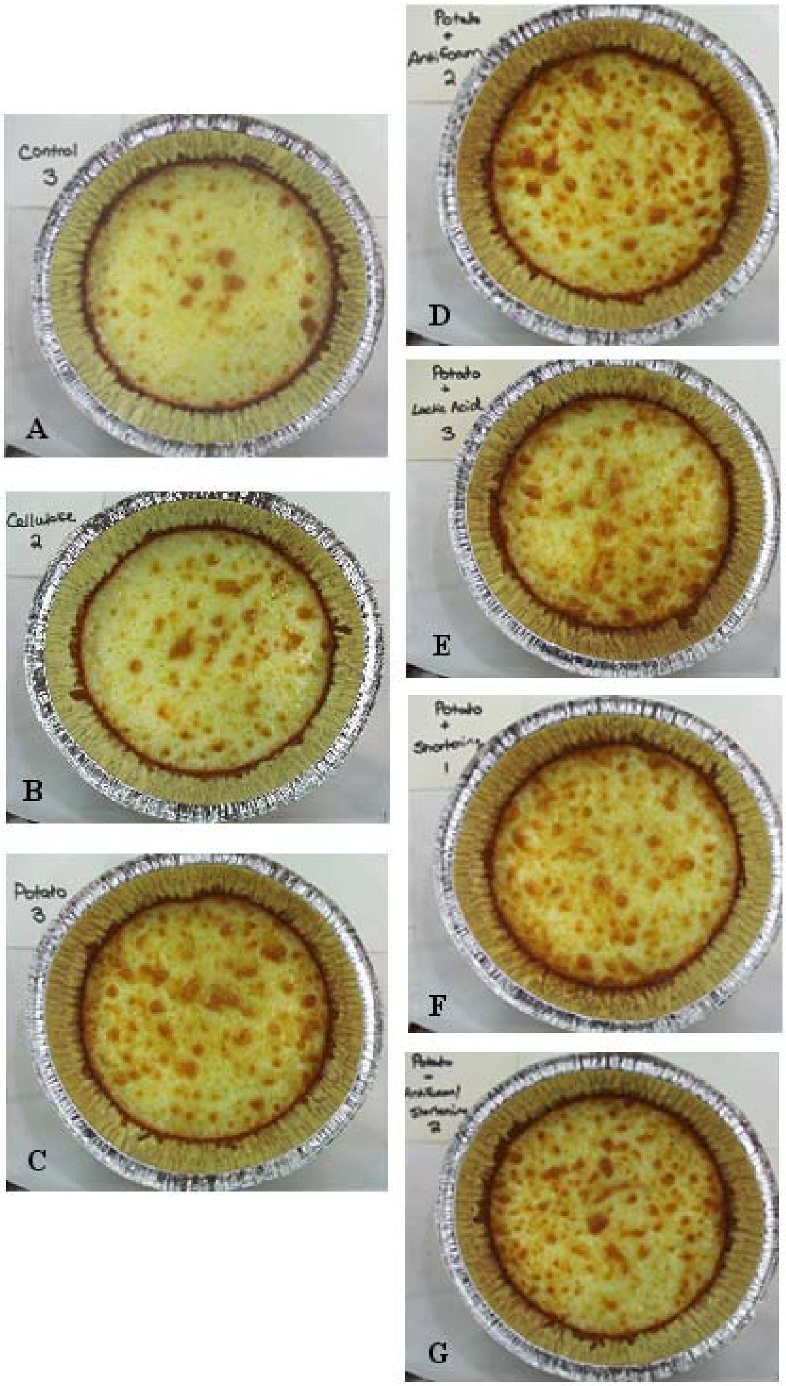

Figure 4-1. Appearance at room temperature of low fat part skim Mozzarella cheese after baking (232°C for 5 min) with no treatment (A), 2% (wt/wt) cellulose anti-caking agent (B), 2% potato starch anti-caking agent (C), 2% potato starch anti-caking agent + 0.05% antifoaming agent (D), 2% potato starch anti-caking agent + 0.05% lactic acid (E), 2% potato starch anti-caking agent + 0.025% spray dried shortening (F), 2% potato starch anti-caking agent + 0.05% antifoaming agent + 0.025% spray dried shortening (G).

Analysis of Physical Changes

Moisture loss of the cheese during baking was measured to determine the degree to which the anti-caking agent treatment would hinder evaporation of water from the cheese surface. Moisture loss on the surface of the cheese shred has been associated with the formation of a skin that leads to entrapped steam formation blisters that will brown excessively (Rudan and Barbano, 1998). All treatments lost a significantly lower percentage of water than the control, which lost 19.2% moisture during baking (Table 4-4). The cellulose treatment lost 18.1% moisture, and 16 to 17% moisture was lost with the treatments containing potato starch. Since both potato starch and cellulose exhibit the ability to bind water, the amount of evaporation would be expected to be lower than the control. Potato starch appears to entrap more water than cellulose during baking, thus reducing the percent moisture loss. Overall, the moisture loss values reported were much lower than those reported by Rudan and Barbano (1998) in LMPS Mozzarella cheese under similar baking conditions. The control cheese in that study was reported to have lost 27.9% moisture during baking compared to the 19.2% lost in this study. These differences may be attributed to the addition of the insulating mat under the cheese during baking to better simulate the conditions of cheese baked on a pizza.

Two adjuncts, lactic acid and shortening, significantly reduced the moisture loss potato starch. Shortening may have reduced the uptake of water by coating the surface of the potato starch with a hydrophobic material, thus blocking some water from being absorbed by the starch granule. Rudan and Barbano (1998) found that there was no change in moisture loss between LMPS Mozzarella cheese treated with vegetable oil and a control LMPS Mozzarella cheese sample, supporting the assumption that the hydrophobic material interacts with the potato starch to prevent moisture loss. The effect of lactic acid may have been due to chemical cleaving of the starch molecule. Reported changes in the physical properties of acid-modified starch include lower granule swelling during gelatinization and lower gel viscosity (Snyder, 1984). The combination of the antifoaming agent and shortening adjuncts did not increase moisture loss suggesting that the effect of the antifoaming agent blocked the ability of shortening to increase moisture loss. The antifoaming agent, dimethylpolysiloxane, is a hygroscopic chemical and thus would not be expected to bind water.

Water activity is a measure of the ratio between the water vapor pressure exerted by the food and the water vapor pressure of pure water (Fox and McSweeney, 1998). Water activity measurements were taken at day 0, 1, and 7 after shredding and packaging of cheese (Appendix Table 3). No differences were noted between treatments on the three days measurements were taken. Water activity before and after baking was also measured to determine the change in the water activity (ΔA_w) for each treatment. Differences in the ΔA_w were noted with the lowest reduction in water activity from baking resulting from the cellulose treatment (-0.06). All other treatments had a significantly higher water activity reduction in the range of –0.09 to –0.08 except for the potato starch/shortening treatment with a ΔA_w of –0.07, which was not significantly different from any of the treatment. Although differences among treatments were found there was no correlation between the change in water activity and the differences in the browning between the treatments. The cellulose treatment may have a lower change in water activity after baking because although more moisture was lost than the potato starch samples, the water may not be bound by cellulose as with potato starch and may be free to exert a vapor pressure.

Table 4-4. Mean values[1] for moisture loss and water activity change (ΔA_w) after baking of low moisture part skim Mozzarella cheese with anti-caking agents and adjuncts for browning control.

Treatment[2]	% Moisture Loss	ΔA_w [3]
Control[3]	19.2[a]	-0.09[a]
2% Cellulose[4]	18.1[b]	-0.06[b]
2% Potato[5]	16.2[d]	-0.09[a]
2% Potato + 0.05% Antifoam[6]	16.1[d]	-0.08[a]
2% Potato + 0.05% Lactic Acid[7]	16.8[c]	-0.08[a]
2% Potato + 0.025%Shortening[8]	16.7[c]	-0.07[a,b]
2% Potato + 0.05% Antifoam/ 0.025% Shortening	16.3[d]	-0.08[a]
SE	0.13	0.006

[1]n=3
[2]Starch and cellulose applied on a wt/wt basis; adjunct(s) applied to cheese on a wt/wt basis of active ingredient
[3]ΔA_w – difference in water activity between unbaked and baked treatments
[3]Control – no anti-caking agent
[4]Cellulose – powdered cellulose
[5]Pot – unmodified potato starch
[6]Antifoam – antifoaming agent, dimethylpolysiloxane
[7]Lactic acid – as calcium lactate
[8]Shortening – spray dried partially hydrogenated sunflower oil
[abcd]Means in columns with different superscripts are significantly different at $p<0.05$

The correlation between color formation and physical changes of the treatments was analyzed by regression analysis. A significant correlation was found between moisture loss and many of the measurements of color determination. The relationship between the Minolta colorimeter L*-, a*-, and b*-values and moisture loss produced R^2 values of 0.60, 0.63, and 0.63, respectively. The correlation between the digital image data and moisture loss was highest for the ΔE (R^2=0.61). The observation that an increase in water loss decreases the amount of browning during baking on the surface of the cheese is consistent with earlier findings in this study (Chapter 3). The cause of excessive browning appears to be due to impedance of water out of the cheese during baking, thus inhibiting evaporative cooling. The higher temperatures cause an increase in the amount Maillard browning. No correlation was noted between the change in water activity and any of the color measurements.

CONCLUSIONS

The addition of adjuncts for the intent of lowering the browning of shredded LMPS Mozzarella cheese coated with a potato starch anti-caking agent were ineffective at lowering the browning to a level produced with the use of cellulose as an anti-caking agent. The adjuncts used in this study were antifoaming agent, calcium lactate, and shortening, as well as a combination of shortening and antifoaming agent. Mozzarella cheese treated with cellulose-based anti-caking agents is the standard in the pizza industry. Since none of the adjuncts produced the ability to decrease the levels of browning on Mozzarella cheese treated with potato starch anti-caking agent to that found with cellulose anti-caking agents, these adjuncts would not be effective in a potato starch anti-caking agent blend.

A significant correlation between moisture loss and measures of browning demonstrate the addition of adjuncts the anti-caking agent did not drastically change the relationship between moisture loss and the subsequent amount of evaporative cooling and the color formation on the surface of the cheese.

Future research on the use of additional adjuncts that may effect the browning of Mozzarella cheese treated with starch-based anti-caking agents during baking is suggested. The modification of the starch molecules through chemical and physical processes to control water uptake could also show a significant impact on the browning of the cheese.

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APPENDIX

Table A-1. Mean water activity values[1] (A_w) during 4°C storage of low moisture part skim Mozzarella cheese treated with various anti-caking agents.

Anti-caking agent[2]	Day 0	Day 1	Day 7
Control[3]	0.97[a]	0.96	0.97[a]
100 % cellulose[4]	0.96[b,c]	0.96	0.97[b,c,d]
80% cellulose/ 20% dextrose[5]	0.96[c]	0.96	0.96[d]
100% potato[6]	0.96[c]	0.96	0.96[d]
80% potato/ 20% dextrose	0.97[a,b]	0.96	0.97[a,b]
Blend A[7]	0.96[b,c]	0.96	0.97[c,d]
Blend B[8]	0.97[a]	0.96	0.97[a,b,c]

[1]n=3
[2]Applied to cheese at 2% wt/wt
[3]Control – no anti-caking agent
[4]Cellulose – powdered cellulose
[5]Dextrose – anhydrous dextrose
[6]Potato – Unmodified potato starch
[7]Blend A – 68% potato starch/ 20% dextrose/ 12% cellulose
[8]Blend B – 88% potato starch/ 12% cellulose
[abcd]Means in columns with different superscripts are significantly different at $p<0.05$

Table A-2. Mean water activity values[1] (A_w) during 4°C storage of low moisture part skim Mozzarella cheese treated with various anti-caking agents and starches.

Treatment[2]	Day 0	Day 1	Day 7
Control[3]	0.97	0.97^a	0.97^b
Powdered cellulose[4]	0.97	0.97^a	0.97^b
Potato starch	0.97	0.97^a	0.97^a
Wheat starch	0.97	0.97^b	0.97^b
Corn starch	0.97	0.96^b	0.97^b
Rice starch	0.97	0.97^b	0.97^b

[1]n=3
[2]Applied to cheese at 2% wt/wt
[3]Control – no anti-caking agent
[4]Cellulose – powdered cellulose
[ab]Means in columns with different superscripts are significantly different at $p<0.05$

Table A-3. Mean water activity values[1] (A_w) during 4°C storage of low moisture part skim Mozzarella cheese treated with anti-caking agents and adjuncts for browning control.

Treatment[2]	Day 0	Day 1	Day 7
Control[3]	0.96	0.96	0.95
Cellulose[4]	0.96	0.95	0.95
2% potato[5]	0.95	0.96	0.95
2% potato + 0.05% antifoam[6]	0.97	0.96	0.95
2% potato + 0.05% lactic acid[7]	0.96	0.96	0.96
2% potato + 0.025% shortening[8]	0.96	0.95	0.95
2% potato + 0.025% shortening/ 0.05% antifoam	0.97	0.96	0.95

[1]n=3
[2]Starch and cellulose applied to cheese on wt/wt basis; adjunct(s) applied to cheese on a wt/wt basis of active ingredient
[3]Control – no anti-caking agent
[4]Cellulose – powdered cellulose
[5]Potato – Unmodified potato starch
[6]Antifoam – antifoaming agent, dimethylpolysiloxane
[7]Lactic acid – as calcium lactate
[8]Shortening – spray dried partially hydrogenated sunflower oil

VITAE

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