IMPACT OF HEATING RATE ON STARCH GRANULE STRUCTURE AND FUNCTIONALITY

A Thesis in

Food Science

by

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ABSTRACT

The quality and shelf life of baked products is affected by the time and temperature of the baking process. In this study, dough was baked at 219 ºC by using different ovens (conventional, impingement or hybrid) and with different dough weight (520g or 80g) for varying times. During baking the temperature profile at the dough center was recorded. The texture, thermal properties and pasting characteristics of baked products with reference to baking conditions were investigated. Small breads baked in the hybrid oven had the highest heating rate (25.1 ºC/min) while large breads baked in conventional oven had the lowest heating rate (6.0 ºC/min). When data were evaluated as a function of heating rate in this study, the enthalpy of amylopectin recrystallization, rate of bread firmness development and the amount of soluble amylose were lower at the slower heating rate. The differences observed in product firmness following storage are potentially a consequence of the extent of starch granule hydration, dispersion and the extent of amylose reassociation; all of which are affected by the heating rate during baking.

Structural attributes of the baked goods are mainly determined by the gelatinized starch granules, which form the basis for the second study. The changes in starch granule hydration and dispersion were followed visually by using a hot stage microscopy and at a molecular level by using the differential scanning calorimetry (DSC). Hot stage microscopy revealed changes in starch granule morphology and size during heating at
either 5 or 25 °C/min when monitored continuously. The results showed that granule morphology was different as a function of the heating rate and granule swelling was governed kinetically. These observations visually demonstrated the significant influence of processing conditions, i.e., heating rate, on starch granule size and morphology; and therefore potentially have implications in determining structure and texture of baked products.

The changes observed visually in starch granules indicate the potential difference in the gelatinization process of the starch granules. The visual changes observed by microscopy were further investigated using the DSC at molecular level. Differential Scanning Calorimeter tracked the processes of starch gelatinization and retrogradation at molecular levels in terms of peak temperature and enthalpy of endothermic events associated with gelatinization as well as retrogradation. The effect of heating rate on baked product structure, texture and firmness development following storage has been reported. However, the differences in the mechanistic processes occurring during starch gelatinization, as a function of heating rate, are unclear. The objective of this study was to investigate the effect of heating rate at different moisture contents on starch retrogradation and gelatinization processes. Starch suspensions at a water: starch ratio of 0.7 or 2.0 were heated by using a DSC at heating rates between 5 °C/min and 40 °C/min for the retrogradation study. The thermal profiles were evaluated, as a function of heating rate, and the retrogradation behavior following storage were also determined. The effect of heating rate was not evident on the retrogradation behavior of starch suspensions at either moisture content. To determine the effects of heating rate on starch-water
interactions, starch suspensions at a water:starch ratio ranging from 0.7 to 3.0 were heated at 5, 15 or 25 °C/min by using a DSC to different final temperatures and rescanned. The deconvoluted G and M1 endotherms and the corresponding additional unfrozen water (AUW) were determined. The results showed that the G and M1 endotherms merged at higher heating rates and at higher moisture contents. A significant interaction was observed between moisture content and heating rate demonstrating that the gelatinization process was governed by moisture content at the lower heating rates and by heating rate at the higher heating rates. Results from the AUW data suggest that the M1 component of gelatinization dominated at lower moisture content and lower heating rates. However, at higher moisture contents, an interaction was observed between moisture content and heating rate. The data suggest that at higher moisture content and at higher heating rate, there is still a kinetic limitation to the complete melting of the M1 endotherm. All these results support the premise that baking process can be a potential tool in developing the baked product quality and shelf life.
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Chapter 1

Introduction

1.1 Baking Industry

The present-day baking industry is a multi-billion dollar business. Two specific trends getting market attention at the present time are the increased popularity of artisan breads and the use of breads in the food service area. Buns and rolls are used in millions per day by major food service companies (burger and sandwich chain stores). Therefore, significant attention is being paid to increasing the shelf stability, even by small margins.

The workhorse of the baking industry is the oven, which was originally made of clay-brick. In the past, wood or coal was the main source of fuel for oven. Modern ovens are fueled by gas or electricity. With increasing mechanization of different stages of dough handling and baking process, different oven types became available such as the deck, rack, or reel oven which helps with large scale production. Today innovative technologies are also used in food service sector where baked goods are served efficiently using either Jet impingement oven or hybrid (Jet Impingement and Microwave combination - JIM) oven combining impingement and microwave heating technologies. These newer technologies assist the food industry and consumers in the creation of better quality products, as well as in the establishment of energy efficient processes and improved control of existing processing operations.
Consumers typically rely on touch or squeeze to determine the quality of baked goods before purchase. This perception of quality by the consumer measures the textural attributes of product. Baking in general is the conversion of raw dough into baked product with a characteristic texture and the texture development occurs in the oven. The dough experiences numerous changes during baking which result in desired finished product quality. Application of innovative heating technologies in baking is limited because the relationship between different heating regimes and the quality of finished product is not clear. One such example is microwave heating, which is an energy and cost efficient process. However, the products baked with microwave generally lack the brown crust formation, which is the main contributor to flavor of baked products, and have toughness, which is an undesirable quality attribute (Sumnu, 2001). Two novel processes jet impingement baking and hybrid baking (Jet Impingement Microwave combination - JIM) are popular in the baking industry. Impingement ovens are successfully used in food service sector for preparing various baked products especially pizza, tortilla, and various flat breads in front of consumer, though for large size products it is not suitable. JIM ovens are becoming popular at the household level and special applications such as space travel. JIM oven technology offers significant potential applications for a broad array of baked food products. Understanding the conventional baking process and changes in dough as baking progresses in conjunction with insight into the mechanism of heating using these novel technologies is essential in successful application of novel baking technologies.
While numerous studies have investigated the development of structure in baked products and applied principles of polymer sciences in their interpretations, very few have investigated sequential changes to polymers during varying baking processes, i.e., different temperature profiles or have linked the impacts of the various structures established during baking to product quality and functionality post-baking. The numerous physico-chemical changes that occur during baking have not been specifically characterized or investigated with respect to the baking process, i.e., heating and cooling regime during baking and the desired quality in finished product.

Thus, understanding the impact of different heating conditions on starch transformation and associated changes in the properties is very critical to control and predict the final product quality. Further, baking conditions provides opportunity to develop new product textures through the use of novel technologies.

1.2 Research Problem

This proposed study is aimed at providing the basic groundwork for a long-term study to develop improved baking processes to enhance shelf stability of baked products. The success of the strategy is dependent upon understanding and characterizing the structural and thermo-mechanical changes that occur in a product matrix, i.e., the matrix of starch and gluten during baking and the post-baking process. Thus, product shelf stability can be significantly enhanced if the processing parameters could be modified to enable “stable” structures in products.
However, further basic research is required to realize these potential benefits. Therefore the fundamental experimental goals of this project are to elucidate the practical importance of the baking process in a baked product, e.g. bread, which is widely accepted by the researchers and characterize the baking conditions for subsequent study.

Starch being a major component in most of the baked products, the broad goal of this research project was to understand the transformation and associated changes in its properties under varying baking conditions.

The research can be followed logically as hypotheses and objectives for each hypothesis as listed below.

**Hypothesis 1**

Different baking conditions do not affect starch properties and the texture as observed by firmness of baked products following baking.

**Objective 1.1**

To record the thermal profiles experienced by dough during baking under different conditions and characterize the thermal profile for comparison of different processes.
Objective 1.2
Determine the effects of different baking conditions on the physico-chemical properties of bread crumbs.

Hypothesis 2
Changes to starch granule swelling and morphology during heating are independent of heating rate.

Objective 2.1
To determine starch granule swelling and morphology at different heating rates using hot stage microscopy.

Hypothesis 3
Starch gelatinization, unfrozen water content following gelatinization, and retrogradation, as measured by using a Differential Scanning Calorimeter (DSC), are independent of heating rate.

Objective 3.1
To determine the effects of heating rate on starch gelatinization.

Objective 3.2
To determine the effects of heating rate on the additional unfrozen water content following partial and complete gelatinization of starch.
Objective 3.3

To determine the effects of heating rate on starch retrogradation.

1.3 Organization of Dissertation

The first chapter of the thesis deals with a concise introduction of the research and its relevance to the baking industry. The chapter concludes with listing the problem, hypothesis, and the objectives for the research.

The second chapter presents a review of the literature on various aspects covered in this research including baking technologies, starch gelatinization and staling.

The third chapter presents the practical aspect of this research; it prepares the ground for the research project based on the relationship between the textural properties and baking process by baking breads by using different ovens and thermal profiles.

The fourth chapter highlights the differences in starch gelatinization process at various heating rates with respect to starch granule swelling and granular morphology as observed under microscope.
The **fifth chapter** explores the differences in starch gelatinization process as observed by DSC when heated at different heating rates. Starch retrogradation is also reported following different heating rate treatments.

The **sixth chapter** discusses and summarizes the observations from the previous three chapters.

The **seventh chapter** puts forward a list of ideas and aspects for future research in this area.
Chapter 2

Review of Relevant Research

2.1 Baking Process

Food industry depends heavily on heating and cooling operations to convert raw ingredients into desired finished products. Though, both operations are useful in imparting quality and serve to preserve products, heating operations are widely applied to bring about desired structural transformations in products. Many cultures around the world have cereal-based products as a part of their meal made from wheat, rice, or corn that is prepared by heating. Preparation of a typical cereal-based product involves heating followed by cooling, and the intensity of heat/cool treatment varies with the desired attributes of a particular product.

The term ‘baking’ generally refers to the collective process of making dough, fermentation, and heating in an oven. It was considered an art in earlier times and with advances in science, the basic principles underlying different stages are now better understood. A key unit operation that normally brings about the desired transformation of raw materials into finished product is the final stage of baking, i.e., heating and cooling. Over the years, research has aided in better understanding the effects of heating and subsequent cooling on major components of cereals, especially starch.
Many researchers have studied the effects of heating on the rheological properties of dough during baking (Bloksma and Nieman, 1975; Bloksma, 1980). Bloksma (1980) investigated the influence of heating on rheological properties of dough during baking. These tests either utilized the difference between initial and final temperatures of dough during baking or temperatures up to starch gelatinization since it is the major change that brings about conversion of dough into a structured baked product. The actual thermal profiles experienced by dough during baking have also been investigated by few researchers (Audidier 1968, Martin et al., 1991, Giovanelli et al., 1997, Kusunose et al., 1999) and has been used to understand the whole gamut of physical and biochemical changes taking place during baking in an oven.

Audidier (1968) described the different processes that take place during baking as thermal kinetics and thermal weight loss kinetics. Different biochemical and physicochemical reactions, including starch breakdown by amylases, starch gelatinization, and protein coagulation, take place within characteristic temperature ranges. The kinetics of these reactions are dependent on the thermal kinetics of baking, i.e., temperature of dough during heating as well as cooling. Swortfinger (1968) prepared the baking map, wherein the temperature experienced by dough was plotted as a function of baking time and different changes were identified on the map (Figure 2.1).

As the temperature increases above 40°C the yeast activity increases and more gas is produced. The gas production stops due to yeast inactivation above 63°C. Carbon dioxide
gas is fully released and thermal expansion takes place resulting in gas cell formation resulting in maximum expansion of dough. Starch and protein are swollen and a slight hint of brown crust formation is evident.

Fig 2.1: Typical baking map indicating various stages of baking as a function of baking time and temperature of dough

A further increase in temperature (75-80 °C) results in complete gelatinization of starch, leading to continuous starch structure and coagulation of protein providing network for starch structure. These changes in starch and protein lead to crumb structure setting and inhibit further expansion. Evaporation of water also increases at higher temperature and is at a maximum, since the crust is not completely formed at this stage of baking. As the
temperature reaches above 90 °C, the time-temperature plot becomes asymptotic and the crust forms due to Maillard reaction that also provides flavor to product. The stages of baking could be described as expansion stage (below 75 °C), evaporation and setting stage (75-90 °C) and finishing stage (above 90 °C).

### 2.2 Baking Ovens

Baking ovens could be divided into two classes: conduction oven, i.e., heat is transferred by contact with hot surface and, convection oven, i.e., heat is transferred by the circulating hot air. These two categories could be used to classify a majority of the ovens used in industry based on conventional baking technologies. With novel technologies, non-conventional processes have also become popular; for example the jet impingement oven, hybrid oven (jet impingement with microwave (jim), microwave oven, or the electric resistance oven (ERO). With the newer heating technologies it is possible to achieve higher efficiency in the baking operation. While the non-conventional technologies provide faster and energy efficient operations, the temperature changes experienced by products are different from that observed during conventional baking. These ovens individually or in combination provide better practical control of the temperature profile of dough during baking over that of conventional baking.
2.2.1 Jet Impingement Oven

The jet impingement oven is a type of convection oven where high velocity jets of hot air are directed over the entire product surface to be baked. It is efficient due to a higher rate of heat transfer and moisture removal leading to reduced baking time and increased throughput. Several authors have investigated the heat and mass transfer phenomena to evaluate the baking process (Gardon and Akfirat, 1964, 1965; Braud et al., 2001; Nitin and Karwe, 2004; Olsson et al., 2004). Implications of the modified heating technique were reported to be improved quality perception of finished product as well as increase in shelf-life (Walker, 1987; Walker and Sparman, 1989; Yin and Walker, 1995; Li and Walker, 1996; Ovadia and Walker, 1998). One limitation of this technology is that quick crust and color development might lead to an under-baked center especially in the case of larger sized products.

2.2.2 Microwave Ovens

Heating in a microwave oven is achieved by the absorption of electromagnetic energy waves by polar molecules; mainly water and polar lipid molecules in typical baked products. Microwave ovens have been successfully used at the household level for general heating purposes, but its application in the baking industry is restricted due to toughness and rubbery texture of microwave baked products (Rogers et al., 1990; Shukla, 1993). Ni et al. (1999) reported migration of moisture from inside to surface, which might be the cause of surface sogginess or rubbery texture. They suggested addition of hot air or infrared heating as a means to avoid the quality problems of rubbery texture in
microwave oven baked products. Microwave ovens are still not widely used for baking operations.

2.2.3 Hybrid / Jet Impingement and Microwave Ovens

The limitations of jet impingement ovens and microwave ovens were overcome upon by combining the two technologies. Rapid temperature increase in the center due to microwave heating eliminates under baking and sogginess is eliminated by the rapid evaporation of moisture from the surface with the formation of a moisture impervious crust. The potential of this technology was illustrated empirically (Walker, 1993).

2.2.4 Electric Resistance Oven

In electric resistance ovens the heat is generated internally by using the dough as the resistance between the electrodes carrying alternating current. Baker and Mize (1939) applied voltage across a small piece of dough and simulated baking behavior in dough to study changes in the physical properties of dough during baking. Though the procedure was adopted by a few researchers, it was used for small pieces of dough until Hoseney and coworkers developed a larger device to bake practical sized loafs (He and Hoseney, 1991; Junge and Hoseney, 1981; Moore and Hoseney, 1986). In their extensive research work using ERO, they characterized the oven for dough temperature increase as a function of different voltage applied, resistance (Ohm) of dough during baking, and CO₂ released during baking. They presented a strong case for use of ERO in understanding the
baking process. Though the advantages of resistance baking in terms of improved shelf life was reported by Martin et al. (1991), the rationale and causes for these improvements were not studied.

2.3 Baking Parameters

Studies on bread quality and shelf life in the past have used different parameters in terms of baking temperature, time and weight of the breads (Table 2-1). Shogren and Finney (1984) standardized a baking test using 10 g flour and compared with 100g flour (~170 g dough) baking test; Walker and Li (1993) baked a number of products in different ovens and reported different time-temperature conditions to obtain acceptable products. Baik and Chinachoti (2000, 2001, 2002) conducted their investigations using breads baked in a bread machine that were baked for 50 min at 160 °C. Thorvaldsson and Skjoldebrand (1996) conducted their studies on larger sized bread loaves (~ 550 g dough). These differences in the heating methods as well as sample weight finally result in different temperature profile experienced by the dough during baking. These products baked under different conditions are difficult to compare unless the temperature profile characterizing the baking process provides the common platform for such comparisons. Starch gelatinization is a kinetic process occurring under non-equilibrium conditions (Levine and Slade, 1990; Slade and Levine, 1993; Shiotsubo and Takahashi, 1984). Therefore understanding the process of gelatinization and relating it with the temperature profile of the dough during baking is a critical step.
Table 2-1: Baking parameters used in different studies

<table>
<thead>
<tr>
<th>Study</th>
<th>Temperature-Time (°C – min)</th>
<th>Weight (g)</th>
<th>Oven description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Baik and Chinachoti, 2001</td>
<td>160 – 50</td>
<td>356.74</td>
<td>Automatic bread making machine (Panasonic)</td>
</tr>
<tr>
<td>Hug-Iten et al., 1999</td>
<td>220 – 35</td>
<td>600</td>
<td>Ventilated oven (Blodgett Co. Inc.)</td>
</tr>
<tr>
<td>Martin and Hoseney, 1991</td>
<td>219 – 25</td>
<td>~500</td>
<td>Reel oven</td>
</tr>
<tr>
<td>Thorvaldsson and Skjoldebrand, 1998</td>
<td>225 – 35</td>
<td>592.5</td>
<td>Conventional oven (Heraeus GmbH)</td>
</tr>
<tr>
<td>Shogren and Finney, 1984</td>
<td>219 – 18/24</td>
<td>10/100</td>
<td>Conventional oven</td>
</tr>
</tbody>
</table>

An extensive listing of varying baking conditions is also presented in appendix A

2.4 Gelatinization Process

Starch, when heated in presence of water, undergoes irreversible changes that are dependent on the amount of water and heat available in the system. Thomas and Atwell (1999) described gelatinization and pasting as distinct stages of change during heating of starch, i.e., thermal processing. The first set of changes during heating are termed as gelatinization and is characterized by the irreversible disruption of molecular order depending on temperature and moisture, and the initial increase in granule size resulting in increased suspension viscosity. These changes render part of the material in granule soluble following heat treatment and thus contribute to food properties such as texture, viscosity, and moisture retention. When a majority of the granules have undergone these changes, the starch is considered “pasted”. Thus, pasting is the phenomenon following
gelatinization. It involves granular swelling, exudation of molecular components from granule, and eventually total disruption of granules (Atwell et al., 1988). The subsequent changes that occur following gelatinization and pasting during storage are termed as retrogradation, where starch polymers in the solubilized starch fraction and the remaining granular fragments re-associate imparting firmness to the gel. The above definitions of the gelatinization process are based on macromolecular level observations in terms of starch-water paste viscosity and gel firmness, which are manifest as a consequence of gelatinization.

2.5 Theories explaining the Gelatinization Process

The above mentioned empirical terms do not elucidate the gelatinization process at molecular level in terms of changes in molecular arrangement in starch granule during gelatinization. Donovan (1979) using a DSC, proposed a model for gelatinization. In this model, the crystalline order of semicrystalline granule is destroyed by stripping of chains from surface of crystallites due to swelling of the amorphous region of the granule. Under excess moisture conditions (≥ 2:1 water:starch) this swelling driven process generated a single DSC endotherm (referred to as G), which is replaced by two endotherms (referred to as G and M1) as moisture decreased from 2:1 (water:starch) to 0.7:1. The M1 endotherm is suggested to be the result of insufficient water for all the crystallites to be disrupted by stripping. Partial disruption of crystallites in the region of locally high moisture gives rise to G endotherm and those remaining undergo melting process at higher temperatures giving rise to the M1 endotherm. This explanation is consistent with
the observations of granule swelling and loss of birefringence associated with gelatinization that supports amorphous region swelling and crystalline order loss respectively.

Based on the same fundamentals of polymer science three other models were proposed which differ in various key features attempting to explain the gelatinization process at a molecular level. Blanshard (1987) suggested the reinterpretation of G and M1 endotherms. Polymer chain mobilization in amorphous regions causes the G endotherm. In excess water, this lead to the gross swelling of granules and the crystallite disruption process as proposed by Donovan. However, in limiting water systems, swelling had little effect on crystallites, which therefore melt at higher temperatures generating M1 endotherm. However, more recent studies (Waigh et al., 2000a, b; Jenkins and Donald, 1998) on the disruption of granular crystallinity during gelatinization suggest that crystallinity is lost throughout both G and M1 endotherms, and contradicts the above theory.

Another approach based on the observation of very narrow temperature ranges for loss of birefringence of an individual granule was proposed by Evans and Haisman (1982). They explained gelatinization process in a single granule as a highly co-operative ‘positive feedback’ mechanism. In excess moisture conditions, they postulated that melting of the least stable crystallite within a granule removed some swelling constraint, allowing granule to absorb more water which in turn lowered melting point of remaining crystallites; thus starting a cyclic process of water absorption and partial melting of
crystallites occurring rapidly within narrow temperature range. In the case of limited water systems, the cooperative melting of different crystallites is restricted; consequently the remaining crystallites melt at a higher temperatures generating M1 endotherm. However, the assumption of crystallite melting as a starting point of gelatinization is not supported by the observation of loss of birefringence associated with onset of gelatinization (Cooke and Gidley, 1992).

Biliaderis (Biliaderis et al., 1986; Biliaderis, 1991) proposed the gelatinization process as a combination of simultaneous melting and recrystallization process depending on the heating rate and temperature of the system. At higher heating rates the G and M1 endotherms merged due to insufficient time available for recrystallization. In excess moisture, the bulk amorphous phase undergoes glass transition whereupon melting and recrystallization processes could occur simultaneously. However, in limiting moisture conditions the difference between glass transition and melting temperatures increased resulting in G and M1 endotherms. However, this theory is contradicted by the absence crystallinity by X-ray studies on partially gelatinized starch in limited water (Liu et al., 1991; Zobel et al., 1988).

Donald and coworkers (Donald, 2001; Waigh et al., 1999; Waigh et al., 2000a, b) proposed a liquid crystalline approach based theory using the analogy of a chiral side-chain polymeric liquid crystal structure. Depending on the moisture content, the phase transitions were described as smectic to smectic+gel in excess water conditions (moisture > 60%), whereas an intermediate stage was expected under limited water condition. The
intermediate structure was nematic for B type starch and isotropic for A type starch (Waigh et al., 2000a). However, under low moisture conditions, the intermediate phase is absent and glassy to amorphous stage transitions is observed. Two levels of molecular organization are observed in starch, i.e., double helical arrangement of two end chains sharing a common branch point and association of such double helices in ordered lamellae. These two structures are disordered at specific temperatures \( T_{ss} \) (dissociation of the helices side-by-side) and \( T_{hc} \) (helix to coil transition). In excess moisture condition \( T_{hc} < T_{ss} \), thus dissociation of helices side-by-side is immediately followed by helix coil transition (Fig. 2.2). For limited moisture conditions the intermediate step depends on type of starch. For A type starch the transition follows from smectic \( \rightarrow \) isotropic \( \rightarrow \) gel (Fig. 2.3), whereas for B type starch the transition follows from smectic \( \rightarrow \) nematic \( \rightarrow \) gel (Fig. 2.4). The intermediate stage does not appear at low moisture where glassy stage is directly converted to amorphous stage (Fig. 2.5).

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![Diagram](image.png)

**Fig 2.2**: Two stage process involved in the gelatinization of starch in excess water \( (T_{hc} < T_{ss}) \) (Waigh et al., 2000a)
Fig 2.3: Three-stage process involved in the gelatinization of A type starch in limited water ($T_{ss} < T_{hc}$) (Waigh et al., 2000a)

Fig 2.4: Three-stage process involved in the gelatinization of B type starch in limited water ($T_{ss} < T_{hc}$) (Waigh et al., 2000a)
The liquid crystalline approach proposed by Donald and coworkers (Donald, 2001; Waigh et al., 1999; Waigh et al., 2000a, b) is widely accepted at present and it explains the transitions during gelatinization at a molecular level. This review of proposed theories highlights that even though we are able to understand the gelatinization process better with recent models based on fundamentals of polymer science, more research is needed to solve questions posed by the present research and to explain the contradictions to existing models.
2.6 Staling

2.6.1 Staling of Baked Products

Staling is a complex phenomenon involving textural and sensory changes in both crust and crumb, and it generally results in decreased consumer acceptance of baked products (Lineback, 1991). Most of the baked products undergo quality deterioration during storage because of either microbial spoilage or staling. This review covers, in brief, staling and the biophysical characterizations associated with it. Bechtel et al. (1953) described the staling process as “a term, which indicates decreasing consumer acceptance of bakery products caused by changes in crumb other than those resulting from the action of spoilage organisms.” Staling can be described based on different quality changes that take place during storage of baked products including crumb-firming, crust staling, and organoleptic staling (Kulp and Ponte, 1981). Consumers mostly use the squeeze test and recognize the staling by increasing crumb firmness. Thus, crumb firming is the most researched aspect of staling. Early research on the subject of staling has been extensively reviewed by Maga (1975) and an excellent compilation of different aspects of staling and different mechanisms proposed were presented. Further, based on new analytical techniques, a large body of work is present on staling which can be seen from reviews by Hebeda and Zobel (1996), Chinachoti and Vodovotz (2000), and Gray and Bemiller (2003). Mechanisms governing staling are still not fully understood as it involves many physical and chemical phenomena such as change in texture (Robertson and Emami, 1974; Fessas and Schiraldi, 1998), water migration (Willhoft, 1971; He and Hoseney, 1990; Martin et al., 1991; Zanoni et al., 1993), starch crystallization (Hoover et al., 1994;
2.6.2 Staling Mechanism and Staling Theories

The theories of staling are proposed and analyzed based on the understanding of baked product system. Staling of bread is the cumulative manifestation of many changes in bread crust and crumb. Mostly consumers notice the force needed to squeeze the loaf, which reflects the firmness of crumb. Crumb firming was initially believed to be mainly caused by moisture loss from the loaf but Boussingault demonstrated early in 1852 (Maga, 1975) that the phenomenon of staling was not specifically due to an overall loss of moisture from product since bread kept in a moisture-proof container underwent normal staling and it could be freshened by heating the product above 60 °C. Further, it was demonstrated conclusively that moisture migration from crumb to crust also played important role in staling of crumb as well as crust (Bechtel et al., 1953). The work of Baker and Mize (1939), and Martin et al. (1991) also supports this theory of firmness increase resulting from moisture migration from crumb to crust. Since moisture migration from crumb to crust leads to crust staling, which can be retarded; however, factors that retard crust staling, promote crumb staling. Thus, in most instances crust staling is tolerated at the expenses of maintaining crumb freshness. These studies clearly indicated the critical role played by moisture in staling.
The second most widely accepted theory, based on starch retrogradation, was proposed by Katz (1928). The theory was based on a series of X-ray diffraction studies involving bread as well as wheat starch gels. The X-ray diffraction patterns of fresh bread resembled freshly gelatinized wheat starch, while the patterns of stale bread were similar to retrograded starch. Supporting the conclusion, further research reports (Hellman et al., 1954) indicated similarity between starch crystallinity development rate and rate of bread firming. These findings led to the hypothesis that change in starch components from amorphous to crystalline forms is important in staling process.

Based on the proposed hypothesis relating starch retrogradation and staling, Schoch and French (1947) also proposed a theoretical model explaining the staling process, which is still useful in explaining the role of amylose and amylopectin in staling. The model is based on the principle of heat reversible aggregation of amylopectin leading to bread staling and freshening following reheating of bread. Starch granules retain individual shape even after swelling in presence of limited water. Due to swelling, the linear amylose fraction diffuses out in to aqueous phase, forming a concentrated solution. Upon cooling, this solution of amylose molecules associates by hydrogen bonding and rapidly retrogrades to set an insoluble gel, contributing to crumb structure. Thus, amylose quickly retrogrades following baking, affecting initial firmness, but plays no further role in crumb firming. The firming is attributed to changes in the physical orientation of the branched amylopectin molecules of starch within the swollen granule. This theory was further corroborated by researchers applying advanced analytical techniques and polymer science principles (Levine and Slade, 1990; Hug-iten et al., 2003; Slade and Levine,
1991). It is well accepted from extensive researches that starch retrogradation has major role in staling of bread.

A few researchers also point towards role of protein in staling process (Maga, 1975; Kim and D’Appolonia, 1977a, b). During baking process the gluten dehydrates while the starch retained moisture (Horsford in 1876 as reported by Maga, 1975). Further, it was theorized that staling might be due to exchange of water from starch to gluten and, upon storage, water from the starch migrated to the gluten resulting in firming. Moisture sorption properties (Cluskey et al., 1959) also support the notion of moisture transfer from starch to gluten, since starch gels lost moisture sorption capacity during storage while that of gluten gels remained constant. However, Senti and Dimler (1960) demonstrated that starch loses approximately 2% water during aging, which might be considered minor change in case of crumb (Pyler, 1973). Further, Kim and D’Appolonia (1977a) reported that increase in protein level reduced the firmness development. They suggested that flour proteins retarded the firming but did not alter the mechanism, which is essentially similar to starch retrogradation reported by Katz (1928) and Eliasson (1983), but effectively serve as diluent to starch leading to reduced firming of crumb. Furthermore, on the role of water in staling, Schiraldi et al. (1996) reported age dependent changes in water fraction in bound form. They proposed that water molecules facilitated cross linking of polymers by acting as slider of an interchain zipper leading to increase in firmness. Thus, water molecules play an important role in firmness development as they facilitate structural alterations.
Initial research by von Bibra in 1861 (as cited by Maga, 1975) demonstrated that a moisture content of at least 30% was required to refresh stale bread and it was thought to be the result of conversion of free water in fresh bread to bound water in stale bread which revert back to free state upon reheating. Recent approaches with principles of polymer science provide fundamental explanation supporting the relationship between temperature and water during dough baking and crumb refreshening. Water acts as plasticizer and helps to melt crystallites and as moisture content decreases the melting temperature increases. While moisture contents below 30% might result in melting temperatures above crumb refreshing temperature, which is typically below 100 °C. Recent reports by Hallberg and Chinachoti (2002) also support the significant role played by moisture migration over that of starch retrogradation that occur within products especially between amorphous domains connecting the crystalline region. These reports along with the findings of Hug-Iten et al. (2001), Hallberg and Chinachoti (2002), and Dragsdorff and Varriano-Marston (1980) question the direct cause and effect relationship between starch recrystallization and firmness, i.e., increase in firmness during storage does not result from extent of recrystallization alone but it also depends on type of crystals and its relative arrangement in the matrix also plays important role.

Thus, the vast research on staling helped in developing strategies to retard staling, i.e., antistaling measures; but still the actual mechanism on staling of bread remains ambiguous and while many theories explain different aspects of staling, not a single theory explains all the biophysical changes and relate different factors that lead to staling
of bread crumb. Though new research points to factors other than starch for staling there is enough evidence relating starch retrogradation to staling of bread crumb.

2.6.3 Factors Influencing the Staling

Most of the earlier research covered various aspects of staling including starch retrogradation, addition of gluten, addition of functional ingredients (emulsifiers, enzymes, low molecular weight carbohydrates, etc.) and also the modification of processing stages. Though the positive impact of this research on staling is perceived, the mode of action is not clear. The review of literature in this area has been summarized in a tabular form for convenience (Tables 2-2 – 2-7).

Table 2-2: Effects of processing conditions on bread staling

<table>
<thead>
<tr>
<th>Factors</th>
<th>Theory / Hypothesis</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mixing time</td>
<td>Optimum mixing slows firming rate</td>
<td>Maga, 1975</td>
</tr>
<tr>
<td>Fermentation time</td>
<td>No significant effect</td>
<td>Freilich, 1948</td>
</tr>
<tr>
<td>Proofing time</td>
<td>Linked with enzyme activity, time and gluten quality</td>
<td>Maga, 1975</td>
</tr>
<tr>
<td>Baking time</td>
<td>Limited role as product after low/high baking time is poor quality</td>
<td>Maga, 1975</td>
</tr>
<tr>
<td>Baking profile</td>
<td>Staling rate slower for breads baked at higher temperature for shorter time</td>
<td>Faridi and Rubenthaler, 1984</td>
</tr>
</tbody>
</table>
Table 2-2: Effects of processing conditions (contd.)

<table>
<thead>
<tr>
<th>Factors</th>
<th>Theory / Hypothesis</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cooking temperature of crumb</td>
<td>Slower staling rate with lower cooking temperature</td>
<td>Giovanelli et al., 1997</td>
</tr>
</tbody>
</table>

Table 2-3: Application of polymer science theory to bread staling

<table>
<thead>
<tr>
<th>Factors</th>
<th>Theory / Hypothesis</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polymeric phase separation</td>
<td>Thermodynamic incompatibility of polymers</td>
<td>Tolstoguzov, 1993;</td>
</tr>
<tr>
<td></td>
<td></td>
<td>MacRitchie, 1984</td>
</tr>
<tr>
<td></td>
<td>Thermodynamic inequilibrium of system</td>
<td>Zasyskin et al., 1997</td>
</tr>
</tbody>
</table>

Table 2-4: Effect of moisture on bread staling

<table>
<thead>
<tr>
<th>Factors</th>
<th>Theory / Hypothesis</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moisture</td>
<td>Slow staling in presence of moisture content &lt;16%</td>
<td>Katz, 1928; Pyler, 1973</td>
</tr>
<tr>
<td>Moisture migration</td>
<td>Loss of moisture from crumb to crust</td>
<td>He and Hoseney, 1990; Czuchajowska and Pomeranz, 1989</td>
</tr>
<tr>
<td>Moisture migration</td>
<td>Among starch matrix in the crumb and between crumb and crust</td>
<td>Chinachoti and Baik, 2001</td>
</tr>
</tbody>
</table>

Table 2-5: Effect of flour compositional factors on bread staling

<table>
<thead>
<tr>
<th>Factors</th>
<th>Theory / Hypothesis</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Starch</td>
<td>Chain aggregation on ageing – forming crystalline phase</td>
<td>Schiraldi and Fessas, 2001</td>
</tr>
</tbody>
</table>
Table 2-5: Effect of flour compositional factors on bread staling (contd.)

<table>
<thead>
<tr>
<th>Factors</th>
<th>Theory / Hypothesis</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Defatting, heat-moisture treatment, amylose leaching and chain length of amylose and amylopectin influenced starch chain interactions</td>
<td>Hoover et al., 1994</td>
<td></td>
</tr>
<tr>
<td>Amylopectin crystallization</td>
<td></td>
<td>Schiraldi et al., 1996</td>
</tr>
<tr>
<td>Changes in amorphous regions important rather than crystallized region</td>
<td></td>
<td>Rao et al., 1992</td>
</tr>
<tr>
<td>Gluten-Starch</td>
<td>Bread firming results from cross-links (hydrogen bonds) between the continuous protein matrix and the discontinuous remnants of starch granules</td>
<td>Martin et al., 1991; Every et al., 1998</td>
</tr>
<tr>
<td>Gluten</td>
<td>Gluten level has positive influence on firming rate and shelf stability</td>
<td>Kulp and Ponte, 1981; Maga, 1975; Prentice et al., 1954; Betchel and Meisner, 1954</td>
</tr>
<tr>
<td>Gluten</td>
<td>Increased loaf volume and resulted softer bread</td>
<td>Maleki et al., 1980</td>
</tr>
<tr>
<td>Pentosan</td>
<td>Acts as moisture sink and retards firming rate</td>
<td>Michniewicz et al., 1992; Patil et al., 1976</td>
</tr>
<tr>
<td></td>
<td>Do not influence retrogradation</td>
<td>Gudmundsson et al., 1991</td>
</tr>
</tbody>
</table>
Table 2-6: Effect of added Ingredients on bread staling

<table>
<thead>
<tr>
<th>Factors</th>
<th>Theory / Hypothesis</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Protein products</td>
<td>Staling rate retarded</td>
<td>Maga, 1975</td>
</tr>
<tr>
<td>Added carbohydrates</td>
<td>Sugars retarded the firming rate but oligosacharides increased firming rate</td>
<td>Kulman and Balasheva, 1938; Salem and Johnson, 1965</td>
</tr>
<tr>
<td>Enzymes</td>
<td>Retard bread staling as they break down amylose/amylopectin</td>
<td>Akers and Hoseney, 1994</td>
</tr>
<tr>
<td>Potato starch addition</td>
<td>High molecular weight and high polymer length – retarded firming</td>
<td>Maga, 1975</td>
</tr>
<tr>
<td>Milk solids</td>
<td>Slower firming rate but not significant</td>
<td>Pelshenke and Hampel, 1962</td>
</tr>
<tr>
<td>Whey solids</td>
<td>Addition of whey solids retard staling</td>
<td>Yousif et al., 1998</td>
</tr>
<tr>
<td>Shortening</td>
<td>Reduces firmness by improving the fine texture and loaf volume</td>
<td>Elton, 1969; Coppock et al., 1954</td>
</tr>
<tr>
<td>Yeast</td>
<td>High yeast level retards staling by increased loaf volume</td>
<td>Maga, 1975</td>
</tr>
<tr>
<td>Surfactant</td>
<td>Complex with starch retards retrogradation</td>
<td>Le Bail et al., 1999; Conde-Petit and Escher, 1994</td>
</tr>
<tr>
<td></td>
<td>Increased loaf volume</td>
<td>Knightly, 1996</td>
</tr>
<tr>
<td></td>
<td>Monoglycerides interact with gluten</td>
<td>Hoseney et al., 1969; Quail et al., 1991</td>
</tr>
</tbody>
</table>
Table 2-7: Effect of crumb structure on bread staling

<table>
<thead>
<tr>
<th>Factors</th>
<th>Theory / Hypothesis</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crumb structure</td>
<td>Coarser crumb – slower firming rate irrespective of starch retrogradation or moisture loss</td>
<td>Robertson and Emami, 1974; Fessas and Schiraldi, 1998</td>
</tr>
</tbody>
</table>

2.6.4 Measurement of Staling

Depending on the quality criteria used there are different methods available for measurement of staling in breadcrumb and starch gels. Karim et al. (2000) reviewed the methods used for starch retrogradation study and broadly classified them in two categories (i) macroscopic technique: monitors alterations in physical properties as manifestations of retrogradation (mechanical or textural changes) (ii) molecular techniques: monitors changes in starch polymer conformation or water mobility in starch gels at molecular levels.

Rheological studies include large deformation studies which show good correlation with sensory textural attributes (Keetels et al., 1996a, b, c) where as small deformation tests also known as dynamic rheological tests can be performed on soft gels which reveals the structure at molecular assembly level. There are large numbers of textural studies that report the texture data using compression testing but due to variations of test parameters it becomes impossible to compare the results (Karim et al., 2000). Another type of large deformation test is measurement of pasting properties where the tendency of starch to
retrograde during cooling following cooking is studied by recording the viscosity change during programmed heating and cooling of starch suspension. The ease of the procedure makes this test popular for study of starch characteristics. Small deformation tests e.g. dynamic oscillatory rheology test provides the information on microstructure of system. Since it is structurally non-destructive test it can be used to follow the structure formation or disintegration in real time as a function of temperature and time.

X-ray diffraction shows regular repeating nature of double helices of molecular structures, but it does not detect irregularly packed structures. Extensive information on the role of starch in bread staling has been gathered using X-ray diffraction technique. However, the sensitivity of X-ray diffraction is relatively low compared to techniques such as NMR and FTIR, which are able to detect even minor extent of recrystallization (Smits et al., 1998). Thermal analysis using differential scanning calorimetry has proven most useful in providing basic information on starch retrogradation. Starch retrogradation study using DSC involves gelatinization of starch in DSC cell and then storing the treated cell to observe retrogradation.

NMR application in the study of starch retrogradation involves various measurements related viz. $^1$H NMR or solid-state NMR involving $^{13}$C or $^{17}$O. All these invariably measured the molecular characteristics and relate the change to molecular rearrangements during staling. FTIR (Fourier transform mid-infra-red) in combination with ATR (attenuated total reflectance) has been used to follow conformational changes during
starch retrogradation. In terms of convenience, simplicity (sample preparation), and precision, NMR and DSC methods were recommended by Karim et al., (2000).
Chapter 3

Impact of Different Baking Processes on Bread Firmness and Starch Properties in Breadcrumb

Abstract

The influence the quality and shelf life of baked product has previously been reported to be effected by the time and temperature of the baking process. In this study, dough was baked at 219 degrees C by using different ovens (conventional, impingement or hybrid) or with doughs of different weights (large or small) for varying times. During baking the temperature profile at the dough center was recorded. Texture, thermal properties and pasting characteristics of baked product with reference to baking conditions were investigated. Small breads baked in the hybrid oven had the highest heating rate (25.1 degrees C/min) while large breads baked in conventional oven had the lowest heating rate (6.0 degrees C/min). When the data are viewed as a function of heating rate in this study, the enthalpy of amylopectin recrystallization, rate of bread firmness and the amount of soluble amylose were all-lower at the slower heating rate. The differences observed in product firmness following storage are potentially a consequence of the extent of starch granule hydration, swelling, dispersion and extent of reassociation; all of which are affected by the heating rate during baking.
3.1 Introduction

Several comprehensive reviews have documented the changes in starch that occur during storage and its relationship to staling of baked products (Chinachoti and Vodovotz, 2001; Kulp and Ponte, 1981; Lund, 1984; Maga, 1975; Zobel and Kulp, 1996). The principles of polymer chemistry have been successfully applied to understand the changes in the starch polymers that help to explain the process of staling (Hoover, 1995; Slade and Levine, 1993). Other key factors that relate to staling and have been studied extensively include: changes in moisture content (He and Hoseney, 1990; Zeleznack and Hoseney, 1986), moisture migration within the product and the possible interactions between starch and gluten (He and Hoseney, 1990; Kim and D’Appolonia, 1970a, b; Martin et al., 1991). Numerous studies have also documented the means by which to minimize staling of baked products by altering changes in starch using maltodextrins (Defloor and Delcour, 1999; Gerrard et al., 1997), lipids (Collar et al., 1998), surfactants (Faheid and Ragab, 1996; Rao et al., 1992; Stauffer, 2000), shortenings and/or emulsifiers (Armero and Collar, 1998; Forssell et al., 1998; Genc et al., 2000), or enzymes (Champenois et al., 1999; Hug-Iten et al., 2001; Morgan et al., 1997).

Tamstorf et al. (1986) conducted studies on dough expansion during the baking process and demonstrated differences in the functionality of surfactants at different temperatures. Furthermore, it has been reported that the critical changes that take place during baking determine the final crumb structure and product quality (Hayman et al., 1998). Seetharaman et al. (2002) reported that the heating process establishes a particular
polymeric structure in a product that subsequently influences staling behavior following storage. The central premise of this research, therefore, is that the structural matrix (starch and gluten) established in the crumb during baking is a function of the thermal history of the crumb during baking and subsequent cooling.

Processing technologies including ohmic cooking (Baker and Mize, 1939; He and Hoseney, 1991), impingement cooking (Li and Walker, 1996; Yin and Walker, 1995), microwave cooking (Ahmad et al., 2001; Baldwin et al., 1986; Lin and Anantheswaran, 1988), impingement-microwave combination cooking (Li and Walker, 1996; Yin and Walker, 1995), or infrared (IR) cooking (Anon, 1970) have been used to process a variety of foods including cookies, popcorn, French fries, or biscuits. These techniques are based on different modes of heating that potentially result in products with improved quality. Martin et al. (1991) reported that breads baked using Electrical Resistance Oven (ERO) staled more slowly than those baked in a conventional oven. Li and Walker (1996) and Yin and Walker (1995) reported improvements in product quality using impingement and hybrid (impingement-microwave combination) ovens when compared to conventional ovens. Microwave baking of bread resulted in a product with unacceptable texture (Ovadia and Walker, 1996) due to its rubbery and tough crust, and firm crumb (Shukla, 1993). However, Willyard (1998) reported slower staling of buns when baked with additional application of microwave energy in combination with conventional baking.

The effects of changes in processing conditions, i.e., baking time and temperature, on starch properties and staling kinetics have also been investigated (Faridi and Rubenthaler,
Different parameters such as pasting characteristics, Differential Scanning Calorimetry (DSC) profiles, and soluble amylose content have been used to evaluate starch properties (Faridi and Rubenthaler, 1984; Seetharaman et al., 2002; Yasunaga, 1968). Fessas and Schiraldi (2000) prepared a baking process map using DSC to simulate the baking of dough. They concluded that changes in heating rate (0.5 – 5 °C/min) do not influence the enthalpy of starch gelatinization, supporting an earlier report by Eliasson (1980). However, when a wider range of heating rates (0.02 – 20 K/min) were explored, Shiotsubo and Takahashi (1984) found that gelatinization is at equilibrium when heating rates were below 0.5 K/min, but kinetically limited at heating rates above 0.5 K/min. Wootton and Bamunuarachchi (1979) reported a decrease in gelatinization enthalpy of wheat starch as the heating rate increased from 8 – 32 °C/min. Also Doublier et al. (1987) observed that heating rate and shear conditions during processing have a significant influence on starch gel characteristics. The impact of heating rate was found to be more dramatic when low shearing was applied. Furthermore, Bloksma (1980) reported that dough viscosity changed when baked at different heating rates. Thus, during baking where limited shearing is encountered as a result of oven spring and gas expansion, heating rate might become an important factor in determining the characteristics of the crumb structure formed.

Investigation on the staling behavior of baked products and starch retrogradation have used baked products ranging in weight from 150 to 520 g, baking temperatures ranging from 160 to 230 °C and baking times varying form 15 to 50 min depending on the weight
and temperature (Baik and Chinachoti, 2001; Hug-Iten et al., 1999; Martin and Hoseney, 1991; Thorvaldsson and Skjoldebrand, 1998). In this study, we investigated whether product weight, baking temperature and time of baking resulted in products with different starch properties and staling behaviors. Thermal profiles of breads baked under different baking conditions were recorded and the starch properties in these baked products were determined.

3.2 Experimental

3.2.1 Modes of Heating

The different heating modes during baking were: natural convection heating using a conventional oven (Sears, Roebuck & Co., IL, USA), forced convection heating using an impingement oven (Enersyst Development Center, TX, USA), and a combination of forced convection with microwave energy using a hybrid oven (Enersyst Development Center, TX, USA). The details of the ovens used in the study are listed in Table 3-1. The Super jet oven had a choice of three levels of air velocity and 0-100% power control for microwave heating which made it possible to use it as an impingement oven with the microwave power set at 0%.
Table 3-1: Specifications for ovens used in bread baking, baking conditions, and heating rates

<table>
<thead>
<tr>
<th>Oven</th>
<th>Oven cavity (mm)</th>
<th>Power</th>
<th>Time (min)</th>
<th>Heating rate (°C/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Small</td>
<td>Large</td>
</tr>
<tr>
<td>Conventional</td>
<td>550 (W) 420 (D) 400 (H)</td>
<td>5.27 KWh (Natural gas)</td>
<td>15</td>
<td>25</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>16.8</td>
<td>6.0</td>
</tr>
<tr>
<td>Impingement</td>
<td>285 (W) 280 (D) 205 (H)</td>
<td>2.0 KW (air heater)</td>
<td>6</td>
<td>12.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>14.7</td>
<td>6.5</td>
</tr>
<tr>
<td>Hybrid</td>
<td>285 (W) 280 (D) 205 (H)</td>
<td>2.0 KW (air heater) 1.2 KW (microwave 2450 MHz)</td>
<td>3.5 a</td>
<td>7 a</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>25.1</td>
<td>16.7</td>
</tr>
</tbody>
</table>

a Microwave power was at 20% in the hybrid oven for both small and large breads.
3.2.2 Baking

Breads were made using commercial wheat flour (Cargill Foods, Minneapolis, MN, USA) following the recipe listed in Table 3-2. The basic properties of the flour were; 14% protein, 13% moisture, 64% water absorption at 500 BU. The dough was made using AACC method 10-10B (AACC, 2000) and the breads were baked using the parameters listed in Table 3-1. Dough was scaled for large breads (520 g) and small breads (80 g) and proofed loaves were baked in ovens preheated to set conditions. Following baking, the breads were cooled to room temperature over 45 min for small breads and 90 min for large breads and sealed in plastic Ziploc® bags until further analysis. Breads were analyzed for moisture content, water activity, firmness, water holding capacity (WHC), retrogradation, and soluble amylose after 2 h and 1, 3, 7, 10, or 15 d of storage. The whole study was duplicated and for each analysis multiple data were collected.

Table 3-2: Bread formulation for each batch of dough

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Amount (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flour</td>
<td>300.0</td>
</tr>
<tr>
<td>Water</td>
<td>192.0</td>
</tr>
<tr>
<td>Sugar</td>
<td>13.5</td>
</tr>
<tr>
<td>Active dry yeast</td>
<td>8.0</td>
</tr>
<tr>
<td>Salt</td>
<td>7.8</td>
</tr>
<tr>
<td>Shortening</td>
<td>5.4</td>
</tr>
<tr>
<td>Calcium propionate</td>
<td>1.0</td>
</tr>
</tbody>
</table>
3.2.3 Temperature Profile

The temperature at the center of the crumb during baking in a conventional or impingement oven was measured using a T-type thermocouple and a data logger (Reading Bakery Systems, PA, USA). The temperature profile during baking in the hybrid oven was measured by removing breads at different time intervals during baking and measuring temperature at the center using a T-type thermocouple. Each reading was taken with a new loaf of bread. All temperature profiles during baking were determined in duplicates.

3.2.4 Moisture and Water Activity

Moisture content and water activity of the center of the loaf were measured. Moisture content was determined using AACC method 44-11 (AACC, 2000). Water activity was measured using the AQUALAB CX-2 instrument (Decagon Devices Inc., WA, USA). All values are reported as the average of three readings for each sample.

3.2.5 Firmness

Bread firmness was measured using the procedure described by Seetharaman et al. (2000) using a TA.XT2 instrument (Texture Technologies Inc., NY, USA) with a 38 mm diameter cylindrical probe at test speed of 0.5mm/min. At least four slices of bread (12 mm thickness each) cut from the center of the loaf were tested and the average values reported.
3.2.6 Thermal Properties of Starch

Breadcrumb samples were stabilized for storage before analysis using a methanol treatment (grinded and washed with methanol) (Seetharaman et al., 2002). Thermal properties of samples were evaluated using a Differential Scanning Calorimeter (PYRIS 1 DSC, Perkin-Elmer, CT, USA). Each stabilized breadcrumb sample (1:2; sample: water; w/v) was scanned from 20 °C – 140 °C at 10 °C/min as described by Seetharaman et al. (2002). All values are reported as average of two readings.

3.2.7 Water Holding Capacity

Water holding capacity of the bread sample was measured as weight of gel obtained from breadcrumb following centrifugation. The crumb was homogenized in a coffee grinder (Braun Aromatic KSM 2; The Gillette Company, Boston, MA, USA) and a ~2 g sample was soaked in 40ml distilled water for 30 min at room temperature. The slurry was centrifuged at 1000g for 10 min following 30 min of holding. The sediment weight was recorded and the weight of water in gel was obtained by subtracting the dry sample weight from the gel weight. WHC was expressed as grams of water per gram of dry sample weight.
3.2.8 Soluble Amylose

Soluble amylose in stabilized breadcrumb samples was analyzed according to Seetharaman et al. (2002), and the values reported as mg amylose/100mg stabilized sample. Each sample was analyzed in duplicate and average is reported.

3.2.9 Pasting Properties

Freeze-dried breadcrumb samples were milled in a coffee grinder and sieved (250 μm sieve) for pasting properties analysis. The samples were analyzed by using a Rapid Visco-Analyzer IV (Newport Scientific, Australia) and the data interpretation was conducted using Thermocline 3.1 software (Newport Scientific, Australia). Each sample was weighed to obtain a 28g suspension with 14% solids. A standard pasting profile of 13 min was used except that the initial mixing step was modified from 960 rpm for 10 s to 160 rpm for 5 min to obtain proper hydration of sample and reproducible results. Each sample was analyzed at least twice and average results reported for peak viscosity, final viscosity, trough, breakdown and setback. Maximum viscosity between 500 and 700 seconds was reported as peak viscosity, minimum viscosity between 600 and 800 seconds was reported as ‘trough’, and viscosity at the end was reported as ‘final viscosity’. The difference between peak viscosity and trough was reported as ‘breakdown’ and between trough and final viscosity as ‘setback’.
3.2.10 Statistical Analysis

Three types of ovens were used to bake six different breads and whole set of experiments was replicated at least twice. The general linear model procedure of SAS (ver 8.2, SAS Institute, Cary, NC, USA) was used for analysis of moisture, water activity, and firmness data. ANOVA revealed significant interaction between processing and storage (results in Appendix D) so each storage period was analyzed separately for processing effect. Fisher’s LSD test was used to compare means at the 5% significance level. Regression analysis was also conducted as a function of heating rate for each storage time by using Excel software.

3.3 Results

The objective of the research was to compare the characteristics of products produced using widely different heating profiles during baking. Three ovens with different modes for heating were used to prepare breads from two dough weights in each oven; 520 and 80 g. The heating curves (Fig. 3.1) and rates (Table 3-1) show the different thermal profiles to which these doughs were exposed during baking. The oven temperature was same for all treatments but the baking time was determined by observation of the crust and the baking time calculations of Walker and Li (1993).
3.3.1 Temperature Profile

The temperature profiles at the center of bread were measured continuously during the baking process and are shown in Fig. 3.1. The internal thermal profile was significantly different in shape for breads baked in different ovens as well as for breads of different weights. The thermal profile at the center of the large dough during baking in a conventional oven can be divided into three distinct phases; phase I, characterized by a very slow temperature increase for up to 4 min; phase II, exhibiting a rapid increase in

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Fig 3.1: Temperature profile of breadcrumb center during baking in different ovens and loaf weight
temperature for a period of 13 min; and phase III, characterized by an asymptotic increase of temperature above 90 °C for a period of 8 min (Fig. 3.1). Large breads baked in impingement oven had a thermal profile similar to large breads baked in conventional oven, except that baking was completed before the temperature reached phase III. Large breads baked in the hybrid oven and all the small breads had a negligible phase I stage with significant increase in temperature within about 1 min of baking followed by a very rapid temperature increase in phase II until the end of baking. Small breads baked in a conventional oven had a thermal profile with phase III of about 6 min, i.e., less than that observed for large bread baked in conventional oven.

The thermal profiles during baking were further characterized by calculating the heating rates. Heating rates were calculated in the linear region of rapidly increasing temperature, i.e., in phase II, between 50 and 80 °C to facilitate comparison between different breads (Table 3-1). The rate of temperature increase at the center of the loaf was significantly different for the different breads baked in different ovens. Small breads baked in the hybrid oven had the highest heating rate (25.1 °C/min) while large breads baked in conventional oven had the lowest heating rate (6.0 °C/min).

3.3.2 Moisture and Water Activity

The moisture content and water activity of the crumb samples were measured at the center of the loaf as for the thermal profiles. Moisture contents of all bread samples decreased after 15 d storage. Small breads baked in the conventional oven had the highest
loss of moisture, whereas large breads baked in the conventional or impingement ovens had the lowest loss. I recognize that moisture loss in small breads baked in conventional oven is higher than those reported in the literature, but the data has been consistent over three separate trials.

When the data is viewed as a function of heating rate (Fig. 3.2), breads baked at lower heating rates had higher moisture after both 2 h and 15 d of storage compared to breads baked using a higher heating rate. Furthermore, breads baked at lower heating rates lost less moisture following storage compared to breads baked at higher heating rates. The amount of moisture lost up to about 7 d of storage was highest for samples baked at intermediate and higher rates of heating.
The heating technique, i.e., conduction, convection or hybrid, also affected the moisture content of the breads. Breads baked in impingement or hybrid ovens lost less moisture than conventional oven baked breads. This is probably due to the early crust formation in breads baked in impingement or hybrid ovens thus reducing moisture loss through the crust. Furthermore, hybrid oven baked breads had overall lower moisture content than the respective breads baked in conventional or impingement ovens. This is probably due to heating both within the loaf by the microwave energy and from the outside by the hot air.

The water activities of bread samples also decreased upon storage. Trends for levels of water activity were similar to those observed for bread moisture content (data not shown).
3.3.3 Firmness

Bread firmness values increased after 15 d storage. Firmness of breads from all treatments were almost the same 2 h following baking. However, a trend was observed wherein firmness was higher when breads were baked at a higher heating rate compared to breads baked at a lower heating rate (Fig 3.3). The regression coefficients for firmness as a function of heating rate are shown in Table 3-3. The differences in firmness values as a function of heating rate are more evident after 15 d of storage than after 2 h of storage.

![Graph showing firmness of breadcrumb as a function of heating rate](image)

**Fig 3.3:** Firmness of breadcrumb as a function of heating rate

Note: Regression lines from top to bottom in order are for storage period 0.08 days - □; 1 day - ○; 3 days - Δ; 7 days – x; 10 days - *; and 15 days - ○, respectively.
Table 3-3: Regression coefficients ($R^2$) of different properties following storage as a function of heating rate

<table>
<thead>
<tr>
<th>Storage time (Days)</th>
<th>Moisture (%)</th>
<th>Firmness (gram)</th>
<th>Amylopectin melting enthalpy (J/g)</th>
<th>Amylose solubility (mg/100g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.08 (2 h)</td>
<td>0.814</td>
<td>0.537</td>
<td>0.598</td>
<td>0.789</td>
</tr>
<tr>
<td>1</td>
<td>0.740</td>
<td>0.862</td>
<td>0.693</td>
<td>0.630</td>
</tr>
<tr>
<td>3</td>
<td>0.804</td>
<td>0.514</td>
<td>0.716</td>
<td>0.625</td>
</tr>
<tr>
<td>7</td>
<td>0.743</td>
<td>0.533</td>
<td>0.739</td>
<td>0.675</td>
</tr>
<tr>
<td>10</td>
<td>0.654</td>
<td>0.850</td>
<td>0.498*</td>
<td>0.707</td>
</tr>
<tr>
<td>15</td>
<td>0.757</td>
<td>0.614</td>
<td>0.358*</td>
<td>0.574</td>
</tr>
</tbody>
</table>

$R^2$ values were not significant P<0.05.

3.3.4 Thermal Properties of Starch

In all bread samples, starch was completely gelatinized as measured by DSC. Fresh and stored breadcrumb samples were analyzed for amylopectin retrogradation enthalpies using DSC. The enthalpy of amylopectin recrystallization was slightly higher in samples baked at higher heating rates compared to samples baked at lower heating rates (Fig. 3.4). For all samples the enthalpy of amylopectin recrystallization increased significantly up to 7 d storage.
3.3.5 Water Holding Capacity

The water holding capacity (WHC) of the crumb was measured 2 h after baking (Table 3-4). In general, as the heating rate during baking increased WHC decreased. However, the mode of heating appeared to have a larger impact on WHC than heating rate. Bread baked in a conventional oven with a heating rate of 6°C/min had a higher WHC than bread baked in impingement oven with a heating rate of 6.5 °C/min. This may be due to the absence of phase III in the baking temperature profile in breads baked in the impingement oven.
### Table 3-4: Water holding capacity of breadcrumb 2 hr after baking

<table>
<thead>
<tr>
<th>Bread</th>
<th>Heating rate (°C/min)</th>
<th>Water holding capacity (g water/ g dry sample)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conventional Small</td>
<td>16.8</td>
<td>3.36 ab&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>Conventional Large</td>
<td>6.0</td>
<td>3.68 a</td>
</tr>
<tr>
<td>Impingement Small</td>
<td>14.7</td>
<td>3.3 ab</td>
</tr>
<tr>
<td>Impingement Large</td>
<td>6.5</td>
<td>2.77 c</td>
</tr>
<tr>
<td>Hybrid Small</td>
<td>25.1</td>
<td>3.02 bc</td>
</tr>
<tr>
<td>Hybrid Large</td>
<td>16.7</td>
<td>2.85 c</td>
</tr>
</tbody>
</table>

<sup>a</sup> Values followed by the same letter (a-c) in the same column are not significantly different (P < 0.05).

### 3.3.6 Soluble Amylose

Soluble amylose contents of samples are plotted as a function of heating rate (Fig 3.5). Breads baked at higher heating rates had higher soluble amylose contents compared to the breads baked at lower heating rates. Furthermore, the decrease in soluble amylose during storage was higher in breads baked at higher heating rates compared to those baked at lower heating rates.
3.3.7 Pasting Characteristics

Breadcrumb samples were analyzed for pasting characteristics 2 h after baking (Table 3-5). The pasting properties are determined by the starch granular and molecular structures. A significant relationship was observed between heating rate and the pasting properties (Fig 3.6). The peak, trough and final viscosities of bread samples increased as the heating rate increased.
### Table 3-5: Pasting properties of breadcrumb 0.08 days after baking

<table>
<thead>
<tr>
<th>Pasting characteristics</th>
<th>Conventional small</th>
<th>Conventional large</th>
<th>Impingement small</th>
<th>Impingement large</th>
<th>Hybrid small</th>
<th>Hybrid large</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heating rate (°C/min)</td>
<td>16.8</td>
<td>6.0</td>
<td>14.7</td>
<td>6.5</td>
<td>25.1</td>
<td>16.7</td>
</tr>
<tr>
<td>Peak viscosity (cP)</td>
<td>2585.5c(^a)</td>
<td>1987.5 e</td>
<td>2756.5 b</td>
<td>2233.0 d</td>
<td>3213.0 a</td>
<td>2543.0 c</td>
</tr>
<tr>
<td>Breakdown (cP)</td>
<td>405.5 d</td>
<td>171.0 f</td>
<td>548.0 b</td>
<td>363.0 e</td>
<td>775.0 a</td>
<td>487.5 c</td>
</tr>
<tr>
<td>Final viscosity (cP)</td>
<td>2913.5 c</td>
<td>2328.5 e</td>
<td>3100.0 b</td>
<td>2630.5 d</td>
<td>3515.5 a</td>
<td>2941.5 c</td>
</tr>
<tr>
<td>Setback (cP)</td>
<td>733.5 c</td>
<td>602.0 d</td>
<td>891.5 b</td>
<td>760.5 c</td>
<td>1077.5 a</td>
<td>886.0 b</td>
</tr>
</tbody>
</table>

\(^a\) Values followed by the same letter (a-f) in the same row are not significantly different (P < 0.05).

---

**Fig 3.6: Correlation between pasting characteristics and heating rate**

Note: (Linear) – linear correlation
3.4 Discussion and Conclusions

Under the hydrothermal conditions experienced during baking, starch crystallites melt, starch granular structure is disrupted, and amylose and amylopectin are partially dispersed (Gomez et al., 1992; Zobel and Kulp, 1996). Amylose and amylopectin are dispersed out of the granule (inter-granular dispersion) and into cavities inside the granule (intra-granular dispersion) (Hug-Iten et al., 1999). Amylose association increases as the concentration of soluble amylose increases (inter- or intra-granularly) and when the temperature of the medium is less than the $T_m$ of amylose crystals (125 – 145 °C) (Morris, 1990). Upon cooling to temperatures less than the $T_m$ of amylopectin (50 °C), the amylopectin inside the gelatinized starch granule begins to associate. The relatively high amylopectin concentration of non-dispersed, gelatinized starch granules increases the rate and extent of amylopectin-amylopectin and amylose-amylopectin associations (Fernandez et al., 1999; Klucinec and Thompson, 1999; Liu and Thompson, 1998).

In this study, the changes in starch structure and function in relation to the temperature profile experienced by the dough during baking, and potentially the consequent influence on staling behavior were investigated. The independent variable was the temperature profile of the dough due to the different baking conditions, resulting in breads with varying moisture content and textural properties following storage. I acknowledge that these different temperature profiles were achieved by heating using different modes of heat; i.e., conduction, convection and/or microwave energy and that these variables may
also be responsible for some of the differences observed. I have further elaborated these differences in the discussion that follows.

Previous studies on bread quality and shelf life have used different parameters with respect to baking temperature, time and weight of the breads. Shogren and Finney (1984) compared a standardized baking test using 10 g flour with one using 100 g flour (~170 g dough) test; Walker and Li (1993) baked a number of products in different ovens and reported different time-temperature conditions to obtain acceptable products. Baik and Chinachoti (2000, 2001, 2002) conducted their studies using breads baked in a bread machine for 50 min at 160 °C. However, most of these studies do not report the temperature profiles during baking which are influenced by the heating method as well as the weight.

Our results show that not only can the rate of heating be significantly altered during phase II of the temperature profile (e.g. 6-25 °C/min), but also that the temperature profile in phase III can be varied (e.g. 0-8 min) by altering the modes of heating or the weights of bread baked in different ovens (Fig. 3.1). For comparison, we estimated the heating rates from some of the published studies based on the temperature profiles reported. Martin et al. (1991) reported heating rates of 3 and 9 °C/min for breads baked in an Electric Resistance Oven and a conventional oven, respectively. Giovanelli et al. (1997) simulated the bread baking process by heating dough in a covered pan with estimated heating rates in the range of 1.5 – 5 °C/min. Leon et al. (1997) reported on changes taking
place during baking using a heating rate of 11.7 °C/min followed by holding at 100 °C for 9 min. Most of the reported heating rates are similar to those observed for large bread baked in conventional or impingement oven in this study. However, as shown in this study, by baking using a range of temperature profiles there are significant consequences for starch structure and functionality.

The differences in starch properties of products baked from the same dough are attributable to differences in the rate of heating achieved using different modes of heating and/or by altering the weight of the dough. It is known that changes to starch granules during baking determine crumb structure (Dreese et al., 1988). Altering the heating rate during baking would potentially vary the kinetics, and the extent of disordering of the amylopectin crystals, granule swelling, amylose leaching and, therefore, the effective crumb structure established within the product. These changes would subsequently impact the textural changes occurring in product during storage.

Breads baked at the higher heating rates, in general, had a lower moisture content compared to breads baked at lower heating rates. These differences in moisture content could be attributed partly to the modes of heating and the initial dough weight. Bread moisture content, therefore is a symptom of the baking conditions as mentioned above and in turn influences product shelf life up on subsequent storage (Maleki et al., 1980; Yin and Walker, 1995; Zeleznak and Hoseney, 1986). Similar observations have also been reported by Walker and Li (1993) and Yin and Walker (1995). When the data from our study are viewed as a function of heating rate, the enthalpy of amylopectin
recrystallization (Fig 3.4), breadcrumb firmness (Fig 3.3) and the level of soluble amylose (Fig 3.5) were all lower at the slower heating rate. The respective regression coefficients (Table 3-3) are also indicative of the differences in the various properties that are potentially due to differences in the mode of heating and indirectly, due to the heating rate. Amylopectin recrystallization enthalpies tended to plateau after 7 d storage, which might explain the decrease in value and significance of the regression coefficient (Table 3-3). Exceptions were observed such for small breads baked using a conventional oven, with a heating rate of 16.8 °C/min or breads made using hybrid oven, where either stage III thermal profile or microwave energy, respectively, could alter the starch characteristics. The unusual firming pattern of breads baked in the hybrid oven could be the result of toughening effect due to the applied microwave energy (Shukla, 1993) and is difficult to differentiate from firmness (Sumnu, 2001). In general, heating rate had an influence on starch properties and consequently firmness development, following baking.

Conventional oven baked large breads showed highest WHC suggesting maximum starch gelatinization while large breads baked in impingement or hybrid ovens had the lowest WHC. Yasunaga et al. (1968) reported that WHC of crumb samples increased with time and temperature of baking and was related to the extent of gelatinization. Large breads baked in the conventional oven experienced a slower heating rate and a longer baking time, potentially resulting in a higher degree of degree of order-disorder transformations of starch molecule and starch granule disruption compared to large breads baked in other ovens. Similarly, small breads baked in hybrid oven had lower WHC than small breads baked in conventional or impingement ovens, corresponding to the shorter baking time in
hybrid oven. Previous research has also documented the relationship between heating rate and starch properties. Biliaderis (1991) suggested that changes in heating rate would change the gelatinization process by altering the time available for order-disorder transitions. The influence of heating rate on starch gelatinization was also demonstrated by Shiotsubo and Takahashi (1984) and Wootton and Bamunuarachchi (1979). Thus baking using different thermal profiles is likely to change the kinetics of the processes involved during the gelatinization of starch granules.

The pasting properties of breadcrumb from the different treatments were significantly different suggesting differences in gelatinization process as a function of thermal regime during baking. Peak viscosities observed were highest for small breads baked in the hybrid oven and were lowest for large breads baked in the conventional oven. Yasunaga et al. (1968) reported a decrease in peak and final viscosity as the baking temperature or time increased. In this study, the baking temperature was kept constant while the baking time increased. There is a strong relationship between heating rate and the different pasting parameters (Fig 3.6), i.e., peak viscosity ($r^2=0.89$), final viscosity ($r^2=0.89$), and trough ($r^2=0.89$). As the dough temperature increases starch granules gelatinize and swell followed by the leaching of amylose (Langton and Hermansson, 1989) that envelops the swollen granules and provides necessary firmness to set the crumb structure in bread (Hoseney et al., 1978). Therefore, the starch granules, when exposed to slower heating rate and longer time above $T_m$ of native starch, experience increased order-disorder transitions and amylose phase separation, leading to formation of amylose structures inside and outside the granules. The amylose structures formed during processing ($T_m >$
95 °C) are difficult to melt at temperatures used in pasting studies (Biliaderis, 1992), which might restrict granule swelling during pasting. Similar observations on the restriction of granule swelling as a result of amylose leaching in the presence of endogenous lipid content have been reported by Becker et al. (2001) and Navarro et al. (1996).

Pasting profiles of the crumb samples also show the presence of a small secondary viscosity peak (Fig 3.7). The secondary peaks had similar shapes irrespective of bread size (dough weight) when baked in different ovens. Bread baked in the hybrid oven exhibited a smaller peak compared to breads baked in the other ovens. The width of this peak increased for breads baked in the impingement and conventional ovens. The presence of small secondary viscosity peak in pasting curve during cooling has also been reported by Yasunaga et al. (1968) and Xu et al. (1992) for breadcrumb and by Takahashi and Seib, (1988) for wheat starch. The changes in viscosity were probably due to the complexation of lipids with solubilized starch molecules followed by crystallization of the complex during the cooling phase (Xu et al., 1992). The differences in the shape of the secondary peak in breads baked in different ovens are also suggestive of changes in the crumb structure as a function of the thermal profile.
In summary, different thermal profiles generated during baking yield products whose moisture content and firmness development following storage are a direct result of the heating rate experienced at the crumb. The differences observed in the product firmness following storage are potentially a consequence of the extent of starch granule hydration, swelling, dispersion and extent of amylose reassociation; all of which are affected by the heating rate during baking.

Fig 3.7: Second viscosity peaks on the pasting curve during the cooling stage
Chapter 4

Effect of Heating Rate on Starch Granule Morphology and Size

Abstract

Changes in starch granule morphology and size during heating were monitored continuously, when heated at either 5 or 25 degrees C/min on a hot stage. The results showed that granule morphology was different as a function of the heating rate and granule swelling was governed kinetically. These observations visually demonstrate the significant influence of processing conditions, i.e., heating rate, on starch granule size and morphology and therefore potentially have implications in determining structure and texture of baked products.

4.1 Introduction

Starch, when heated in the presence of water, undergoes irreversible changes that are dependent on the amount of water and heat available in the system. Thomas and Atwell (1999) described gelatinization and pasting as distinct stages of change during heating of starch, i.e., thermal processing. The first set of changes during heating is termed as gelatinization and is characterized by the irreversible disruption of molecular order depending on temperature and moisture, and the initial increase in granule size resulting in increased suspension viscosity. These changes render part of the material in granule soluble following heat treatment and thus contribute to food properties such as texture,
viscosity, and moisture retention. When a majority of the granules have undergone these changes, the starch is considered to be “pasted”. Thus, pasting is the phenomenon following gelatinization. It involves granular swelling, exudation of molecular components from granule, and eventually total disruption of granules (Atwell et al., 1988). The subsequent changes that occur following gelatinization and pasting during storage are termed as retrogradation, where starch polymers in the solubilized starch fraction and the remaining granular fragments re-associate imparting firmness to the gel.

Wheat starch has a bimodal size distribution comprising of A-type and B-type granules whereas cornstarch has a normal size distribution. The pasting properties of wheat starch are reported to be a function of A- and B-type granules and a strong positive correlation was reported between A-type granules and starch pasting parameters (Shinde et al., 2003). Morphological changes have also been documented for A-type granules during heating (Bowler et al., 1980). Starch granule size increased with increase in temperature and above a temperature of 70 °C, the granules tended to fold extensively. In addition to type of starch granule, physical parameters such as temperature, rate of temperature increase, and shearing during heating also influence the viscosity of starch suspensions (Doublier et al., 1987; Suh and Jane, 2003). Doublier et al. (1987) used different heating and shearing rates and observed that heating rate significantly influenced the flow characteristics. A higher heating rate resulted in a higher apparent viscosity. Similarly, Suh and Jane (2003) also reported higher peak viscosity at faster heating rate during pasting.
Influence of processing conditions on baked product texture has been reported (Seetharaman et al., 2002; Patel et al., 2005). The authors hypothesized that the different heating rates experienced by dough during baking result in different starch granule dispersions and subsequently have an impact on product texture and shelf life. Studies using non-conventional baking processes (Martin and Hoseney, 1991; Martin et al., 1991; Yin and Walker, 1995) have shown that baked product texture varied under different baking conditions as a result of different starch granule morphologies which were due to altered heating regime. The objective of this research was to demonstrate the visual evidence of differences in the starch granule swelling and morphological changes as a function of heating rate in real time that potentially provides an explanation for the differences in product texture.

4.2 Experimental Procedures

Wheat starch (Midsol-50; Midwest Grain Products, Inc., Atchison, KS, USA) suspensions were prepared by suspending ~10.0 mg starch in 1.0 ml of water by using a vortex mixer. The suspension was transferred on to a slide, covered with a coverslip and sealed with Cytoseal 60 (Richard Allan Scientific, Kalamazoo, MI, USA) to prevent moisture loss during heating. The sealed specimen was then mounted on a Linkam LTS 350 hot stage (Linkam Scientific Instruments, Tadworth, Surrey, UK) and observed under 40x magnification using Olympus BX41TF microscope (Olympus Optical Co. Ltd., Shinjuku-ku, Tokyo, Japan) during heating. Different heating rates (5 or 25 °C/min) were achieved by using Linkam LNP and Linkam TMS94 temperature controller (Linkam
Scientific Instruments, Tadworth, Surrey, UK). The actual temperatures at each heating rate were measured by using a T-type thermocouple placed on slide and sealed with a cover slip on top and have been used in the results. The images were captured using SPOT Insight QE camera (Diagnostic Instruments Inc., Sterling Heights, MI, USA) and the granule dimensions were calculated using the SPOT 3.5.6 for windows (Diagnostic Instruments Inc., Sterling Heights, MI, USA) software. It was repeated twice and average values were reported for granule dimensions.

4.3 Results and Discussion

The microscopic images of wheat starch granules heated at 5 or 25 °C/min are shown in Fig. 4.1. The arrow marks facilitate tracking the morphological changes of A- and B-type granules through the different frames. The typical native wheat starch morphology with two types of granules, large lenticular A-type and small spherical B-type as has been previously reported (Bowler et al., 1980; Franco et al., 1998; Velde et al., 2002; Williams and Bowler, 1982), is visible in the micrograph. The granule size did not increase before 50 °C but above that progress in swelling could be observed visually. Significant variability was observed among the granules in their respective size increase with increase in temperature above 50 °C as would be expected. Most A- and B-type granules appear swollen at 60 °C when heated at 5 °C/min while only a few A-type granules were swollen when heated at 25 °C/min. At 65 °C many of the B-type granules did not swell when heated at 25 °C/min. At 70 °C, the typical folding of A-type granules was observed when heated at 5 °C/min. Similar results have been reported before at slower heating
rates (Bowler et al., 1980; Choi and Kerr, 2004). However, the extent of folding was much less when heated at 25 °C/min even at 80 °C and the circular granule contours are clearly visible. Granules heated at 5 °C/min, on the other hand, appear extensively folded and wrinkled.
<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>5 °C/min</th>
<th>25 °C/min</th>
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<td><img src="image2" alt="Image" /></td>
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<tr>
<td>65</td>
<td><img src="image7" alt="Image" /></td>
<td><img src="image8" alt="Image" /></td>
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</table>

**Fig 4.1:** Light micrograph of wheat starch at different temperatures during heating at 5 °C/min or 25 °C/min. (Note: Magnification (40x X 10); bar in each micrograph is 50 μm length.)
The granule size increase of A- and B-type granules was plotted as a function of time to highlight these differences based on time during heating (Fig. 4.2a, b). Wheat starch granule size increase is presented as absolute change in dimensions as well as percentage change from original native granule at 25 °C. The data pointes in Fig. 4.2 (a, b) are average values calculated at 30, 40, 50, 55, 60, 65, 70, or 80 °C. Granule dimensions were
not measured above 80 °C since deformation, folding, and disruption of granules made it difficult to calculate the size. A-type granules showed substantial size increase in size between 50 and 70 °C when heated at 5 °C/min; from 5.3% to 103.4% change in 250s, whereas at 25 °C/min the change was from 9.1% to 148.1% within 50s. Similarly, for B-type granules heated at 5 °C/min, granule size changed from 2.2% to 113.6% in 250s, and at 25 °C/min heating rate it changed from 2.4% to 116.5% within 50s. Swelling form B-type granules occurred at a higher temperature than for A-type granules, which is in agreement with previous reports that suggested that B-type granules were more resistant to gelatinization (Chiotelli and LeMeste, 2002; Eliasson and Karlsson, 1983; Peng et al., 1999; Wong and Lelievre, 1982).

Therefore, the two key observations reported here based on visual observations are: (1) extent of granule swelling and folding are different when heated at different heating rates; and (2) granule swelling is a kinetic phenomenon, i.e., at higher heating rates, granule swelling occurs at a higher temperature. This delay is not due to a temperature lag at the higher heating rate because the temperatures reported are actual measured temperatures. The changes in granule morphology reported in this study need to be interpreted in the context of time taken to reach a specific temperature at the different heating rates. For example, the difference in time required to heat from 25 °C to 50 °C between 5 and 25 °C/min is 240 s, while the difference in time increases to 614 s at 90 °C. Therefore, the residence time at a given temperature range is greater at slower heating rates. Granule swelling at 60 °C when heated at 5 °C/min occurred over 420 s. Therefore, the particular changes associated with starch gelatinization, i.e., glass transition, swelling, amylose
leaching and granule folding occur over a time interval of more than 5 min. These same events will have to occur over a much shorter time frame (84 s) if heated at 25 °C/min (Figure 4.2a, b). 

![Graph showing average size and change in granule size of A- and B-type wheat starch granules as a function of heating rate.](image)

**Fig 4.2a:** Average size and average change in granule size of A- and B-type wheat starch granules as a function of heating rate.

Note: (Δ) – A-type wheat starch granule; (○) – B-type wheat starch granule; open symbols represent 25 °C/min and closed symbols represent 5 °C/min heating rates; solid line represent average granule size (μm); dotted line represent average change in granule size (%); each data point represents data at temperatures ranging from 30, 40, 50, 55, 60, 65, 70, or 80 °C.
However, the data reported here show that there is a kinetic limitation to granule swelling, and consequently to amylose leaching, and likely other associated processes that are reflected in altered paste viscosity as has been reported earlier (Doublier et al., 1987; Suh and Jane, 2003).

Fig 4.2b: Average size and average change in granule size of A- and B-type wheat starch granules as a function of heating rate.

Note: (Δ) – A-type wheat starch granule; (○) – B-type wheat starch granule; open symbols represent 25 °C/min and closed symbols represent 5 °C/min heating rates; solid line represent average granule size (μm); dotted line represent average change in granule size (%); each data point represents data at temperatures ranging from 30, 40, 50, 55, 60, 65, 70, or 80 °C.
Several studies have reported that granule swelling and amylose leaching occur concurrently (Ghiasi et al., 1982a; Sakonidou et al., 2003; Tester and Morrison, 1990). Furthermore, the kinetic limitations at higher heating rates will likely influence the extent of amylose leaching and the nature of amylose reassociation. One can conceive an image of amylose leaching out of the granule and rapidly reassociating on the granule surface and/or phase separating from amylopectin within the granules at higher heating rates; while at slower heating rates, a more extensive amylose network could be formed due to the slower increase in the temperature and phase separation from amylopectin (Miles et al., 1985a, b). These alternative scenarios would likely explain the differences in gel texture and property at higher starch concentrations. We recognize that results from this study are based on a dilute system and the particular changes in morphology and polymer leaching will be different in the product system at higher starch concentrations. However, research from our laboratory has demonstrated differences in product texture and shelf life as a function of the heating rate during baking (Patel et al., 2005; Seetharaman et al., 2002). These observations, therefore, at least set stage for possible alternative scenarios to interpreting textural differences in products. Other results from our laboratory also demonstrate similar trends in granule size and morphology changes as a function of heating rate for normal corn and waxy corn starches (data not shown).

4.4 Conclusions

The results presented here provide visual evidence for differences in starch granule morphology and size increase as a function of heating rate. More extensive folding of
granules was evident when starch was heated at 5 °C/min compared to those heated at 25 °C/min. Furthermore, the increase in granule size occurred at a higher temperature when heated at 25 °C/min compared to 5 °C/min. These differences potentially result in altered patterns of amylose leaching and network formation thus providing an explanation for differences in gel properties and baked product texture.
Chapter 5

Effect of Heating rate at Different Moisture Contents on Starch Retrogradation and on Starch-Water Interactions during gelatinization

Abstract

The objective of this research was to investigate the effect of heating rate at different moisture contents on starch retrogradation and the gelatinization process. Starch retrogradation was not influenced by either moisture content (water:starch ratio of 0.7 or 2.0) or heating rate (5 °C/min, 20 °C/min or 40 °C/min). In order to further understand the effects of heating rate on starch-water interactions, starch suspensions at a water:starch ratio ranging from 0.7 to 3.0 were heated at 5, 15 or 25 °C/min by using a DSC to different final temperatures and rescanned. The deconvoluted G and M1 endotherms and the corresponding additional unfrozen water (AUW) were determined. The results showed that the G and M1 endotherms merged at higher heating rates and at higher moisture contents as expected. A significant interaction was observed between moisture content and heating rate. The results suggest that the gelatinization process is governed by moisture content at the lower heating rates and by heating rate at the higher heating rates. Results from the AUW data suggest that the M1 component of gelatinization dominated at lower moisture content and lower heating rates. However, at higher moisture contents, an interaction was observed between moisture content and heating rate. The data suggest that at higher moisture content and at higher heating rate, there is still a kinetic limitation to the complete melting of the M1 endotherm.
5.1 Introduction

Starch gelatinization is understood as the conversion of native semicrystalline structure through a thermal process typically in the presence of water. Several models have been proposed to describe the molecular processes involved in the process of gelatinization (Donovan, 1979; Blanshard, 1987; Evans & Haisman, 1982; Biliaderis et al., 1986; Waigh et al., 2000a). The most recent description used the side-chain liquid crystalline model to explain gelatinization (Jenkin & Donald, 1998). Following gelatinization and upon storage, starch polymers tend to reassociate and this phenomenon is termed as retrogradation. Starch retrogradation is an important phenomenon, both scientifically and technologically, due to its relationship to product texture, sensory perception and nutritional quality. Consequently numerous studies have investigated this phenomenon; most studies have focused on dilute systems and only a few have focused on concentrated starch-water systems.

Starch gelatinization and retrogradation processes are kinetic in nature and depend on time, temperature, and moisture (Shiotsubo & Takahashi, 1984; Farhat et al., 2000). During baking the kinetic dependence becomes relevant where temperature and time play major role in determining the product structure and texture (Seetharaman et al., 2002; Patel et al., 2005). Patel et al. (2005) reported variations in heating rate ranging from 5 °C/min to 25 °C/min under practical conditions during baking and demonstrated differences in product texture and shelf life.
The different heating rates under limited moisture conditions are therefore likely to influence the mechanistic aspects of starch gelatinization. Biliaderis et al. (1986) based on their investigation at different heating rates proposed that starch gelatinization is a combination of simultaneous melting and recrystallization processes. These events result in two separate melting endotherms G and M1 at slower heating rates and which merge into one peak at faster heating rates. Tananuwong & Reid (2004) deconvoluted the G and M1 endotherms by using a DSC procedure and reported that the additional unfrozen water (AUW) content was dependent on the initial moisture content and larger AUW was found following M1 transition.

The objective of this research was to study the effect of heating rate at different moisture contents on starch retrogradation and gelatinization process.

5.2 Materials and Methods

5.2.1 Sample Preparation

Wheat starch used in the study was Midsol-50 which is a natural unmodified wheat starch (MGP ingredients, KS). The same starch was used for gelatinization as well as retrogradation studies. For the samples with low water content (0.7 and 1.0) starch and water were mixed and equilibrated overnight.
5.2.2 Sample Temperature Correction at Different Heating rates

Benzophenon (Sigma chemical Co., St. Louis, MO, USA) and oxalic acid (Fisher Scientific Co., Fair Lawn, NJ, USA) with melting temperatures of 48°C and 101.5 °C, respectively, were used to determine the actual sample temperature under different rates of heating. Samples were heated in sealed stainless steel pans from 25 °C to 120 °C at 5, 20, or 40 °C/min. The onset temperatures of melting endotherm at each heating rate was measured and compared to the respective actual melting temperatures of each compound.

At the highest heating rate the temperature lag at 50 °C was 1.8 °C and at 90 °C the lag was 4.9 °C. Therefore in the analysis of the data the measured DSC temperatures were corrected to represent actual temperatures.

5.2.3 Retrogradation Study as a Function of Heating Rate

Samples (0.7:1 or 2:1 water:starch ratio) were heated by using DSC (Pyris 7, Perkin Elmer, Norwalk, CT) from 25 °C to 95 °C at 5, 20, or 40 °C/min. Samples were then cooled rapidly to 25 °C at 100 °C/min and stored at 25 °C or 4 °C for retrogradation study. The stored samples were analyzed following 0, 1, 3, or 7 days by heating in DSC from -40 °C to 160 °C at 10 °C/min. Peak onset temperature and the gelatinization and retrogradation enthalpies were calculated by using the Pyris™ Software for windows (ver. 3.80). All analyses were conducted at least in duplicate and the average values are reported.
5.2.4 Starch-Water Interaction during Gelatinization

The starch-water interaction during the gelatinization process was characterized with AUW values and the DSC endotherm was deconvoluted as described by Tananuwong & Reid (2004). The $T_1$ is the temperature near the peak of the first endotherm (G endotherm) and $T_2$ is the temperature above the conclusion temperature of the overall gelatinization endotherm (G+M1 endotherm), at each heating rate respectively (Table 5-1). The M1 endotherm is the endotherm recorded when scanned to the final $T_2$ temperature, following the first scan up to G endotherm. The DSC samples were heated at heating rates of 5, 15, or 25 °C/min in a DSC (Pyris 7, Perkin Elmer, Norwalk, CT) with Pyris™ Software for windows (ver. 3.80). The samples were heated from -40 °C to $T_1$ or $T_2$ temperatures (Table 5-1), cooled to -40 °C at 30 °C/min and reheated to $T_2$. The G+M1, M1, and ice melting enthalpies were calculated by using the Pyris™ Software for windows (ver. 3.80). The amount of frozen water was calculated using area under ice melting curve and the known heat of fusion of ice 334.7 J/g. AUW as a result of partial or complete gelatinization (AUW$_G$, AUW$_{M_1}$, AUW$_{G+M_1}$) was calculated as the difference between sequential scans.
Table 5-1: T1 and T2 temperatures used in the DSC temperature program

<table>
<thead>
<tr>
<th>Water content (g water/ g dry starch)</th>
<th>Temperatures at different heating rates (°C)</th>
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<th>15 (°C/min)</th>
<th>25 (°C/min)</th>
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<td>T1 T2 T1 T2</td>
<td>T1 T2 T1 T2</td>
<td></td>
</tr>
<tr>
<td>0.7</td>
<td>58 103 62 107 68 113</td>
<td>60 95 66 99 70 103</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.0</td>
<td>60 95 66 99 70 103</td>
<td>60 95 66 99 70 103</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.5</td>
<td>58 81 64 97 69 95</td>
<td>58 81 64 97 69 95</td>
<td></td>
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<tr>
<td>2.0</td>
<td>58 81 64 97 69 95</td>
<td>58 81 64 97 69 95</td>
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</tr>
<tr>
<td>3.0</td>
<td>58 81 63 85 70 95</td>
<td>58 81 63 85 70 95</td>
<td></td>
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</tbody>
</table>

5.2.5 Statistics

All samples were analyzed in duplicate and average values are reported. The graphs represent error bars extending one standard deviation above and below the mean value.

5.3 Results and Discussion

5.3.1 Effect of Different Heating rate on Retrogradation

The retrogradation study was conducted at a water:starch ratio of 2.0 and 0.7 representing excess and limited moisture conditions, respectively. Amylopectin recrystallization as a function of heating rate did not show any particular trend. However, the changes in amylopectin recrystallization upon storage on the basis of storage time, storage
temperature, and moisture content were typical of what has been reported in the literature (Fig 5.1, 5.2); i.e., amylopectin recrystallization increased with storage time (Giovanelli et al., 1997; Levine & Slade, 1990; Zeleznak & Hoseney, 1986), was higher at the lower storage temperature (Farhat et al., 2000; Levine & Slade, 1990; Zeleznak & Hoseney, 1987), and lower at the higher moisture concentration (Zeleznak & Hoseney, 1986). Amylopectin recrystallization increased rapidly during the first day of storage at either temperature of storage and thereafter the rate of increase was slow (Giovanelli et al., 1997, Zeleznak & Hoseney, 1987).

Fig 5.1: Amylopectin recrystallization at 25 °C storage for different storage period

Note: ● – 5 °C/min (0.7:1 water:starch); ■ – 20 °C/min (0.7:1 water:starch); ▲ – 40 °C/min (0.7:1 water:starch); ○ – 5 °C/min (2:1 water:starch); □ – 20 °C/min (2:1 water:starch); Δ – 40 °C/min (2:1 water:starch).
Amylopectin recrystallization is thought to be one of the factors responsible for staling of baked products and is generally reflected as increased firmness in product texture. The absence of any functional relationship between heating rate and amylopectin recrystallization suggests that the amount of crystallinity is not critical to firmness development in baked product. Hug-Iten et al. (2001) reported that breads with smaller

Fig 5.2: Amylopectin recrystallization at 4 °C storage for different storage period

Note: ● – 5 °C/min (0.7:1 water:starch); ■ – 20 °C/min (0.7:1 water:starch); ▲ – 40 °C/min (0.7:1 water:starch); ○ – 5 °C/min (2:1 water:starch); □ – 20 °C/min (2:1 water:starch); △ – 40 °C/min (2:1 water:starch).
amylopectin crystals did not increase firmness while breads with larger crystals exhibited increased firmness development. However, Seetharaman et al. (2002) and Patel et al. (2005) reported the influence of heating rate on firmness development in baked products. Since heating rate influenced baked product texture, but is apparently not related to amylopectin recrystallization, it is important to further understand the changes to starch granules during gelatinization as a function of heating rate.

It has been reported that the order-disorder transition of crystallites continues well beyond the end temperature of DSC endotherm (Jenkins & Donald, 1998; Waigh et al., 2000a). Therefore it is likely that the final temperature of 95 °C used in this study did not completely melt all of the ordered structures. These remnant ordered structures could serve as a nuclei for amylopectin recrystallization during storage and could explain the lack of differences in the enthalpy of amylopectin recrystallization at different heating rates.

5.3.2 Deconvolution of DSC Endotherm

Gelatinization is a non-equilibrium process and depends on moisture content and heating rate (Biliaderis et al., 1986; Shiotsubo & Takahashi, 1984). Donovan (1979) reported that the gelatinization endotherm is composed of two components, G and M1 endotherms. With increasing heating rates and with increasing moisture contents, the G and M1 endotherms merged as seen in the DSC profile (Fig. 5.3, 5.4). The G and M1 components
of these endotherms were deconvoluted by using the technique described by Tananuwong and Reid (2004).

Fig 5.3: G and M1 portion of gelatinization endotherm as a function of heating rate (water:starch ratio 1)
Fig 5.4: G and M1 portion of gelatinization endotherm as a function of moisture content (5 °C/min heating rate)

Fig. 5.5 shows the total gelatinization enthalpy (G+M1) at different moisture contents when heated at different heating rates. The total gelatinization enthalpies when heated at 15 or 25 °C/min were not significantly different at all moisture contents investigated. However at 5 °C/min, the enthalpy peaked at a water:starch ratio of 1 and decreased at the ratios above 1. The M1 enthalpy at different moisture contents when heated at different heating rates is shown in Fig. 5.6. The M1 enthalpy decreased with increasing heating rate at all moisture contents. At 5 and 15 °C/min, the M1 enthalpy peaked at a water:starch ratio of 1 and decreased at higher water contents, similar to that observed for
G+M1. The M1 endotherm at 5 °C/min and 25 °C/min comprise 73% and 29%, respectively, of total gelatinization enthalpy at a water:starch ratio of 1. Therefore, the changes in the G+M1 and M1 enthalpies at water:starch ratio of 1 at slow and fast heating rates clearly indicate the interactions between water and heating rate. This interactions highlight differences in the mechanistic aspects of gelatinization as governed by moisture and/or heating rate.

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**Fig 5.5:** Effect of heating rate on gelatinization enthalpy for total gelatinization (G+M1) at different water:starch ratios (0.7, 1, 1.5, 2, and 3)
Jenkins & Donald (1998) and Waigh et al. (2000a) described the gelatinization process at a molecular level based on smectic, nematic, and isotropic helix to coil transitions at different moisture regimes. The results for G+M1 endotherm in this study at higher moisture content (≥1.5 water:starch ratio) suggest that heating rate is not a factor at these moisture contents, since the temperature for T_{hc} (Temperature for helix coil transition) transition is less than temperature for dissociation of T_{ss} (Temperature for helix side-by-side dissociation) in the crystallites (Waigh et al., 2000a). Furthermore, as discussed above, the onset temperature of G+M1 endotherm increased with increasing heating rate (Fig. 5.3). Therefore, the onset of T_{ss} is higher at higher heating rates and as soon as T_{ss} is
reached, the $T_{hc}$ transition would occur instantaneously thus decreasing the M1 component at higher heating rate.

The events occurring at a water:starch ratio of $<$1.5 exhibit a different trend and therefore require a different set of explanations. At a water:starch ratio of $<$1.5, it is likely that $T_{hc}$ is higher than $T_{ss}$. Therefore, the dissociation of $T_{ss}$ occurs first followed by $T_{hc}$ transition.

Biliaderis et al. (1986) following studies using heating rate as variable, proposed that at slower heating rates there is recrystallization occurring simultaneously with melting that in turn gives rise to the second melting peak (M1). The very high proportion of M1 endotherm when heated at 5 °C/min at a water:starch ratio of 1 (73%) supports the argument of simultaneous crystal formation. This is likely because of the slower heating rate and the increased time available for recrystallization. The same mechanism, however, does not appear to apply at a water:starch ratio $>$1, because the recrystallization of amylopectin is maximum between 45 to 55% moisture and is lower below 45% and above 55% moisture contents as reported by Zeleznak & Hoseney (1986). The decrease in the proportion of M1 endotherm with increasing heating rare is likely due to kinetic limitation of the recrystallization process. The lower G+M1 and M1 values at a water:starch ratio of 0.7 compared to 1 is likely due to limited moisture content that in turn minimizes the extent of recrystallization as explained earlier.
5.3.3 Starch-Water Interactions

Figures 5.7 to 5.9 show the plots of different AUW contents as a function of heating rate. The AUW\(_{G+M1}\) increased with heating rate at a water:starch ratio of 0.7 and 1.5 while they were not significantly different at the other moisture contents. The AUW\(_{G+M1}\) values were higher at water:starch ratio less than 1.5 by almost a factor of two. AUW\(_G\) values increased significantly with increasing heating rate at a water:starch ratio of 1.5 and the values were not significantly different at all the other water contents. AUW\(_{M1}\) decreased significantly at a water:starch ratio greater than 1. The AUW\(_{M1}\) component was a larger proportion of AUW\(_{G+M1}\) at a water:starch ratio less than 1.5. The changes in AUW values as a function of water content at all heating rates followed a trend similar to that reported by Tananuwang and Reid (2004).
Fig 5.7: Effect of heating rate on AUW$_{G+M1}$ at different water:starch ratios (0.7, 1, 1.5, 2, and 3)
Fig 5.8: Effect of heating rate on AUW$_G$ at different water:starch ratios (0.7, 1, 1.5, 2, and 3)
Results reported earlier show that the M1 endotherm merges into the G endotherm with either increasing moisture content or increasing heating rate (Fig. 5.3 & 5.4). Therefore, the AUW$_{M1}$ values at the higher moisture content should be similar at all heating rates, since the M1 endotherm has merged with the G endotherm. The effect of temperature lag at higher heating rates should not be a factor since all samples have been scanned to their respective final T2 temperatures. However, the results in Fig. 5.9 show that AUW$_{M1}$ decreased with increasing heating rate even at a water:starch ratio higher than 1.5. This suggests that at higher heating rates there is a decreased binding of water by the starch resulting in a decreased AUW$_{M1}$ value. Therefore, it is likely that there are residual crystalline structures in the samples heated at 25 °C/min at a water:starch ratio greater
than 1.5. This observation supports the earlier data (Figs. 5.1 & 5.2) presented in this study wherein retrogradation, as measured by amylopectin recrystallization enthalpy, was not influenced by heating rate. These results also support the hypothesis proposed by Patel et al., (2005) that at higher heating rate the residual crystalline matter acts as nuclei and induces smaller amylopectin crystals which do not contribute to the baked product firmness. Therefore, even though the enthalpy of recrystallization is similar at the different heating rates, the textural properties are influenced by the heating rate.

5.4 Conclusions

The key observations from this study point to the following conclusions.

1. Retrogradation, as measured by amylopectin recrystallization, is not influenced by heating rate.

2. A significant interaction was observed between moisture content and heating rate in their effects on the gelatinization process. The results suggest that the gelatinization process is governed by moisture content at the lower heating rates and by heating rate at the higher heating rates.

3. Results from the AUW data suggest that the M1 component of gelatinization dominated at lower moisture content and lower heating rates. However, at higher moisture contents, an interaction was observed between moisture content and heating rate.

4. The data also suggest that at higher moisture content and at higher heating rate, there is still a kinetic limitation to the complete melting of the M1 endotherm.
Chapter 6
Discussion and Conclusions

Although bread staling has been studied for more than a century and a half, staling is still a major cause of economical loss to both the baking industry and the consumer. Much of the earlier research targeted shelf life improvements by using various raw materials, ingredients and through improved packaging. A majority of these researchers did not alter the baking conditions because of the possible risk of under baking or over baking (Maga, 1975; Yasugana et al., 1968).

Development of non-conventional baking technologies led to optimization studies where baking oven conditions and baking times were optimized for different baked products (He and Hoseney, 1991; Junge and Hoseney, 1981; Yin and Walker, 1995) such that comparable quality was obtained to that baked in conventional oven. Most of these studies considered the changes in modes of heating and modified the baking conditions (time and temperature) to take the advantage of the economy of non-Conventional process as well as the convenience. The changes in quality were noticed for different products and the difference was attributed to starch granule morphology and extent of granule disruption (Faridi and Rubenthaler, 1984; Martin et al., 1991; Yasunaga et al., 1968). However, none attempted to understand the impact of conventional or non-conventional heating method on starch gelatinization during baking, which plays critical
role in establishing textural attributes of the finished products (Dreese et al., 1988; Hayman et al., 1998).

Changes in starch when heated in presence of sufficient water are collectively referred to as gelatinization. Thus, gelatinization includes many individual events such as glass transition of amorphous regions, hydration, granule swelling, loss of birefringence, leaching of polymers, and granule solubilization, followed by formation of polymer network up on cooling. Though these changes collectively represent gelatinization process, it is not clear whether under a given condition of moisture content and heat, how these events are related with each other. Different theories of gelatinization have been proposed to explain these relationships as explained previously in section 2.5. The latest of these theories proposed by Donald and co-workers based on chiral side-chain liquid crystal model comprehensively explained most of the observed changes in starch during heating. Since gelatinization is not an equilibrium process these changes depend on heating conditions. Further, these changes are difficult to follow individually as a function of heating because of temperature and moisture interaction (5.4 conclusions). We believe that these individual events associated with gelatinization under different heating conditions are essentially not similar and will result in different starch properties.

In previous research, Seetharaman et al. (2002) illustrated this by comparing hamburger buns and tortillas; similar products but baked by using two distinctly different conditions. The differences in starch properties due to different baking conditions were successfully demonstrated based on pasting and thermal properties measured following baking. A
caveat in this study was the difference in bun and tortilla formulation. In the next study (Patel et al., 2005; Chapter 3) we addressed the formulation difference by investigating breads, with extensive research available for reference, baked from same dough under different baking conditions.

In our study starch properties were measured in terms of amylopectin recrystallization, pasting, and amylose solubility as a function of heating rate. Amylopectin recrystallization, pasting viscosity, and amylose solubility were observed to increase with increasing heating rate, corresponding with higher firmness at faster heating rate. All these starch properties measured indicate relationships between extent of starch granule solubilization and amylose leaching as a result of different processing conditions. At higher heating rates more amylose remained inside the starch granule that could be easily solubilized in dilute alkali. Pasting viscosity increased with heating rate due to less granule dispersion at higher heating rates during baking. Subsequently upon storage amylopectin recrystallization was observed to increase with heating rate, due to less granule dispersion and more residual ordered structures that provide nuclei for recrystallization of amylopectin. These changes due to heating rate at molecular level are likely reflected as increased firmness in texture related changes during storage.

The baking step does not result in complete dispersion of starch granules for most baked products due to intermediate moisture contents. Under these conditions, two starch gelatinization mechanism models, ‘boil-in-bag’ (Atkin et al., 1998) and ‘liquid-crystal-side chain’ (Waigh et al., 2000b), could be successfully employed to explain the
influence of heating rate on baked product textural quality at starch granular level and molecular level, respectively.

However, in this study microwave heating led to outlier data points due to possible molecular modifications in food which are not clearly understood to-date. The influence of microwave on starch at granular and molecular level during gelatinization in excess as well as limited moisture systems has been investigated in our laboratory (Palav and Seetharaman, 2006 in review).

The influence of heating rate on starch granule swelling and morphological changes was further investigated using a hot-stage microscopy (Patel and Seetharaman, 2006; chapter 4). Starch granules form the structural building blocks for most of the baked products when observed under a microscope and are held together by starch exudates and/or the gluten network (Bechtel et al., 1978; Moss, 1975; Varriano-Marston et al., 1980). This highlights the role of swelling and morphological changes in starch granule during baking in the development of typical textural attributes. Furthermore, Genovese and Rao (2003) conclusively demonstrated that fractal dimensions of starch granule play a major role along with volume fraction and rigidity in determining the rheological properties of starch suspensions rather than exudates at moisture conditions similar that of interest in our study. The hot-stage microscopy provided visual evidence supporting our hypothesis that heating rate influence starch granule morphology and size increase (Fig 4.1 and 4.2a, b). Slow heating rate of 5°C/min resulted in extensive morphological changes in granule shape, i.e., extensive folding whereas at faster heating rate of 25°C/min starch granules
still retained their rounded shape with limited folding. Furthermore, the increase in granule size occurred at a higher temperature when heated at 25°C/min compared to 5°C/min. These differences potentially resulted in altered patterns of amylose leaching and network formation thus providing a likely explanation for differences in gel properties and baked product texture. These differences in granule morphology and amylose leaching reflect change in the molecular order-disorder transformations during gelatinization at molecular level that can be investigated by using a DSC.

Variations in gelatinization process were further investigated as a function of heating rate by using a DSC (Chapter 5). Starch retrogradation, as measured by amylopectin recrystallization, was not influenced by heating rate. The retrogradation was observed to increase during first 3 days and afterwards it leveled off. Firmness of breads (section 3.3.3) also followed the trend and increased during storage. However, firmness did not level off after 3 days in all samples which clearly indicates that heating rates applied during baking altered the starch granule structure in a manner that even though the extent of crystallinity is same it does not result in same firmness due to nature of the crystallinity. The importance of amylopectin recrystallization is confounded when analyzed by using a DSC since the procedure does not distinguish the size, location and arrangement of crystalline regions. Some researchers have shown results that raise the question on relationship between the amylopectin recrystallization and firmness development. A rapid increase in crystallinity was observed by X-ray analysis that was corroborated by development of birefringence in bread when treated with amylases. However, the product did not show corresponding firmness development (Hug Iten et al.,
The small crystalline regions induced by hydrolyzed polymers favored recrystallization but due to numerous small crystalline regions the texture remained soft. Similarly, faster heating rate limits granule dispersion along with accumulation of amylose inside the granule, which results in amylose interspersed between amylopectin crystalline regions. Further, due to faster heating rate, the helix to coil dispersion is incomplete leading to more residual crystalline structures, which provide nuclei for crystal growth. Thus, due to more nuclei large number of small crystalline arrangements are developed which would show same crystal melting enthalpy but not similar in structural quality.

A significant interaction was also observed between moisture content and heating rate in their effects of the gelatinization process. The results suggest that different stages of gelatinization process (granule swelling, water uptake, helix-coil dissociation, helix-helix dissociation, loss of birefringence, granule rupture) are governed by moisture content when heated at lower heating rate. However, at higher heating rate different stages of the gelatinization process are altered as evident from DSC endotherms. Further, the extent of granule dispersion was indirectly obtained from AUW data. The results suggest that the M1 component of gelatinization dominated at lower moisture content and lower heating rates. However, at higher moisture contents, an interaction was observed between moisture content and heating rate. The results also suggest that at higher moisture content and at higher heating rate, there is still a kinetic limitation to the complete melting of the M1 endotherm.
The results from the above mentioned studies (chapters 3-5) conclusively state that the baking conditions play a role in determining the textural quality and shelf life of baked products.

The different aspects of baking process identified as heating rate, final heating temperature, and time at final temperature influence the starch gelatinization with respect to swelling and morphology of granules, endothermic transitions at molecular level, or viscosity which manifests in terms of final product quality and shelf life. The heating rate experiments clearly show delay in swelling at faster heating rate which is also observed from DSC endotherms where the G endotherm peak temperature increased with increasing heating rate. Furthermore, at slower heating rate the granule morphology was altered extensively corresponding the larger time periods available for molecular transitions to take place as evident by increased M1 enthalpy at slow heating rates. Thus, at higher heating rates the order-disorder transitions are not as extensive as the same at slower heating rate indicating the possible presence of residual ordered structures. These ordered structures serve as a nuclei and in case of faster heating rate more number of nuclei result in large number of small crystals which is opposite for slow heating conditions where we get small number of large crystals. Thus, even though the amount of crystallinity appeared same for all heating rates the type of crystallinity determines the textural property during storage. The granule structures that determine the textural properties are in turn also influenced by final heating temperature and time at that temperature.
Similar to heating rate, final temperature and time at final temperature represented by stage III in the thermal profile (Fig 3.1) towards the end of baking was also investigated for starch paste rheological properties. Pasting experiment results (appendix B) show that by selecting a combination of temperature and holding time at that temperature, a particular viscosity of system can be attained, i.e., desired viscosity can be attained using combination of time-temperature parameters. During long holding the granule disruption was observed to be a function of temperature and a significant drop in viscosity was observed during first 15-20 min of holding, and after that a gradual decrease is observed. These observed differences were significantly reflected in cold paste viscosity too, i.e., during cooling and holding at 50 °C depending on the final heating temperature retrogradation was different. Thus, different aspects of baking profile, i.e., heating rate, final temperature and time at final temperature are critical in obtaining good quality final product.
Chapter 7

Future Research

The present research clearly indicates that baking conditions in terms of heating rate, final temperature, and time at final temperature play role in determining the textural quality and shelf life of finished product, by altering the gelatinization and retrogradation processes encountered during baking and storage.

The next step of experiments should measure dynamic rheological properties ($G'$ and $G''$) at different treatments replicating the variety of baking conditions encountered in the present research. The results would provide relationship between the conditions of baking and structural properties at molecular level being influenced by characteristic molecular relaxation as a direct consequence of baking treatments. The experiment would involve a set of variables including heating rate, final temperature, time at final temperature, cooling rate, cooling temperature, storage temperature, and moisture.

Another rheological experiment would be designed to measure dynamic rheological properties as well as large scale deformation properties of starch water suspensions at above mentioned factors. Here the treated samples would be equilibrated at different water activities ranging from 0.2 to 0.9. The dynamic rheological properties of the treated samples would reveal relationships between $T_g$ and treatments which could be correlated with the large scale deformation results. This would clarify the understanding
of relationship between baking conditions and textural properties in terms of molecular mobility and interactions.

NMR based experiments would be designed with similar factors as previous sets of experiment. The results from NMR studies would explain the influence of baking conditions in terms of molecular mobility and starch water interactions. This relationship between baking condition and molecular mobility and molecular structures would support the results from previous two rheological studies. Moreover, it would corroborate as well as clarify the relationship between the baking conditions and textural properties in terms of molecular mobility and molecular associations.

As mentioned in section 2.5 the mechanism of gelatinization and time of different stages as the gelatinization progresses under different moisture and heating rate conditions is still unclear. To understand the impact of amylose in this mechanism we heated starch in iodine solution with different concentrations. Due to inability of iodine complexed amylose to leach out of granule the gelatinized granules were still observed to retain partial molecular order in granule resulting in Maltese cross when observed under birefringent light. The micrograph is shown in appendix C and manuscript is also submitted for publication. These results support our hypothesis and also corroborate that the gelatinization process as understood at present does not describe the set of changes taking place during cooking of starch and starch based products.
Based on the understanding from the results of these experiments the ultimate goal would be to propose baking processes with definite parameters which would produce a final product with desired characteristics. Thus, baking process could be customized (time and temperature cycles during baking) for attaining the desired final product properties in terms of texture and shelf life. The ultimate baking process could be a multi-stage baking process involving controlled stages of heating, holding, and cooling.


### Appendix A

**Baking parameters used in various studies**

<table>
<thead>
<tr>
<th>Study</th>
<th>Mass (g)</th>
<th>Temperature (°C)</th>
<th>Time (min)</th>
<th>Oven Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>Larsen and Greenwood (1991)</td>
<td>794g</td>
<td>230</td>
<td>25</td>
<td>MDD baking</td>
</tr>
<tr>
<td>Oliver and Allen (1992)</td>
<td>180g</td>
<td>225</td>
<td>20</td>
<td>Rotating hearth oven</td>
</tr>
<tr>
<td>Yamada and Preston (1992)</td>
<td>170g</td>
<td>195</td>
<td>25</td>
<td>Heat sink oven</td>
</tr>
<tr>
<td>Morrison et al. (1989)</td>
<td>~425g</td>
<td>CBP</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gan et al. (1989)</td>
<td>460g</td>
<td>230</td>
<td>25 min</td>
<td></td>
</tr>
<tr>
<td></td>
<td>56g</td>
<td>225</td>
<td>20 min</td>
<td></td>
</tr>
<tr>
<td>Westerlund et al. (1989)</td>
<td>500g</td>
<td>210</td>
<td>22min &amp; 35min</td>
<td>Convection oven (0.8m/s air velocity); 20s steam at start</td>
</tr>
<tr>
<td>Tait and Galliard (1988)</td>
<td>900g</td>
<td>225</td>
<td>30min</td>
<td>Rotary test baking oven</td>
</tr>
<tr>
<td>Haglund et al. (1998)</td>
<td>700g</td>
<td>210</td>
<td>38-40min</td>
<td></td>
</tr>
<tr>
<td>Armero and Collar (1998)</td>
<td>100g</td>
<td>190</td>
<td>20min</td>
<td></td>
</tr>
<tr>
<td>Wikstrom and Bohlin (1999)</td>
<td>100g</td>
<td>220</td>
<td>20min</td>
<td></td>
</tr>
<tr>
<td>Author, <strong>et al.</strong>, (Year)</td>
<td>Weight (g)</td>
<td>Temperature (°C)</td>
<td>Time (min)</td>
<td>Oven Type</td>
</tr>
<tr>
<td>---------------------------</td>
<td>------------</td>
<td>-----------------</td>
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<td>-----------</td>
</tr>
<tr>
<td>Faegestad, <strong>et al.</strong>, (2000, Faergestad, <strong>et al.</strong>, 1999)</td>
<td>150g, 100 and 150g</td>
<td>220C</td>
<td>20min</td>
<td>Rotatong hearth oven preheated to 250C</td>
</tr>
<tr>
<td>Engelsen, <strong>et al.</strong>, (2001)</td>
<td>~425g</td>
<td>230C</td>
<td>25min</td>
<td></td>
</tr>
<tr>
<td>Alava, <strong>et al.</strong>, (2001)</td>
<td>454g</td>
<td>244c</td>
<td>25min</td>
<td>Direct gas fired reel tray oven</td>
</tr>
<tr>
<td>Sahi, (2003)</td>
<td>~800g</td>
<td>243C</td>
<td>30min</td>
<td>Gas fired reel oven</td>
</tr>
<tr>
<td>Elmehdi, <strong>et al.</strong>, (2003)</td>
<td>CC ref</td>
<td>205C</td>
<td>30 min</td>
<td></td>
</tr>
<tr>
<td>Kihlberg, <strong>et al.</strong>, (2004, Kihlberg, <strong>et al.</strong>, 2006)</td>
<td>240g</td>
<td>220C</td>
<td>20min</td>
<td>97-98C crumb temperature</td>
</tr>
<tr>
<td>Sliwinski, <strong>et al.</strong>, (2004)</td>
<td>Calculate</td>
<td>240C</td>
<td>45 min</td>
<td></td>
</tr>
<tr>
<td>Andersson, <strong>et al.</strong>, (2004)</td>
<td>100g</td>
<td>242C</td>
<td>12 min</td>
<td></td>
</tr>
<tr>
<td>Shogren, <strong>et al.</strong>, (1969)</td>
<td>218 – 15</td>
<td>18</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CC 20 – 1943 194</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Magnus, <strong>et al.</strong>, (1997)</td>
<td>230 - 20</td>
<td>100</td>
<td></td>
<td>Rotating hearth oven</td>
</tr>
<tr>
<td>Pollock, and Geddes, (1960a)</td>
<td>250g</td>
<td>232C</td>
<td>25 min</td>
<td></td>
</tr>
<tr>
<td>Pollock, and Geddes, (1960b)</td>
<td>40g</td>
<td>232C</td>
<td>15min</td>
<td></td>
</tr>
<tr>
<td>Wiseblatt, and Kohn, (1960)</td>
<td>18.5oz</td>
<td>232C</td>
<td>25min</td>
<td></td>
</tr>
<tr>
<td>Reference</td>
<td>Weight</td>
<td>Temperature</td>
<td>Time</td>
<td>Notes</td>
</tr>
<tr>
<td>------------------------------------------</td>
<td>--------</td>
<td>-------------</td>
<td>------</td>
<td>--------------------------------------------</td>
</tr>
<tr>
<td>Irvine, and McMullan, (1960)</td>
<td>165-170g</td>
<td>220C</td>
<td>25min</td>
<td></td>
</tr>
<tr>
<td>Pomeranz, (1960)</td>
<td>580g</td>
<td>220C</td>
<td>50min</td>
<td></td>
</tr>
<tr>
<td>Minett, et al., (1976)</td>
<td>590g</td>
<td>230C</td>
<td>35min</td>
<td></td>
</tr>
<tr>
<td>Patil, et al., (1976)</td>
<td>10g and 17g</td>
<td>218C</td>
<td>15min</td>
<td></td>
</tr>
<tr>
<td>Khan, et al., (1975)</td>
<td>Pound loaves</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ling, et al., (1976)</td>
<td>~180g</td>
<td>218C</td>
<td>25min</td>
<td></td>
</tr>
<tr>
<td>Klamczynski, and Czuchajowska, (1999)</td>
<td>355g</td>
<td>175C</td>
<td>54min</td>
<td>Quick bread (egg, sugar added)</td>
</tr>
<tr>
<td>Lu, and Grant, (1999)</td>
<td>160g</td>
<td>218C</td>
<td>25min</td>
<td></td>
</tr>
<tr>
<td>Zghal, et al., (1999)</td>
<td></td>
<td>204C</td>
<td>30min</td>
<td></td>
</tr>
<tr>
<td>Hayashi, and Seguchi, (1999)</td>
<td>120g</td>
<td>210C</td>
<td>30min</td>
<td></td>
</tr>
<tr>
<td>Kusunose, et al., (1999)</td>
<td>165g</td>
<td>220C</td>
<td>25min</td>
<td></td>
</tr>
<tr>
<td>Bakers digest 45-26 1971</td>
<td></td>
<td></td>
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<td></td>
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<td>Bakers digest 1971 45-20</td>
<td></td>
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<td></td>
</tr>
<tr>
<td>Macritch.F, and Gras, (1973)</td>
<td>~50g</td>
<td>185C</td>
<td>17min</td>
<td></td>
</tr>
<tr>
<td>Authors</td>
<td>Year(s)</td>
<td>Weight</td>
<td>Temperature</td>
<td>Time</td>
</tr>
<tr>
<td>-------------------------</td>
<td>---------</td>
<td>--------</td>
<td>-------------</td>
<td>--------</td>
</tr>
<tr>
<td>Ranhotra</td>
<td>1972</td>
<td></td>
<td>232°C</td>
<td>20min</td>
</tr>
<tr>
<td>Kilborn, and Tipples</td>
<td>1972, 1979</td>
<td>170g</td>
<td>221°C</td>
<td>25 min</td>
</tr>
<tr>
<td>Orth / Mander</td>
<td></td>
<td>170g</td>
<td>Same (?) Australian team</td>
<td></td>
</tr>
<tr>
<td>Patel, and Johnson</td>
<td>1975</td>
<td>400g</td>
<td>211°C</td>
<td>25 min</td>
</tr>
<tr>
<td></td>
<td></td>
<td>150g</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Betschart, et al.</td>
<td>1975</td>
<td>150g</td>
<td>220°C</td>
<td>25 min</td>
</tr>
<tr>
<td>Tabekhia, and Dappolonia</td>
<td>1979</td>
<td>50g</td>
<td>221°C</td>
<td>30 min</td>
</tr>
<tr>
<td>Dick, et al.</td>
<td>1979</td>
<td>170g</td>
<td>221°C</td>
<td>20 min</td>
</tr>
<tr>
<td>Sahlstrom, et al.</td>
<td>1999</td>
<td>600g</td>
<td>220°C</td>
<td>25 min</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Bago Line BEX 1.0 Denmark</td>
<td></td>
</tr>
<tr>
<td>Wang, and Sun</td>
<td>1999</td>
<td>170g</td>
<td>221°C</td>
<td>24 min</td>
</tr>
<tr>
<td>Vadlamani, and Seib</td>
<td>1999</td>
<td>170</td>
<td>218°C</td>
<td>24 min</td>
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<td>Uthayakumaran, et al.</td>
<td>1999, 2001</td>
<td>2.4g</td>
<td>200°C</td>
<td>17min</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Micro baking method</td>
<td></td>
</tr>
<tr>
<td>Nelles, et al.</td>
<td>1998</td>
<td>900g</td>
<td>230°C</td>
<td>30 min</td>
</tr>
<tr>
<td>Hareland, and Puhr</td>
<td>1998</td>
<td>500g</td>
<td>204°C</td>
<td>22 min</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Rotating oven</td>
<td></td>
</tr>
</tbody>
</table>
| Author(s) and Year | Sample Weight | Temperature | Duration | Equipment/
Procedure |
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Barrett et al., 2000</td>
<td>70g</td>
<td>175°C</td>
<td>40 min</td>
<td>Rotary oven</td>
</tr>
<tr>
<td>Hugo et al., 2000</td>
<td>950g</td>
<td>230°C</td>
<td>30 min</td>
<td></td>
</tr>
<tr>
<td>Mikhaylenko et al., 2000</td>
<td>Finney 1984</td>
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<td></td>
</tr>
<tr>
<td>Zghal et al., 2001</td>
<td>~375g</td>
<td>223°C</td>
<td>27 min</td>
<td></td>
</tr>
<tr>
<td>Bugusu et al., 2001</td>
<td>120g</td>
<td>219°C</td>
<td>25 min</td>
<td></td>
</tr>
<tr>
<td>Antes and Wieser, 2001, Kieffer et al., 1998</td>
<td>17g</td>
<td>230°C</td>
<td>10 min</td>
<td></td>
</tr>
<tr>
<td>Repeckiene et al., 2001</td>
<td>200</td>
<td>186°C</td>
<td>45 min</td>
<td>Rotary test baking (Henry Simon)</td>
</tr>
<tr>
<td>Campbell et al., 2001</td>
<td>250g</td>
<td>225°C</td>
<td>25 min</td>
<td>Simon rotary test baking oven (Robinson Milling Systems Ltd., UK)</td>
</tr>
<tr>
<td>Kim et al., 2005</td>
<td>130g</td>
<td>220°C</td>
<td>20 min</td>
<td></td>
</tr>
<tr>
<td>Barrett et al., 2005</td>
<td>70g</td>
<td>175°C</td>
<td>20-25 min</td>
<td>Rotary oven</td>
</tr>
<tr>
<td>Park et al., 2005</td>
<td>CC 81 699</td>
<td></td>
<td></td>
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<tr>
<td>CC 83 290-301</td>
<td>Fargesta et al ref.</td>
<td>220°C</td>
<td>Rotating hearth oven</td>
<td></td>
</tr>
<tr>
<td>Ahlborn et al., 2005</td>
<td>600g</td>
<td>190°C</td>
<td>50 min</td>
<td>Staling Low protein Gluten free</td>
</tr>
<tr>
<td>----------------------</td>
<td>-------------</td>
<td>------</td>
<td>----------</td>
<td></td>
</tr>
<tr>
<td></td>
<td>450</td>
<td>210C</td>
<td>60 min</td>
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<tr>
<td></td>
<td>600</td>
<td>220 – 240 C</td>
<td>40 min</td>
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<td>What diff they found?</td>
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<tr>
<td>Xie, et al., (2004)</td>
<td>210g</td>
<td>218C</td>
<td>26 min</td>
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<td></td>
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<td>Staling (starch, prot, storage temp – staling effect)</td>
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<tr>
<td>Sahlstrom, et al., (2004)</td>
<td>35g</td>
<td>220C</td>
<td>12 min</td>
<td></td>
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<tr>
<td>Dobraszczyk, et al., (2003)</td>
<td>400g Chorleywood Bread Process</td>
<td>220C</td>
<td>12 min</td>
<td></td>
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<tr>
<td>Watanabe, et al., (2004)</td>
<td>AACC 10-10B</td>
<td>200C</td>
<td>20 min</td>
<td></td>
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<tr>
<td>Moore, et al., (2004)</td>
<td>400g</td>
<td>230C</td>
<td>30 min</td>
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<td></td>
<td>500g</td>
<td>190C</td>
<td>45 min</td>
<td></td>
</tr>
<tr>
<td></td>
<td>500g</td>
<td>180C</td>
<td>45 min</td>
<td></td>
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<td>Study</td>
<td>Weight</td>
<td>Temperature</td>
<td>Method</td>
<td>Equipment</td>
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<tr>
<td>Seguchi, and Abe, (2004)</td>
<td>130g</td>
<td>210C</td>
<td>Structure</td>
<td>DN 63 (Yamato Scientific Co. Ltd. Japan)</td>
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<td>Zhang, et al., (2004)</td>
<td>1220g</td>
<td>218C</td>
<td>Jet air oven</td>
<td>(aim of the study)</td>
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<tr>
<td>Baik, and Chinachoti,</td>
<td>~360g</td>
<td>160C</td>
<td>Bread machine</td>
<td>(Baker’s production)</td>
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<tr>
<td>(2003)</td>
<td></td>
<td>50min</td>
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<tr>
<td>Sharadanant, and Khan,</td>
<td>160g</td>
<td>218C</td>
<td>Staling –</td>
<td>Gums, frozen dough</td>
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<tr>
<td>(2003)</td>
<td></td>
<td>25 min</td>
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<tr>
<td>Wennermark, and Jagerstad,</td>
<td>420g</td>
<td>250C-</td>
<td>Tunnel oven</td>
<td></td>
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<tr>
<td>(1992)</td>
<td></td>
<td>220C</td>
<td></td>
<td></td>
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<tr>
<td>JFS 56- 1699-1701 &amp; 1706</td>
<td></td>
<td>Microwave</td>
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<td></td>
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<tr>
<td>Zanoni, et al., (1991)</td>
<td>205g</td>
<td>205C</td>
<td>Electric oven</td>
<td>Moretti Model, Miulan – Italy</td>
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<tr>
<td>Yue, et al., (1991)</td>
<td>~170g</td>
<td>221C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Abbott, et al., (1991)</td>
<td>23g</td>
<td>204C</td>
<td>Bread rolls</td>
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<tr>
<td>Rasco, et al., (1990)</td>
<td></td>
<td>AACC 10-10B</td>
<td></td>
<td></td>
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<tr>
<td>Sernasaldivar, et al.,</td>
<td>~170g</td>
<td>250C</td>
<td>Gas fired oven</td>
<td></td>
</tr>
<tr>
<td>(1988)</td>
<td></td>
<td>10 min</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>24min</td>
<td></td>
<td></td>
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<tr>
<td>Authors, Year</td>
<td>Bread Mass</td>
<td>Temperature</td>
<td>Time</td>
<td>Details</td>
</tr>
<tr>
<td>---------------</td>
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<td>-------------</td>
<td>------</td>
<td>---------</td>
</tr>
<tr>
<td>Saab, and Dasilva, (1981)</td>
<td>100g</td>
<td>220°C</td>
<td>20 min</td>
<td></td>
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<tr>
<td>Murata, et al., (1979)</td>
<td>1420g</td>
<td>210°C</td>
<td>43 min</td>
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<tr>
<td>Khan, Rhee, Rooney, and Cater, (1975)</td>
<td>540g</td>
<td>218°C</td>
<td>25 min</td>
<td></td>
</tr>
<tr>
<td>Mandala, (2005)</td>
<td>60g</td>
<td>198°C</td>
<td>20 min</td>
<td>Air oven</td>
</tr>
<tr>
<td>Zanoni, et al., (1993)</td>
<td>341g</td>
<td>203°C</td>
<td>30 min</td>
<td></td>
</tr>
<tr>
<td>Zanoni, et al., (1994)</td>
<td>- do -</td>
<td>- do -</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Morad and</td>
<td>500g</td>
<td>221°C</td>
<td>Two bread making</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Time</td>
<td>Temperature</td>
<td>Notes</td>
<td></td>
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<tr>
<td>--------------------------</td>
<td>----------</td>
<td>-------------</td>
<td>--------------------------------------------</td>
<td></td>
</tr>
<tr>
<td>D’Appolonia (CC 57)</td>
<td>20min</td>
<td>230C – 25min</td>
<td>processes</td>
<td></td>
</tr>
<tr>
<td>Maleki et al (CC 57)</td>
<td>100g (325g)</td>
<td>230C 18; 21; 24 min</td>
<td>Over baked breads tend to firm more – 3 min more at higher temp. – more granule disruption</td>
<td></td>
</tr>
</tbody>
</table>
Appendix B

Starch pasting observed at different temperatures for prolonged time and for prolonged cooling at 50 °C.

Figure B.1  Breakdown of wheat starch paste at 5 min intervals from the peak viscosity during 90 min holding stage as a function of holding temperature.
Figure B.2 Pasting curves of wheat starch produced with extended hold after cooling at 50°C.
Appendix C

DSC and microscopy of starch in iodine solution

Figure C-1: Differential Scanning Calorimeter thermograms of wheat starch solutions with water (a), with 0.02% (b), and 0.2% (c) iodine solutions. In the insertion: polarized micrograph of wheat starch granule after DSC, heated to 95 °C at 5 °C/min in presence of 0.2% iodine solution (B. K. Patel, Cereal Chemistry®)
Appendix D

Alternate statistical analysis for data in chapter 3

A) SAS model #1

\[ Y_1 Y_2 \ldots = \text{Oven Loaf\_weight Storage\_period} \]
\[ \text{Oven*Loaf\_weight Oven*Storage\_period} \]
\[ \text{Loaf\_weight*Storage\_period;} \]

Repeat Y #;

Table of \( (Pr > F) \) values from statistical analysis.

<table>
<thead>
<tr>
<th>Effects</th>
<th>Firmness</th>
<th>Moisture</th>
<th>Retrogradation enthalpy</th>
<th>Soluble amylose</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oven</td>
<td>&lt;0.0001</td>
<td>&lt;0.0001</td>
<td>0.0116</td>
<td>&lt;0.0001</td>
</tr>
<tr>
<td>Loaf weight</td>
<td>&lt;0.0001</td>
<td>&lt;0.0001</td>
<td>&lt;0.0001</td>
<td>0.0006</td>
</tr>
<tr>
<td>Storage period</td>
<td>&lt;0.0001</td>
<td>&lt;0.0001</td>
<td>&lt;0.0001</td>
<td>&lt;0.0001</td>
</tr>
<tr>
<td>Oven*Loaf weight</td>
<td>&lt;0.0001</td>
<td>&lt;0.0001</td>
<td>0.4348</td>
<td>0.7376</td>
</tr>
<tr>
<td>Oven*storage period</td>
<td>0.1887</td>
<td>0.0174</td>
<td>0.4246</td>
<td>0.3209</td>
</tr>
<tr>
<td>Loaf weight*storage period</td>
<td>0.0256</td>
<td>&lt;0.0001</td>
<td>0.0696</td>
<td>0.1379</td>
</tr>
</tbody>
</table>

All three main effects - oven, loaf weight, and storage period - were significant for firmness, moisture, retrogradation enthalpy, and soluble amylose (P<0.05).

The interactions between oven and loaf weight, as well as loaf weight and storage period, were significant for firmness and moisture content, but not significant for retrogradation enthalpy and soluble amylose. The interaction of oven and storage period, in contrast, was not significant for any factor.

The impact of storage period on all the responses has been reported by many researchers and is well recognized. Several of these reports have been documented in the literature review section and will therefore not be further discussed here. The impact of oven and
loaf weight can be attributed to baking time, characteristic to each oven as well as loaf weight used to bake. Thus the changes to moisture content (or other responses) are a consequence of baking environment collectively experienced by the loaf during baking. Furthermore, the differences in the initial product moisture content are known to influence other attributes including bread firmness, retrogradation enthalpy, and soluble amylose.

The goal of the study was to demonstrate the impact of processing conditions on the textural and functional properties (retrogradation and soluble amylose) of breads. To avoid the confounding effect of storage period the analysis was performed separately for each storage time. The graphs were also presented to illustrate the impact of heating rate on the bread properties. Mostly in all the graphs presented the trend observed for 2hr is similar to those observed for subsequent storage periods, i.e., the impact of baking conditions is not negated by changes during storage. This supports our premise that changes occurring during baking play a significant role during staling and these changes in turn depend on baking conditions.

B) WHC statistical analysis

Table of (Pr > F) values from statistical analysis.

<table>
<thead>
<tr>
<th>Effects</th>
<th>WHC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oven</td>
<td>0.0032</td>
</tr>
<tr>
<td>Loaf weight</td>
<td>0.2824</td>
</tr>
<tr>
<td>Oven*loaf weight</td>
<td>0.0352</td>
</tr>
</tbody>
</table>
VITA

Bhavesh K Patel

Education:

M.S., University of Mysore, India; July 1999
B.Tech., Gujarat Agricultural University, India; April 1994

Professional experience:

Production Supervisor, Sugam Dairy, Vadodara, India; May 1994- May 1995
Shift Officer, Viday Dairy, Anand, India; March 1996-July 1997
Food Technologist, Parrys India Ltd. Chennai, India; July 1999- Jan 2000
R&D Officer, Pillsbury India Ltd., Mumbai, India; Jan 2000- July 2001

Other achievements:

Trained 2 undergraduate students during summer 2002 (Governor Program)
Presented 3 posters at Annual Professional meetings (IFT and AACC)
Served as Student Representative on Carbohydrate Division Committee, IFT 2003
Served as Vice President of Food Science Club at Penn State University
Worked with Dr. Seetharaman on multiple consultation projects in Food Industry
Four years research experience at Penn State University