Evaluation of Rheological and Thermophysical Properties of Rehydrated Staled Bread Powders

By

Sabine El Hage

Department of Bioresource Engineering
Macdonald Campus, McGill University
Montreal, Canada

August 2019

A thesis submitted to McGill University in partial fulfillment of the requirements of the degree of Master of Science

Abstract

Staled bread powder (SBP) from crumb was evaluated to study its potential thickening abilities in food formulations. For this research, whole wheat and white wheat SBP were studied and compared at three concentration levels of 5%, 10%, and 20% in aqueous solutions. The rheological properties were evaluated by conducting flow and dynamic tests. Results showed an increased viscosity as a function of concentration for both types of samples. However, whole wheat bread powder demonstrated a slightly higher viscosity level than white bread SBP samples with values of 0.0078 Pa.s, 0.95 Pa.s, 4.73 Pa.s, and values of 0.019 Pa.s ,0.65 Pa.s, 3.77 Pa.s; for 5%, 10% and 20% whole wheat SBP and white SBP, respectively. Dissolution capacity was increased at higher concentrations solutions, and it was almost the same for 20% SBP samples for whole and white SBP. However, results showed that at lower concentrations, the water holding capacity of whole wheat SBP is lower than for white SBP. Cooking properties were measured in terms of the syneresis after a thermal treatment and cold storage. The syneresis of the samples for all concentrations and both types of SBP linearly increased during cold storage up to 14 days. Also, a non-linear behavior was seen between time-dependent syneresis models and concentration. Thermal properties of SBP from whole wheat and white dried crumb were investigated using a Differential Scanning Calorimeter. Direct relationship between the endothermic curve obtained from DSC tests, and, the rate of staling phenomenon could be observed. White SBP showed a greater extent of staling due to its large area under the curve, and a more abrupt endothermic curve. A cubic trend in the heat capacity measurement was also observed which denoted a similar pattern to that of aqueous starch solutions.

RÉSUMÉ

La poudre de pain rassis (SBP) a été évaluée pour étudier ses capacités potentielles d'épaississement dans des formulations et conceptions alimentaires. Pour cette recherche, les SBP de pain de blé entier et de pain blanc ont été étudiées et comparées aux trois niveaux de concentrations de 5%, 10% et 20% en solution aqueuse. Les propriétés rhéologiques ont été évaluées par des essais d'écoulement et de dynamiques. Les résultats ont montré une augmentation de la viscosité en fonction de la concentration pour les deux types d'échantillons. Cependant, le pain de blé entier présentait un niveau de viscosité légèrement supérieur à celui des échantillons de SBP de pain blanc, avec des valeurs de 0.0078 Pa.s, 0.95 Pa.s, 4.73 Pa.s, et des valeurs de 0.019 Pa.s ,0.65 Pa.s, 3.77 Pa.s; pour 5%, 10% et 20% de SBP de pains de blé entier et blanc, respectivement. La capacité de dissolution a augmentée avec des solutions plus élevées, et était presque identique pour les échantillons avec 20% de SBP de pain de blé entier et de pain blanc. Cependant, les résultats ont montré qu'à des concentrations plus faibles, la capacité de rétention d'eau de la SBP du blé entier était inférieure. Les propriétés de cuisson ont été mesurées en termes de synérèse après traitement thermique et stockage au froid. La synérèse des échantillons pour les concentrations et les deux types augmente linéairement pendant le stockage au froid jusqu'à 14 jours. De plus, un comportement non linéaire a été observé entre les modèles de synérèse dépendant du temps et de la concentration. Les propriétés thermiques de la SBP du blé entier et de la mie blanche séchée ont été étudiées en utilisant un calorimètre à balayage différentiel. La SBP de pain blanc a montré une plus grande stagnation par rapport à la SBP de blé entier en raison de sa courbe endothermique qui a été observée avec un comportement plus abrupt. Une tendance cubique dans la mesure de la capacité thermique a également été observée, ce qui s'apparente au modèle similaire de solutions aqueuses d'amidon.

LIST OF PUBLICATIONS AND PRESENTATIONS

El Hage S. and Orsat V. Characterization of Rheological Properties of Staled Bread Powder (SBP), 2018, Canadian Society of Bioengineering (CSBE), Guelph, ON, Canada.

El Hage S. and Orsat V. Utilization of Staled Bread Powder (SBP) as Sustainable Food Additive, 2018 Niagara, ON, Canada.

ACKNOWLEDGEMENTS

I would like to express my deepest gratitude to my supervisor Dr. Orsat because of her valuable guidance and her constant encouragement all along my journey in my program. She taught me how to persevere, most importantly how to be passionate about my goals. Her guidance and her kindness will always be appreciated and never forgotten. I am proud to be her student.

Besides the academic, I admire her because of all the other exceptional life lessons she taught me.

I would like to thank my external supervisor Dr. Ramaswamy, for his honorable support.

I would like to thank my friends which were one of the most valuable assets I gained during my studies here at McGill University.

I would like to extend my sincere regards to my colleagues in food engineering. Thank you for all the support and beautiful days we spent together.

I also wish to convey my profound gratitude and appreciation to my husband Dr. Hamed Vatankhah for freely sharing his scientific and spiritual support from the first day of my studies at McGill. He put his best efforts to mentor me on how to overcome the most difficult situations of life. He was always passionate about my progression and always believed in me throughout all my student life at McGill University.

This thesis is dedicated to my family, especially my beautiful parents, Sam and Katia. Words cannot express my love and appreciation to you. I thank you. Through all these years of hard work and nightless nights, you were supporting and caring so much about me. I wish my graduation will bring the best gift to your lives. As always, I hope to make it up to you one day, that way, I forever feel complete. You mean the world to me.

TABLE OF CONTENTS

NOMENCLATURE

θ	enthalpy of retrogradation
A_o, A_t and A_∞	experimental values of the property at times zero, *t* and infinity
k	rate constant
n	Avrami exponent.
σ	compressive stress,
E, $E_C(t)$	crumb elastic modulus at time t
ε	compressive strain represented by,
K_i	constants which are fitting parameters
Φ_1	remainder crystal growth at time t,
Φ_2	new crystal growth at time t
k_1	growth rate constant of Type 1 crystals
k_2	growth rate constant of type 2 crystals
$\Phi1^{max}$	value of Φ1(t) at storage time t=∞.
μ	apparent viscosity (Pa.s)
k	flow consistency index
n	flow behavior index
μ_0 and μ_∞	limits of the viscosity with a given shear rate,
$\dot{y}$	shear rate (s^{-1})
ʎ	constant calculated from the reciprocal of the shear rate (Pa.s)
b	represents the flow index.
I	is the graphical integral values
m	is the constant factor
c	is the concentration
n	is the exponent
m	the constant factor
n	exponent
$\frac{dq}{dt}$	heating rate(J/s)
m	mass (g)
C_p	heat capacity (J.°C^{-1}. g^{-1})
$\frac{dT}{dt}$	rate of temperature change (°C/s)

LIST OF FIGURES

Fig 4.5 The calculated heat capacity using Eq based on the DSC values presented in Figure 4.10. Figure (a) and (b) show the calculated values for whole bread and white bread, respectively.

LIST OF TABLES

CHAPTER 1
INTRODUCTION

Every year, Canadian bread manufacturers lose several thousands of dollars due to the phenomenon of bread staling. A thorough understanding of the staling process and finding alternative ways to reuse the waste bread as a food ingredient can be a very promising solution for the food industry.

Staled bread is a complex phenomenon that is mainly due to water evaporation and starch retrogradation. There are different solutions to overcome the financial loss of this unfortunate phenomenon. Some of these solutions target the formulation and processing during bread baking. For instance, there are several anti-staling agents which are used to delay the staling process. Moreover, solutions focusing on packaging and storage are also available to delay staling. Despite all efforts to delay this phenomenon, it is not possible to fully eliminate and overcome this loss. Thus, sustainable solutions of re-using the staled bread come into action. One of the possible ways to re-use staled bread is transforming it into staled bread powder -which from now on will be called SBP- and using it as a sustainable thickener in food formulations.

Bread waste can still be considered as a healthy and nutritive food where it has a fair amount of carbohydrate content, proteins and other nutrients that make it a healthy alternative to use in ready-to-eat soups or any other paste-like foods. Moreover, this sustainable way of re-using bread waste by transformation into staled bread powder is not only ecologically friendly but it can also be economical to be used in food formulations. Rather than processing with the often used chemical, physical or microbial processing involved in the production of some hydrocolloid gums, this innovative additive does not require the use of harsh chemicals, nor the use of expensive industrial tools of production, and with its sustainable re-use, represents a benign ingredient for the food industry as part of a circular economy approach.

1.1 Research hypothesis

The present research work aims at comparing the physical characteristics of staled bread powder (SBP) produced from staled whole-wheat and white wheat breads as a potential food thickening agent in pasty-like food products. The conducted experiment is monitoring the potential of SBP compared to other available commercial thickeners used in the food industry such as locust bean gum (LBG).

1.2 Research objectives

1.2.1 Rheological evaluation of aqueous SBP solutions

The rheological properties of Staled Bread Powder (SBP) from whole-wheat and white breads, dissolved in water, were evaluated and compared to the existing shear-thinning behavior of hydrocolloid gums commonly used in pasty foods. The rheological behavior is evaluated by investigating the dynamic viscosity and its behavior under varying shear rates, as well as the viscoelastic properties (flow and dynamic rheological properties) of the SBP solutions.

1.2.2 Understanding the microstructure of SBP

The morphology of crystallized starch granules during retrogradation is ordered, while during bread making, amylose leaches out of the granules. Therefore, reheating the retrograded starch can serve to render some of the intact starch-containing amylopectin and amylose in a more amorphous state which is desirable during cooking for thickening soups or sauces. Determination of the microstructural properties, using scanning electron micrograph (SEM), is needed to evaluate and compare the extent of the SBP crystallinity and its effect on the texture of both types of bread powders.

1.2.3 Measurement of dissolution capacity properties of SBP

The higher the water retention capacity, the higher is the thickening ability and capacity to reduce water losses from a food product. Evaluation of hydration and dissolution capacity of SBP is crucial in order to maintain the moisture content of products. This test is needed to monitor the importance of SBP as a food ingredient to minimize loss of moisture.

Adverse effects such as retrogradation and crystallization occur if moisture is lost, affecting yield and quality of the final product.

1.2.4 Assessment of cooking properties of SBP

The cooking properties of SBP, to be used as a food thickener, are important to consider when they are used in a food matrix that requires heat processing. Hence, to observe the characteristics of cooked SBP, it is needed to monitor the percentage of syneresis of the gel-formed samples resulting from various levels of thermal treatment, followed by a cold storage period (up to 14 days).

1.2.5 Thermophysical characterization of SBP using differential scanning calorimetry (DSC)

The lower the enthalpy of heating and melting of the retrograded starch could possibly promise better mixing properties for further processing and cooking applications. Thus, it is essential to perform an analysis to evaluate the transition and melting temperatures of the processed SBP starch granules using Differential Scanning Calorimetry (DSC).

CHAPTER 2

Literature Review

2.1 Introduction

2.1.1 Background

The main components of bread are flour and water. Choosing the proper percentage of flour, water, yeast, and salt is very important in obtaining the proper texture. The final texture is also dependent on the baking conditions. The temperature and humidity of the oven also play an important role in obtaining the desired texture. In addition, the proofing condition is a necessary step in order to produce enough CO_2 in the dough and obtain a homogeneous and porous crumb. The proofing step is a fermentation step in which the yeast –mainly *Saccharomyces cerevisiae*- ferments the dough sugars and converts them into water vapour and CO_2.

Salt is an important ingredient in bread although it is used in lower dosage. Besides the desired taste, salt can improve the texture of the bread by strengthening the gluten and achieving a strong gluten network, as a medium for further expansions within bread with temperature and CO_2.

Fat, or shortening is also used in many baked breads in order to increase the machinability of the dough and facilitate the handling and baking steps. Nowadays, there are other constituents which are added to dough to improve the physical and/or nutritional properties of the final products. For instance, emulsifying agents and anti-staling additives are introduced to improve the mechanical and textural properties of the finished product during the shelf-life period.

Fresh bread is presented in paper bags in the marketplace (baguettes, ciabattas, etc.). The reason behind such packaging policy is the higher consumer attraction and fresh nature of the product presentation. The main disadvantage of this type of packaging is the high moisture loss of the product during storage which leads to a shorter shelf-life. Thus, the amount of bread waste is noticeably high all over the world. In Canada, the rate of food waste is between 30 to 40 %. According to National Zero Waste council, close to 10% of produced bread is unfortunately estimated to be wasted (National Zero Waste council, 2017).

2.1.2 History

Bread is life: Babylonians were the first to pass on the art of fabricating bakery products to the ancient Egyptians, whom in turn created the first organized bakeries. In this period, bread was used mainly for religion, rituals, and ceremonies. Bread is still the ultimate religious symbol of Christianity, for instance, where it is a sacred symbol of the body of Christ that has to be consumed along with wine.

Thousands of years ago, consuming cakes was expensive and was mainly restricted to higher social classes while lower classes were confined to consume flatbreads (Cauvain and Young, 2008). For centuries, bread has been the most consumed food product in the world. It is a primary source of carbohydrate and can be prepared from several food ingredients. Different bread formulations have been developed, however, the general components needed are water, flour, salt, and yeast. Wheat flour is the most popular used flour for bread production, but other cereals can be used such as barley, buckwheat, cassava, and sorghum flours among many others.

In a USDA survey conducted in 2010, calories coming from cereals and grains (Oldways Whole Grains Council, 2013) were revealed to represent an approximate average consumption of 23.4% of a daily diet. Thus, it is highly appreciated and recognized, that the baking industry has developed bread as an integral connection within our important food chain. Nowadays, several types of breads are sold in grocery stores like bagels, packaged sliced bread, refrigerated biscuit dough and frozen bread dough lasting on shelves for a variety of storage periods.

Nowadays, an average annual net loss of bread for each Canadian bread manufacturer is 37400 Canadian dollars (Government of Canada, 2017). These losses are due to bread aging which is a factor playing a significant role in the economic losses to bread producers, Therefore, understanding the staling process and knowing which factors are important in delaying or enhancing this process are quite crucial.

Crucial not only to bakers but also to the suppliers, distributors, and consumers of the bread industry. This problem is the primary focus of this review. The following literature review will cover the significant reasons of bread staling, the analytical methods used to measure and control staling, and finally touch base on the application of additives affecting the rate of bread aging.

2.2 Major bread components

2.2.1 Granular starch

The granules of starch are made up of two main polymers, amylose and amylopectin. Both of them are polymers built up from glucose monomers. Inside the granule of starch, are found alternate ordered and disordered regions describing the semi-crystalline nature of a native granule of starch. Amylose consists of chains that have extensive attractive forces by hydrogen bonds from water. The swelling of the granule disrupts the molecular orders within it, and an amorphous gel is formed. On the other hand, amylopectin also has high hydrogen bonding, but with its branched structure (compared to the linear shape of amylose), has a smaller ability to form a gel with fewer available bonds (Catsberg, 2013). The formation of this amorphous gel is due to the breakage and reassociation of the hydrogen bonds upon water uptake during heating and leads to the pasty nature of starch (Aguirre, et al., 2011).

Starch is an important component of wheat flour. During dough making, if the granules of starch are appropriately mixed with water in excess while heating, the amylose tends to leach out of the granule towards the interstitial water between the granules and retrogradation of starch is triggered (Lai and Lin, 2006).

2.2.2 Protein

Gluten, on the other hand, is in a continuous phase in the dough. During the mixing of the dough, gluten’s components known as glutenin and gliadin form the gluten matrix. They develop the rheological properties of the dough during mixing. They entrap the gas during fermentation and expend the volume of the dough before baking during the kneading and proofing steps.

Proteins play an important role in defining bread quality. Actually, the gluten matrix can interact with starch upon heating and the denaturation of gluten upon heating results in the disulfide linkage formation. Those linkages lead to the formation of a gluten matrix which combines to starch to impart the desirable chewy texture to the bread. Glutenin contributes to the elastic character of the gluten complex in bread while gliadin contributes to its extensibility. These components impart the optimal viscosity, cohesiveness, and elasticity important to bread quality (Cauvain, 2012; Wieser, 2007).

2.2.3 Water

Water redistribution during bread staling causes quality changes in bread components. Water can migrate from gluten to starch and from starch to crumb and finally to the crust. This dehydrates the crumb and imparts a firmer texture to the bread, typical of stale bread.

2.2.4 Fats

Lipids are essential in bread as they provide benefits during the processing and storage of bread. The sources of fat originate from the wheat flour, shortening, and surfactants. Lipids coming from wheat represent 2-2.5% and are composed of non-polar and polar lipids, where polar lipids make up almost 70% of the total wheat lipids such as phosphatidylethanolamine (LPE). On the other hand, some of the non-polar lipids are free-fatty acids (FFA), mono-, di- and triacylglycerols. In bread, fats represent less than 5%, and they are essential for the lubrication of the dough, texture development and aid to increase loaf volume (Pareyt et al., 2011).

2.3 Staling phenomenon

Described as a non-microbial deterioration of quality during storage, bread staling is a physicochemical process that can remarkably decrease consumer's acceptance. Therefore, a deep understanding of the staling phenomenon first may extend awareness for those involved to alleviate food waste from bread.

Staling is a complex phenomenon that triggers many changes in bakery products. Consumer's acceptance is mostly related to the crumb staling. The staling indicator is the measurement of the crumb firmness (Gray & Bemiller, 2003). The crumb is a porous material with flexible elastic cell walls. This elasticity is mainly due to the presence of sufficient amount of water in the fresh crumb. However, upon storage, crumb elasticity is subjected to several physicochemical changes. As many researchers have suggested, crumb elasticity is critically affected by the time in storage and storage conditions (Colwell, et al., 1969). It is commonly known that bread shelf-life is affected by the environmental conditions.

In a study by Harros et al. (2002), the recrystallization of starch was defined using the kinetics of starch. They have illustrated the Avrami equation where the firmness of bread crumb and enthalpy of retrogradation were fitted. The physical changes of granules of starch transformation during the retrogradation process of starch in bread can be represented by Eq. 2.1 (Harros, et al. 2002):

$$\Theta=(A_\infty - A_t)/(A_\infty - A_o)\exp(-kt^n) \qquad \text{Eq. 2.1}$$

Where θ is the enthalpy of retrogradation. A_o, A_t and A_∞ are experimental values of the property at times zero, *t*, and infinity (or limiting value), *k* is a rate constant, and *n* is the Avrami exponent.

In the study done by Nussinovitch et al., 1992, the moisture determination of bread as a function of storage time has been considered. In the study, it was established that most of the physicochemical changes involved in staling occurred within the first 24h, right after the bread is taken out of the oven (Nussinovitch, et al., 1992). Moreover, the highest staling rate and starch crystallinity obtained were found when bread was stored at 4 ºC by Chung et al., (2003). The authors investigated the effect of storage time on the loss of crumb elasticity. The research was done using mechanical means, such as compression and decompression to measure the recoverable work (Chung, et al., 2003).

After baking, the gelatinized starch from bread crumb starts cooling. The amylopectin, accounting for almost 70% of the starch, starts forming double helices chains with a linear length of 10 glucose units. Sometimes, these doubles helices can form between adjacent clusters or in the same amylopectin branch cluster upon cooling termed as retrogradation (Maga & Ponte, 1975). These interactions over prolonged storage time can trigger the recrystallization formation of starch in bread rendering bread harder and less pleasing to consume. Amylopectin further realigns in an ordered array, influencing the rigidity of the swollen granules to become more compact and form stacked double helices next to each other. It is noticeable that the formation of cross-links by hydrogen bonds and liaison between amylose and amylopectin have an impact on the mechanical strength of their interfaces, which in turn influence the mechanical properties of bread.

Wȕrsh and Gumy (1994) investigated the rate of starch retrogradation. They have focused on the amylopectin component in the starch granule and have studied its effect in the process of staling. These authors concluded that longer starch chains, such as amylopectin, retrograde faster than smaller chains like amylose. Moreover, they have shown that any subsequent firming does not involve the amylose fraction, rather the amylopectin with longer chains and number of branches (Würsch and Gumy, 1994). However, another study by Ghiasi and others, demonstrated in the book by Cauvain and Young (2007), that the amylose to amylopectin fraction was changed in flour by using waxy barley starch which allowed a better understanding of the involvement of the amylose fraction in the staling of bread. However, in the reported study by Ghiasi, the evaluated bread staling was only for bread no longer than one day old (Cauvain and Young, 2007). Although these authors have highlighted well the effect of the amylose to amylopectin ratio on staling of bread, they did not consider the degree of starch granule swelling, the hydration of starch, the level, and type of saccharide ingredients, moisture content, the presence of solutes, the flour's hydrocolloids and the lipids content (Cauvain and Young, 2007).

One of the first scientists to support the theory of crystallization of bread crumb was Katz, in 1928. In his experiments, he proved by evaluating x-ray diagrams, that starch appeared both in amorphous and crystalline forms in fresh bread, whereas in stale bread the crystalline form predominates (Chinachoti and Vodovotz, 2000).

Later, scientists approved his view by proposing that staled crumb is caused by the recrystallization of amorphous starch realigning in an ordered array. Over time, this ordered association makes the bread crumb slowly lose its textural quality (Hug-Iten and Conde-Petit, 2003).

Bread shelf-life is not only due to starch recrystallization but is also dependent on water concentration and water loss. Water in bread plays a crucial role because it acts as a plasticizer to increase the flexibility of the starch polymer as illustrated by Levine and Slade

(1990). After bread making, water starts redistributing inside the bread. Water migrates from the crumb to the crust to varying degrees as a function of the storage conditions. Water loss impacts as much the bread as the starch retrogradation. Upon cooling, bread becomes firm as a function of time, temperature, and the ingredients used for the formulation of the bread product.

Water migration in bread is driven by different mechanisms such as illustrated in the study of Monteau, et al. (2017). Monteau and others (2017) have recently developed models involving many assumptions and equations to better represent the process of staling. Illustrated in a better way than earlier studies, the authors have considered molecular diffusion (gas phase) from Fick's law and the pressure gradient from Darcy's law. They explained that mass transfer in porous media is not only due to diffusion through porous media, but that pressure also is a response phenomenon. They have therefore added a convection term to the diffusion term based on Darcy's law. Hence, they presented two scenarios for their study. In the first model, the process is presented at constant pressure and pre-specified conditions, and it is about the migration of water in the crust via water vapor permeability. The second scenario presents the crumb and crust under variable pressure values through the two different layers of the bread, the crust and crumb. Results showed that by comparing the two mentioned mathematical models, the water loss from the crust escaped to the surrounding atmosphere and the crust absorbed the other portion of water remaining in the crumb. Authors also reported that the first model was not realistic due to predicted boundary conditions. The second model is assumed to be more realistic in this case because it considers the real geometry of the crust as distinct area from the crumb with its governing physical characteristics. However, to obtain realistic results, they should consider the thickness of the crust because its thickness would impact significantly the water vapor permeability.

The difference between crust and crumb, regarding water content and water movement, has been suggested by Hamdami and others (2004), where they explained that the moisture distribution within bread dough will change with time during baking (Hamdami, et al., 2004). The crust will contain less water than the crumb because when the dough is exposed to the oven's high temperatures, the water in the outer layer (crust) evaporates. Therefore, due to gas expansion during baking, the volume of the bakery product increases from the porous dough matrix. However, the size of the crust pores will vary; the crust has a denser, less porous and a firmer structure than the crumb after baking. When the baked bread is exposed to colder temperatures during storage, the aging process of bread starts. Water is not lost during this period, actually, only redistribution will occur. This redistribution takes place between the crumb and crust as well as between gluten and starch.

2.4 Gluten effect on starch retrogradation

After gelatinization of starch, when amylopectin starts to retrograde and form crystals, water molecules incorporate into the crystals. This redistribution shifts water molecules from the continuous gluten structure to the starch/amylopectin structure. This shift triggers changes in the gluten network (Gray and BeMiller, 2003; Ronde, et al., 2011). Therefore, the presence of gluten is considered to have a significant impact on bread quality (Curti, et al., 2014). In this interesting study, gluten-enriched breads were monitored at two different levels of gluten; the first level was 5% gluten, the second level was 15% gluten. Results have shown that the presence of higher levels of gluten in samples of bread enhanced the loaves' volume, and gave a more uniform crumb. They observed the presence of smaller pores that promoted a more uniform crumb. Texture analysis suggested that when higher gluten concentrations were present in the bread sample, it remained softer with fewer changes occurring in the crumb springiness and cohesiveness, up to a week of storage as confirmed in a following study by Carini et al. (2017). Thus, the authors concluded that higher concentrations of gluten in the bread formulations have better potential for preserving fresh bread qualities.

2.5 Thermal properties of bread

Retrogradation of starch involves the formation of chain entanglements, short-range molecular ordering, and crystallization of double helices that aggregate. A variety of physical techniques have been employed to monitor these phenomena and other associated thermophysical changes. Many standard methods are employed to monitor these phenomena such as DSC, DTA, X-ray diffraction, several spectroscopic methods including NMR, FTIR, and Raman spectroscopy. DSC is presented in greater details here, as it was used in the experiments conducted in this thesis.

Differential scanning calorimetry (DSC) is used for the thermal analysis of a wide range of food products, including bread. It monitors changes in physical transitions of starch and keeps track of changes due to interactions of starch polymers with other constituents in a composite matrix such as crumb and crust (Koletta, et al., 2014). DSC is a tool sensitive to the molecular ordering of chains like helical conformation (Biliaridis, 2009). Quantitative measures of phenomena like gelatinization and glass transition are given based on heat flow related to the ordered and disordered transitions (Biliaridis, 2009).

DSC and DTA (differential thermal analysis) are closely related analytical methods. Phase transitions occur in both methods, triggered by the temperature changes between the control and the sample to analyze. However, contrarily to DTA, the temperature difference represented for DSC is used to derive the energy difference supplied (Roos and Drusch, 2015). DSC is an instrument that consists of sample holders, heater, sensor, temperature difference detection unit and temperature controller (Abdulagatov, et al., 2015). This equipment can detect phase transitions as a function of temperature. It detects transitions including melting and glass transitions (Roos and Drusch, 2015). The output gives graphical representations of many peaks and inflection points reflecting the thermally induced transitions. Monitoring energy or heat capacity changes, DSC has been used to study several starch retrogradation processes mostly during bread staling (Wang and others, 2015.). Expression and understanding of the DSC peaks can be useful to monitor the extent of staling in different types of bread, for example whole wheat versus white bread samples (Stevens and Elton, 1971).

The effect of staling in bread has been investigated using DSC equipment. Quantifying the retrogradation process of starch in bread on DSC was done by Ellison and Torkelson (2003), where they were able to keep track and monitor bread during storage. Bread was pre-frozen, and the glass transition temperature was monitored all along the experiment. Authors suggested that above the glass transition temperature, molecular mobility is enhanced and consequently, molecular rearrangements for nucleation can take place (Ellison and Torkelson, 2003).

Three steps describe crystallization, the nucleation, propagation, and crystal ripening (Biliaderis, 2009). If the slow crystallization of amylopectin occurs then it is proposed that the nucleation step in the mechanism of crystallization is slowed down (Collar, et al., 2015).

This nucleation-growth process of amylopectin is enhanced by freezing treatment at temperatures above the glass transition temperature (Tg) (Levine and Slade, 1990). Thawing and storage at higher temperatures result in enhanced crystal ripening process therefore in an increased recrystallization rate in comparison with unfrozen systems. Therefore, optimum glass transition and melting temperatures need to be monitored to balance the nucleation and crystal growth of amylopectin (Najafabadi, et al., 2014).

The temperature at which the starch polymers experience phase transition is the glass transition temperature (Tg). Tg describes the transition from a rubbery state to a rigid state. Tg is one of the most important parameters describing amorphous materials. It measures the transition from a rubbery, viscous amorphous solid, to a brittle, glassy amorphous solid with solid-like mechanical properties (Cornell, 2012). It is perhaps the most important measured parameter because it has been proven to be an essential factor in the stability of food. Also, Tg is related to the mechanical properties and behaviour of amorphous polymers, determinants of stability during processing.

On the other hand, melting temperature (Tm) or latent heat is also an important parameter that is quantified by DSC measurements. It is useful because it corresponds to the transformation of a solid material, having an aligned molecular chain, to a viscous liquid in which the structure is disordered. Moreover, the enthalpy of melting can be measured to estimate the degree of starch crystallization (Höhne and Glöggler, 1989). Changes in enthalpy result from providing enough energy as heat to a system up to a specific amount that triggers a change in its state, transforming it from a solid to a liquid at constant pressure (Dincer and Rosen, 2002). The more the enthalpy of melting increases, regarding retrogradation of starch, the more crystallization occurs, at a faster rate and to a greater extent. On the other hand, the lower the enthalpy of melting is, the better the ability of starch to rehydrate and produce an amorphous and pasty-like liquid (Eliasson and Gudmundsson, 1996).

Tg is also extremely sensitive to water content. Moreover, water content is an efficient plasticizer of starch, and can cause a drastic depression in the glass transition temperature if water content is high due to the plasticizing effect of water on amorphous starch, however if the water content is lower, then the glass transition temperature would not decrease as drastically (Vieira, et al., 2011; García, 2012).

Abundant studies have investigated the glass transition temperatures of bread during storage (Chinachoti and Baik, 2000; Chinachoti and Vodovotz, 2000; Roos and Drusch, 2015). Chinachoti and Vodovotz (2000) have studied the thermal properties including glass transition temperature and change in heat capacity as a function of moisture redistribution and amylopectin recrystallization during aging of bread (Chinachoti & Vodovotz, 2000). They found that upon aging, the enthalpy associated with amylopectin recrystallization increased with time of storage. Finally, they concluded that the recrystallization of starch during storage affects the rigidity of the amorphous network, leading to a higher glass transition temperature (Chinachoti and Baik, 2000). Consequently, a decrease in crystallinity in starch should decrease the observed glass transition temperature at a corresponding water content (Roos and Drusch, 2015). Water content gradually increases in the crust while it decreases in the crumb, this indicates a water migration from the crumb towards the crust. In both cases, water content tends to an asymptotic value, which can be attributed to the equilibrium crust-crumb moisture.

2.6 Hydrocolloids

Hydrocolloids can form viscous dispersions and gels when adding a certain amount of water. Hydrocolloids have advantages over another additive because they are simple to use and relatively affordable. Examples of hydrocolloids are xanthan, guar, pectin, carrageenan, locust bean gum, and gum Arabic, all known as food grade thickeners.

Thickening agents are used for fluid products such as ready-to-eat soups, sauces, gravies and salad dressings to increase viscosity and enhance textural properties. They include naturally and synthetically derived gums such as fermentation derived gums, animal gums, plant or seed gums, cereal gums, plant extracts, seaweed extracts or cellulose derived gums such as carboxymethyl cellulose (Li, 2016). Retrograded starch can be used in foods to contribute to regulate the texture and consistency and improve the quality of the final products for consumers. Gums are commercially used in the form of instant powders, where they can be diluted in an aqueous mixture without having to compromise or affect any other properties of the dilute solution (Rahman, 2009).

Hydrocolloids are used as thickening agents, emulsion stabilizer, ice and crystal formation inhibitors, water absorption agents, etc. They are considered as long chains polysaccharides with the power of entanglement. Their interaction is related to their concentration in the dilute solution which contributes to viscous properties (Saha, 2010). Gums such as xanthan, locust bean and gum arabic are common examples of gums used in the formulation of foods to stabilize and control moisture, provide proper texture, and improve the overall quality attributes and stability of the products. The interaction between polymers dictates the viscosity. Characteristics of the gums, such as size and shape of their polymeric molecules, influence their properties. The higher the molecular weight the higher the increase in viscosity of the entangled molecules (Sworn, 2009).

For increased capacity as thickening agents, gums can be combined to other commercial thickeners such as starch to create a synergistic effect. The synergism of using two or more gums together in a food formulation can be an advantage in order to reduce processing time during cooking and increase the potential thickening properties. For instance, in sweet dessert sauces, the most compatible combination between thickening agents are when combining starch and xanthan gum. The processing time is lower and provides more viscosity than if both were used individually (Imeson, 2012).

The thickening hydrocolloids are affordable and effective to use in the food industries since they can be functional even as low as 0.02-0.5% concentrations and do not impart undesirable aftertaste to the food formulations (Saha, 2010).

2.6.1 Gum arabic

Gum arabic (GA) is a natural gum exudate which is among the first thickening, and emulsifying stabilizers used in the food industry (Dickinson, 2009). GA is a liquid from the stems and branches of acacia trees found across the Sahelian belt of Africa. It is characterized as striated nodules of off-white to orange-brown color. Nowadays, gum Arabic is used in confectionery to reduce crystallization of sugars, it is also known to impart no undesired taste as well as impart emulsifying properties to the food. It is advantageous to use GA because it has the extensive ability of creating a stable emulsion. Actually, it has the capacity of emulsification due to its slightly acidic complex polysaccharide with calcium, magnesium and potassium salts that are combined to approximately 2% of protein, more specifically, nitrogen which creates the ability for emulsification. During the emulsification process, the hydrophobic parts, including the protein, adhere to the oil portion, meanwhile the carbohydrate hydrophilic parts of the gum protrude in the water phase. This hydrophilic part is known as the arabinogalactan protein complex of gum arabic (Ma, 2015). However, GA is not stable in cold water when dispersed, therefore, to ensure rapid dispersion and hydration, GA solutions require a continuous agitation step. On the other hand, GA is stable in acid solutions, therefore for its use in food applications, vinegar or citrus oil are preferred for successful emulsions.

Gum arabic is being used as an emulsifier since the 1980s. Used in a variety of applications, GA has been found, like most of the other available gums, to have a particular rheological behavior, namely shear thinning, at low shear rates, and a Newtonian behavior at higher shear rates than 100 s^{-1}.

2.6.2 Locust bean gum

Locust bean gum (LBG) is another hydrocolloid thickener recognized by its high viscosity at low concentrations. LBG is a seed gum, originating from a plant from the middle eastern regions, known as *Ceratonia siliqua*. LBG, a polysaccharide, is extracted from the seed endosperm of the carob beans from the carob tree (Barak, 2014). They are very abundant in the Mediterranean region since ancient times. It is advantageous to use LBG in the food industry because it is non-toxic and has a low cost of an average of 10-50$ per kilogram of LBG gum. Also, LBG does not require high dose of usage for food applications, thus, only 0.5% in an aqueous hydrating solution is enough to raise viscosity. This gum has shown a synergistic effect when it is used with many other gums such as xanthan gum (Copetti et al., 1997). When LBG and xanthan gum are combined, there is an increase in gel strength, especially with the increase in the concentration of LBG. Other combinations with LBG are possible including with gellan gum along with xanthan combination, since xanthan and LBG together form an elastic, and cohesive gel, while adding gellan gum provides a more desirable texture and can be used extensively in dessert gels for instance. The combination of gellan/xanthan/LBG is the most applied combination known to date (Imeson, 2012).

2.6.3 Carrageenan

Carrageenan is a polysaccharide extracted from seaweed. In ancient times, it was used to form milk puddings, salads or gels. Carrageenan is not absorbed by the human body and serves as a bulking agent in food. Carrageenan has a backbone of branched galactose joined together by alternative glyosidic linkages. All carrageenan is produced from red seaweeds, and they differ from one another as a function of their chemical bonds. The difference comes from the position of the functional group, an ester sulfate, in the molecular structure. The other factor that differentiates the types of Carrageenan is in the amount of 3,6-anhydro-D-galactose groups that it contains. The difference in molecular structure of the Carrageenan hydrocolloids results in a wide range of thickening properties. The applications are wide and vary within the same family due to their chemical interactions. Nowadays, this gum is widely used in the food industry for thickening and stabilizing food formulations, mostly used in dairy desserts like milkshakes, chocolate milks, ice creams, as well as meat analogs and many other applications (Imeson, 2012). One of the popular applications of carrageenan is in meats, in which the gum is injected and dispersed with the brining solution without too high of a viscosity (Galera, 2016).

2.6.4 Alginates

Alginate is an ionic charged form of alginic acid and is a polysaccharide extracted from brown algae. Most of the commercial food applications related to alginate are mainly based on the ionic interactions with cations. The cations form a network with the ionic alginates, for instance, mostly with calcium chloride forming cross-linkages with sodium alginate and resulting in a weak gel formation with a backbone structure (Day, 1998). With the formation of a weak gel, the application of sodium alginate is also known to be heat-stable. Therefore, the gel formed between alginate and calcium chloride can withstand its shape and rheological properties all along the thermal processing. Alginate, on its own is an advantageous hydrocolloid to use as a gelling agent and does not require a lot of heating. Alginate has the ability to form gels in cold water, therefore using alginate in baking custard for instance or pie fillings can form a stable and improved structure (Onsoyen, 1997).

2.6.5 Xanthan gum

Xanthan gum is produced by fermentation of simple sugars by species of the *Xanthomonas campestris* bacteria. It is widely used as a thickening agent for salad dressings for instance. Xanthan gum is temperature stable and provides stability to viscous fluids, while it is also more pseudoplastic in its flow. It is often combined with other hydrocolloids and starches to provide different textures. Generally, xanthan gum is combined with guar gum to form a synergistic and enhanced stabilizing and thickening effect with higher viscosity, often used in salad dressings and sauces. The combination of both gums not only reinforces the structure, but their properties combined can reinforce their molecular structure ensuring their stability during processing.

Xanthan gum is used in bakery products to add viscosity to the dough to enhance baked production with known improvement of the texture of the final product (Demirkesen et al., 2010). It also improves the minimum requirement of energy and time of baking of the dough and can serve as a bread crumb improver for gluten-free bread (Gadallah, 2016). In baking products, the most widely used hydrocolloids include xanthan gum, LBG, guar gum, and carboxymethyl cellulose (CMC). Hydrocolloids are mostly used in bakery products to reduce lumps in the batter during mixing and prevent the products from collapsing, or shrinking after the baking process has ended (Vidaurre-Ruiz, 2019).

2.6.6 Guar gum

Guar gum is obtained from the endosperm of the guar or cluster bean, *Cyamopsis tetragonoloba,* which has been cultivated in the semi-arid regions of northwest India and Pakistan. The guar plant is a fast-growing plant that can grow annually. The gum powder can be used as an additive in food formulations, pharmaceuticals, paper and textile. In food applications, guar gum can be used to thicken and stabilize food because of its mechanism of hydrogen-bonding formation with water molecules. Guar gum is an advantageous additive to enhance food products due to its health benefits, anti-cancer controlling properties, anti-diabetes and promotion of bowel movements. With guar gum, the concentration needed is within 0.5-1% concentration range (Barak & Khatkar, 2014). In terms of its processing, guar seeds are removed from their pods, then commercially processed with straight-forward process: roasting, differential attrition, sieving and polishing. In the food industry, guar gum mimics fiber characteristics in food. The matrix stability that it offers is used in various food products such as beverages, processed cheeses, dairy products and bakery products, as well as salad dressings and sauces.

2.6.7 Carboxymethyl cellulose (CMC)

Carboxymethyl cellulose (CMC) is a cellulose derivative that can act as a thickener, water-binding, as well as emulsion stabilizer in food. CMC is a chemically manipulated hydrocolloid that is soluble in either cold or hot water. The rheological character of CMC is following shear-thinning properties. However, it is always important to consider the molecular weight and degree of substitution of CMC in aqueous dispersions. The molecular weight and substitution of CMC are important factors to consider because their variation affect the shear character in food. In other words, products with lower degree of substitution result in shear character following thixotropic behaviour and a viscosity decrease with a temperature increase (Kulicke et al. 1996; Alexander 1999). In food applications, CMC has a wide range of applications in therapeutic foods and ice creams (Ghannam & Esmail, 1997).

2.7 Starch thickeners

2.7.1 Corn starch

The predominant source of native starch used in the food industry comes from corn seed (maize). Commercial corn starch is white in its powder form. Corn starch is mainly used for thickening milk dishes, soups, gravies, and sauces. In addition to its thickening properties, corn starch needs to be processed in different ways to liberate the simple sugars and can then be used as a sweetener in bakery products (González-Montemayor et al., 2019). The processing methods of corn starch liberation into simple sugars use enzymes such as amylase and glucoamylase to hydrolyse the complex molecule. Also, maize starch is used for cooked bakery puddings and dough products. When cooking, corn starch develops a thick viscous and translucent appearance, and during the process of cooling, the texture results in a more resilient thick product (Moore, 1984). Adding thickening agents such as corn starch to bakery products not only regulates their texture but also extends their shelf-life by improving their organoleptic properties (Fiolet, 2017). They prevent bakery product from bottom cracking and contribute to giving cake products volume stability (Wilderjans, 2008).

2.7.2 Potato starch

Potato starch can be obtained by grating potato finely and rinsing it several times. The collected water is then centrifuged to separate the starch that settles from the water content. In the food industry, potato starch is considered functional for thickening, coating, gelling, adhesion, and encapsulation. Upon heating to above the gelatinization point, potato starch granules start to swell with water uptake and increase in viscosity. The main application of potato starch is mostly for thickening soups. The advantage of such thickening additive is that it does not impart coloration in the food product because it is transparent (Moore, 1984).

2.7.3 Tapioca starch

Tapioca starch is obtained from the cassava root which is a tuber rich in starch and grown in regions of South America, Africa, and Asia. The tubers are shredded, and the starch is rinsed out in cold water. The moist starch is heated in rotating drums where irregular-shaped flakes half-transparent are obtained and processed to dry into a powder. Tapioca flakes and grains are colored yellow-brown by the drying process. However, tapioca powder is white with no specific smell or taste. During cooking, dried Tapioca flakes and pearls do not lose their structure through the partial thickening (Grace, 1977). This starch is used for porridges and soups.

2.7.4 Native starch vs. modified starch

Adding native starch to foods could help them develop a viscous consistency. However, upon longer storage time, the native starch may undergo aging. The aging phenomenon is described as when the starch granules start losing water molecules due to syneresis and the starch granules crystallization portion grows creating packed forms of crystals. The crystallization process can lead the native starch stiffening. To expand the uses of starch in the food industry, native or natural starches need to be modified to diversify their functionalities. Native starches from corn, wheat, potato and cassava (tapioca starch), for instance, have limited resistance to the processing conditions such as physical pressures applied in modern food processing. They are not as efficient in their use for thickening due to their instability during shearing and thermal treatment. They also have a tendency to easily retrograde during the cooling process which causes limitations in their use and can cause a decrease in the overall final product quality (Arocas, 2009).

Hermansson and Svegmark (1993) were the first scientists to discover that the modification of native starch, using potato starch, can be more functional and efficient than using native potato starch as a gelling agent (Svegmark & Hermansson, 1993). The authors illustrated the structural importance of the amylopectin and amylose microstructures. They have concluded that amylose has a straighter structure than amylopectin, thus having a greater tendency to create a compact microstructure. Higher levels of amylose thus favour a decrease in the retrogradation of starch compared to amylopectin (Svegmark & Hermansson, 1993)

Modified starch is starch that is changed to have a chemical structure closer to that of amylose structure and less of the amylopectin branched structure. This process can be done chemically, including cross-links, substitutions, and acid hydrolysis oxidation or can be done physically such as pregelatinizing and annealing. The modification produces a modified starch which can be used as a thickening agent, having an increased resistance to mechanical shear, elevated temperatures during sterilization, acid hydrolysis, enzyme hydrolysis and deep-frozen storage time and to increase the crystallization phenomenon (Hoover, 2010). Therefore, to increase resistance during processing, the native starch needs to be chemically, physically or enzymatically modified.

2.8 Rheological properties of foods and thickened formulations

The thickening ability of an ingredient is the phenomenon that occurs due to the occurrence of polymeric cross-linking forming a thicker fluid that can relatively trap water within the structure making it more viscous (Saha, 2010). The flow of the fluid becomes viscoelastic which behaves as both a liquid and a solid promoting elasticity and pseudoplasticity.

Rheological behaviors such as pseudoplasticity and shear thickening are derived from rheological measurements based on the shear stress as a function of shear rate. Rheological behaviors are derived from similar parameters namely; apparent viscosity, consistency index, flow behavior index, shear rate and shear stress. From rheological testing, it is possible to interrelate and describe the properties of formulations during processing, application development and storage to optimize the product's properties for quality and economic values.

2.8.1 Newtonian vs. non-Newtonian fluids

Newtonian fluids are fluids whose viscosities do not depend on the applied shear rate, but rather depend on temperatures and composition of the product. Newtonian fluids are also characterized by a fluid viscosity that does not vary with the applied shear rate under constant temperature and pressure. With non-Newtonian fluids the viscosity changes as a function of varying shear stress and/or shear rate, at constant temperature. If it is the case that the viscosity decreases with an increase in shear rate, the fluid behavior is defined as pseudoplasticity or a shear thinning behavior.

Pseudoplastic behavior is recognized to present an irreversible structural breakdown. The decrease in viscosity occurs as a result of the change in molecular alignment that takes place within the paste foods (Wang, 2016). However, if the viscosity increases with an increase in shear rate, the fluid is defined as a shear-thickening fluid. Sometimes they are referred to dilatant fluids.

With pasty foods an important parameter to consider is the yield stress, which is denoted as σ_0. Yield stress is defined as the minimum shear stress that is required to initiate flow. The yield stress influences strongly the models that can be chosen to model the rheological behavior such as Herschel-Bulkley or Bingham, used to facilitate process calculations. The numerical method to obtain the yield stress of a paste is to plot a graphical illustration of the apparent viscosity as a function of shear stress. The yield stress is then calculated from the point (from zero shear rate) where viscosity becomes infinite. On the other hand, to evaluate the mouthfeel of paste foods, it is highly crucial to study their flow behavior. Therefore key properties to measure in this case are the flow behavior index and viscosity. These parameters, as mentioned in the latter description of yield stress, can as well be numerically calculated and substituted using the mathematical equations of the respective rheological models described by the flow. The flow behavior index can dictate the rheological behavior depending on the value calculated. If the calculated value is lower than 1, then the flow is following shear thinning behavior, if the n value is larger than 1, the behavior is following shear thickening, if n-value is 1, it is a newtonian fluid.

Therefore, these parameters play an essential role in the flow conditions analysis of the food matrix in which the natural thickener is added to, in food formulations (Rao, 1977). The characterization of the samples is done using the relationships between the shear stress and the shear rate, specific to the behavior curve that is produced for each tested sample. The test results highly depend on the food sample behavior under shear deformation. For instance, some food samples have a viscosity that decreases with shear rate, known as shear thinning behavior. Other models, such as shear thickening are related to the food viscosity that increases with shear rate. When tested under a rheometer, gel strength is measured by its viscoelastic properties, and by compression testing.

The assessment of the viscoelasticity of paste foods consists of non-destructive methods to test the behavior of the paste where only small amplitude oscillation is given to the samples to study the thickening character and texture development. This test measures the oscillatory motion by controlling the level of stress that can be applied to the paste.

Food pastes exhibit both viscous and elastic behaviors at the same time, and this results from an applied force to a viscoelastic paste. Once the force is applied to the paste and is removed, the paste will not instantaneously adopt its original dimensions. The rheological properties of the food paste consist of elastic and viscous components also known as modulus, hence, these are most commonly used parameters to characterize the effectiveness of a thickener.

The elastic moduli (G') and the viscous moduli (G'') are the main parameters that provide properties of a viscoelastic paste. The value of G' is defined as the conservative modulus. On the other hand, the G", refer to the dissipative modulus. In fact, the lower this value of G", and higher G' results in a more rigid-like food paste. Similarly, pseudoplasticity is used to predict the flow behavior. The flow behavior index denoted by "n" can predict the flow, where the smaller the n, the more the system is pseudoplastic, however larger n values express lower pseudoplasticity. The adjustments done to these values can be done using different gums (guar gum, xanthan gum, CMC etc.).

2.9 Influence of ingredients and additives

Chinese steam bread (CSB) is a popular traditional Chinese bread, and the texture of this type of bread is already very firm. During storage, the firmness of this bread increases rapidly which leads to rapid loss of freshness. Fan Zhu (2016) developed a strategy to increase the shelf-life of such a firm bread. A new formulation for CSB was thus developed, incorporating anti-staling agents, including enzymes, hydrocolloids, oligosaccharides, lipids and surfactants, soy and waxy wheat flours (Zhu, 2016). The bread's reformulation with additives had a positive impact on the amylopectin retrogradation due to a slowing down of water redistribution and evaporation from bread during storage. This slower dehydration process is due to controlled water activity and lowering of the mobility of water with additives such as enzymes, like xylanase, or hydrocolloids like xanthan gum which are able to slow down moisture migration and shelf life deterioration, each ingredient using their own specific function.

During gelatinization, some amounts of amylose leach out of the starch granules, and during retrogradation, some of them form double helices and stabilize the structure into a more stable rigid network of starch (Debet and Gidley, 2007). Anti-staling agents such as enzymes and emulsifiers would interfere with the association of amylose, and amylopectin to hinder the recrystallization process. The enzymes trigger the production of low-molecular-weight molecules to interfere with the amylopectin retrogradation and with the protein-starch interaction to reduce the firming rate (Hug-Iten et al., 2003).

A study by Giannone and others, (2016) was done to incorporate alpha-lipase enzyme coming from fungal, microbial, or cereal origin in durum wheat bread to evaluate its anti-staling potential (Giannone, et al., 2016). Durum wheat is usually used for pasta making because of its grain hardness. It is usually preferred over soft wheat because it has a longer shelf-life due to higher water-binding capacity (Erbas, et al., 2005). It was found earlier that including lipase in bread acted upon bread's lipid to enhance the emulsifying properties. Moreover, it imparted a positive effect on the freshness of the bread. It was found that alpha-amylase-lipase enzyme works synergistically better than alpha-amylase alone to prevent staling (Bellido et al., 2016).

Bellido and others (2016), have found that water activity of bread samples enriched with alpha-amylase-lipase had a softer and more chewable texture than the control bread sample.

Regarding the physical changes, alpha-amylase-lipase could reduce both hardness and chewiness of the samples of bread even after 90 days of storage. Alpha-amylase increased the rate of amylose leaching out of the granule of starch during the processing of starch to form a gel. Therefore, more porosity is created when there are alpha-amylase acting upon amylose. Some studies have indicated that alpha-amylase alone is said to increase porosity, increase the gelatinization process, therefore, it is understood to accelerate the retrogradation process (Maga & Ponte, 1975). In other terms, it breaks down the starch to release the amylose from the granule of starch.

Pourfarzad and others (2009) investigated the influence of glycerol, sorbitol, maltitol and propylene glycol on the shelf life and quality of barbari, an Iranian flat bread fortified with soy flour (Pourfarzad, et al., 2011). Iranian flat bread contained 85-88% wheat flour with 11.2% protein, 10.52% moisture, 26.7% wet gluten, and 0.79% ash. They found that propylene glycol added to the fortified flat bread at 0, 1 and 5g/100g wase able to decrease bread staling by reducing water activity to 0.871 (1g/100g propylene glycol) and to 0.867 with 5g/100g propylene glycol in comparison to the control sample at 0.883. The evaluation of crumb hardness and moisture indicated that propylene glycol was able to diminish bread staling. It is due to its smaller molecular weight, that propylene glycol is more effective to increase osmotic pressure and decrease water activity. Results showed that the propylene glycol imparted greater effect on quality and shelf-life of this type of Iranian bread.

In another study, three flours with different protein contents were prepared into flatbreads, then baked (Salehifar, 2011). The thermophysical properties were monitored by measuring the enthalpy of crystallization, peak temperatures (Tp) and onset point temperatures (To), during subsequent storage of the breads using DSC thermograms. In the first and third day of storage, the enthalpy of recrystallization increased with time of storage due to retrogradation for the three formulations. Three endothermic peaks were observed on the DSC thermograms of the starch-water mixture. The first at 55-60°C corresponding to the gelatinization of starch crystallites. The second peak was at 65-75°C representing the melting of remaining crystallites and the last peak (about 100°C) was attributed to dissociation of amylose-lipid complex. It was found that the recrystallization enthalpy of starch, as measured by DSC, decreased with increasing levels of protein explained by the distribution of water within the mixed system. As they have monitored, increasing the protein content of flours caused an increase in the water absorption capacity of the flour. The water absorption in the first formulated flour, with a protein content of 9.5%, was 64.05% compared with the flour with 13.5% protein, which was 74.5%, showing a significant difference. This difference in the water absorptions was due to the different protein contents. The results lead to the understanding that higher protein amount in bread showed less retrogradation while lower amounts of proteins increased retrogradation.

Kerch and others (2010) found that chitosan and chitosan oligosaccharides can affect redistribution and state of water and structure in bread crust and crumb. Chitosan can facilitate dehydration of both starch and gluten and facilitate moisture migration from the crumb to the crust. Therefore, this redistribution of water affects the intensity of Maillard reactions in bread crust and the rate of bread staling. However, chitosan oligosaccharides have a lower effect on the staling of bread than does chitosan alone. In fact, what chitosan oligosaccharides do is that they prevent the complexation of amylose-lipid by adsorption of chitosan onto the starch surface.

2.11 Conclusion

Bread staling is responsible for contributing to food waste worldwide. Basically, Bread is made of considerable portion of starches and proteins. Starch and starch–gluten interactions play a significant role in the staling mechanism and the positive/negative effects imparted by different ingredients such as hydrocolloids, enzymes, oligosaccharides or dietary fibers. Thus, it could be hypothesized that the existence of important food components such as starch and proteins could bring the possibility of using available staled bread to thicken food formulations and by this means, contribute providing a sustainable solution to decrease the bread loss.

Connecting text

Chapter 2 introduced the basis of bread staling, ways of prevention and measurement techniques to monitor the staling of bread. It provides the general understanding for which the actual research topic was based on which is the reuse of staled bread crumb used as a food additive and thickening agent in other paste food products.

For this present experimental study, white and whole wheat dried bread crumb were selected and compared.

Chapter 3 presents the rheological properties of dried crumb SBP of whole and white bread as paste solution where the steady-shear flow rate and the viscoelastic properties were evaluated using an AR2000 rheometer. Finally, a comparison is made with a commercially available locust bean gum (LBG) at different concentrations in aqueous solutions.

Chapter 3
Rheological Properties of Staled Bread Powder (SBP)

Abstract

The aim of this study was to conduct rheological studies on aqueous solutions made with 5%, 10% and 20% of staled bread powder (SBP) obtained from crumbs of stale white and whole wheat breads. The flow and dynamic properties were evaluated, and the latter was compared to solutions prepared with locust bean gum (LBG) at 0.25%, 0.5, and 1% concentration levels. The results showed a sudden drop in the viscosity of SBP samples indicating a shear thinning flow behaviour. Overall, bread powder samples were seen to be effective in increasing the apparent viscosity of solutions. In general white bread showed a slightly higher viscosity level (0.0078, 0.95, 4.73 Pa.s) than whole wheat SBP samples with a value of 0.019, 0.65, 3.77 Pa.s for 5%, 10% and 20% of SBP in solutions, and did not show any particular changes in the flow behaviour at the selected concentration levels. The dynamic oscillation rheological tests revealed the existence of crossover points for all SBP solution samples.

3.1 Introduction

Food thickeners are important additives to be used in industrially formulated foods to ensure good consistency and texture of pasty foods. It is crucial to study their rheological properties because understanding their behavior can lead to product and processing optimization, as well as final product's overall quality enhancement.

Measurements of rheological parameters provide fundamental insights on the structural integrity and textural behavior of thickeners based on their viscosities and how this interacts with flow behaviors. Generally, the role of a thickening agent is to adjust the viscosity in the food matrix in which it acts upon and relative to the application it needs to influence. Therefore, food scientists define a thickening agent as an agent that is used in high-moisture foods to increase their viscosity.

Many studies to date have measured and characterized the rheological behavior of food thickeners such as the commonly used hydrocolloidal gums like xanthan gum, locust bean gum, and guar gum (Dickinson, 2006; Katzbauer, 1998; Saha and Bhattacharya, 2010; Steffe, 1996). All previous authors have concluded, from their study on the rheological properties of thickening agents, that they all had similar flow behaviors for the commercial thickeners they tested. They found that they followed a power-law model with shear thinning behavior or pseudoplastic flow behavior.

The thickening agent properties influence the textural properties of the food product. If the thickening agent rheological behavior is shear thinning, the behavior of the sample will follow a similar pattern. However, if the thickener does not provide the desired texture, it will affect the sample and render the food products defective or unworthy. For that purpose, for the development of any new thickening agent, it is important to monitor their viscosity parameters.

Actually, viscosity, in this case, is a key parameter to measure to predict the behavior of a thickener when added to a food formulation such as in the study reported by Arocas (2009) on clean label starches evaluated in white sauces under shear destruction, heating and freeze thaw conditions. It was observed that the viscosity of the sauce can change during different processing conditions. Results shown by the authors concluded that the usage of hydrocolloids reduced the structural modifications occurring after thawing, more specifically, xanthan gum was seen to be more effective in retarding the effect of syneresis.

Actually, the gums used decreased the swelling of the starch granules causing a delay in pasting. In general, the use of xanthan gum increased in pasting temperature (PT), affecting the total hot and cold peak viscosities, as well as was able to reduce relatively the total setback (from the minimum to maximum viscosity). Total setback is an indicator of short-term retrogradation. A positive correlation was found between total setback and water separation. Xanthan gum was able to decrease the retrogradation and, consequently, improved the freeze/thaw stability (Arocas, 2009).

For our studied applications with SBP, the trend of the viscosity changes needs to be monitored with increased shear rates since it could affect the food formulation as compared with existent commercial thickeners. With increased shear rates the potential viscosity behavior that should be seen is lowered.

Generally, the viscosity is a value obtained from the slope of the graph plotting shear stress as a function of applied shear rate. The viscosity of most commercial gums used for fluids obey the power-law model. The Power-law model, also known as the Ostwald de Waele model is the empirical model to describe a shear-thinning fluid. The viscosity component of the Power-law equation is provided in Eq. 3.1;

$$\mu = k\dot{\gamma}^n \qquad \text{Eq. 3.1}$$

Where μ (Pa.s) is the apparent viscosity at shear rate denoted as $\dot{\gamma}$(s^{-1}). In this equation, the important parameters to consider are k and n, where "k" is the flow consistency index and "n" is denoted as the flow behavior index (Holdsworth, 1971).

When the n-value flow behavior index is below 1, the fluid exhibits shear thinning behavior, when it is above 1 then the fluid exhibits shear thickening behavior while for an n-value of 1, the fluid does not show non-Newtonian behavior but rather a Newtonian fluid behavior or Bingham plastic behavior (which requires a yield stress to achieve flow).

The Power law model does not include a yield stress factor denoted as μ_0 (Chhabra, et al., 1999), which is found in the Herschel-Buckley empirical model which quantifies the amount of stress that the fluid may need and experience to begin flow. The Herschel-Buckley general equation is presented in Eq. 3.2;

$$\mu = \mu_0 + k\dot{\gamma}^n \qquad \text{Eq. 3.2}$$

For example, in a study done by Wei and others in 2001, the flow behavior of fruit fillings was assessed in order to investigate the effects of hydrocolloidal gums that were added to the fruit fillers (Wei, et al., 2001). The authors illustrated that the shear rate and shear stress relationships of the fruit fillings containing the incorporated hydrocolloidal gums were modelled well by the Herschel-Bulkley (power law model) equation with yield stress. The necessary yield stress for the fruit fillings ranged between 39-51 Pa, the consistency index ranged from 52-104 Pa.s and flow behavior index was below 1, at 0.4.

Contrarily to both the Herschel-Bulkley and Power-Law models, the Carreau-model takes into account significant deviations at high and very low shear rates to the power-law model. Such curve is fitted by the following equation (Eq. 3.3);

$$((\mu\dot{\gamma} - \mu_\infty)/(\mu_0 - \mu_\infty)) = (1 + (\lambda\dot{\gamma})^2)^{(n-1)/2} \qquad \text{Eq. 3.3}$$

Where $\mu(\dot{\gamma})$ is the apparent viscosity in Pa.s; μ_0 and μ_∞ are zero and infinite shear viscosity, shear rate denoted as $\dot{\gamma}$ (s^{-1}) and λ is the time constant calculated from the reciprocal of the shear rate at which the zero shear rate component is expressed in Pa.s (Dolz et al., 2007).

For example, a study conducted by Roman and others in 2015 focused on fat alternatives in food emulsions, concentrating of extruded flours. In their study, they evaluated a mayonnaise like emulsion where flour-water ratios were monitored. Results showed that at lower shear rates, the emulsion had Newtonian flow, whereas with increasing shear rates the flow behavior was better fit by the power-law (Roman et.al, 2015). This combined behavior is best characterized by a model known as the Carreau model presented in Eq. 3.3.

At a molecular level, the shear thinning behavior with increasing shear rates causes the molecules of the fluid to be less resistant to flow with an increase of the orientation of the molecules. It is this molecular behavior that causes the power-law flow. However, due to different concentrations of the thickening agent added to the solution, it can differ and impact the extent of the behavior of the shear thinning in the fluid solution. The more particles are dissolved in a solution the more they will impart a shear thinning behavior.

The Power law is often attributed to low starch concentrations solutions when the yield stress is negligible. Several authors use the Power-law model to describe the flow of lower concentrations pseudoplastic fluids; fruit pulps, juices, etc., where the flow properties of low-pulp concentrated orange juice were studied depending on the effect of temperature and different levels of concentrations (Vitali and Rao, 1984).

Generally, bread dough has a starch/gluten blend with water and their interaction plays an important role. The interaction of starch in wheat dough is defined as non-Newtonian and is largely responsible for the behavior of the dough during breadmaking (Watanabe, 2003). Wheat bread doughs, as stated in the literature such as in Weipert (1990), follow a viscoelastic nonlinear behavior and are known to be non-Newtonian in their fluid behavior with shear thinning and with a thixotropic (time-dependent) character (Weipert, 1990).
When the viscoelastic behavior is studied for fluid systems, and dynamic oscillatory rheometry is introduced, the elasticity of the dough as well as its viscosity are measured. It has a high correlation with the flour's baking behavior. Both the G' and G'' modulus, as well as the loss tangent value are of particular interest.

G', or storage modulus, represents the elastic component of the dynamic measured viscosity. The G'', or the loss modulus, represents the viscous component of the dynamic measured viscosity. Therefore, at low strain, G' is higher than G'' in the dough while G" is predominant at higher strain. Actually, the viscoelasticity of the dough includes internal resistances which vary between viscous liquid and an elastic solid (Menjivar, 1990). The ratio defined by the loss modulus over the storage modulus is defined as the loss tangent, which dictates the viscoelastic behavior (Lee & Klostermeyer, 2001). Wheat varieties (whole wheat vs. white) have a different viscoelastic and steady-state flow properties (Moreira et al., 2011). Generally, the doughs possessing a higher moisture content possess a looser texture, therefore, they possess lower complex viscosities but higher loss tangent (Bourne, 2002).
Usually, at the crossover point, when the viscous moduli is equal to the elastic moduli, the loss tangent is equivalent to 1, this equivalence leads to the gelling point, and both values of G' and G" are similar in this case. As Song and Zheng (2007) illustrated in their study

of dynamic rheological properties of wheat flour dough and proteins, a lower tangent ratio represents a higher quality of flour used to make the dough, than in the case of a higher loss tangent (Song and Zheng, 2007).

The objective of this study was to investigate the rheological properties of staled bread powder (SBP) made of whole wheat and white flours. In this regard, the steady-shear flow rate testing is used where the SBP of whole wheat is compared to the steady-state flow of white wheat SBP. In addition, viscoelastic properties are studied on SBP white and whole wheat dried crumbs. The obtained results are useful to evaluate the thickening properties of SBP samples compared with Locust Bean Gum solutions.

3.2 Materials and Methods:

3.2.1. Materials

Food grade Locust Bean Gum (LBG) was supplied by Tic Gums, Montreal, QC. Regular fresh whole wheat bread and white bread was supplied by Compliments from IGA bakeries.

3.2.2. Sample preparation

Both white and whole wheat bread samples were stored for 14 days at room temperature (~25°C) to allow them to stale fully. After the period of storage, the bread crumb was separated from the crust and passed through a food processor (Braun brand) to form smaller size particles. Finally, the produced fine powder was passed through a sieve (mesh size; 20µm) to homogeneously separate the particles. The homogeneous particles thus produced (≤20µm) from staled bread were dispersed slowly, to prevent flocculation, in deionized water. The solutions were prepared on a w/w basis to three different concentrations of the bread powders using 5%, 10% and 20% concentrations. The samples were hydrated for 2 hours under gentle magnetic stirring (~400 rpm).

Food grade purified and powdered LBG was dispersed in deionized water and stirred under 600 rpm for approximately 8 hours for full hydration. The tested concentration levels of aqueous LBG solutions were 0.25, 0.5, and 1% (w/w).

3.2.3 Flow and dynamic rheology measurements

Analysis of the steady-flow and dynamic properties of SBP (white and whole wheat) compared to LBG was conducted using a Rheometer (AR2000, TA instruments, USA). Measurements of dynamic properties including the loss modulus (G"), the storage modulus (G') and tan δ (G"/G'), were performed as a function of frequency in the range of 1-100 Hz at room temperature (22°C). Measurements of flow behavior include shear stress as a function of shear rate in the range of 0.1 (1/s) to 100 (1/s) at room temperature (22 °C). All rheological tests were done following a 2 min resting period to achieve an equilibrium state. Both flow and dynamic tests were done in triplicate.

3.2.4 statistical analysis

Statistical analysis was carried out using Microsoft Excel software. Significance of trends were confirmed if comparison of means of sets differed $P<0.05$ (student's t-test).

3.3 Results & Discussion

Viscosity measurements showed a rheological behavior indicative of non-Newtonian fluids. The flow behavior indices obtained from the rheological measurements were found to be following the shear-thinning behavior. As for the potential as a thickening agent in food products such as salad dressings or soup thickening, the flow behavior index was lower than 1, thus shear thinning, further indicating that the apparent viscosity decreases as the shear rate increases.

3.3.1 Steady-shear flow rate

The rheological behaviours of tested samples are shown in Figure 3.1 indicating that the viscosity of all the samples followed a shear thinning behavior for both white and whole wheat stale bread powders at all concentrations tested.

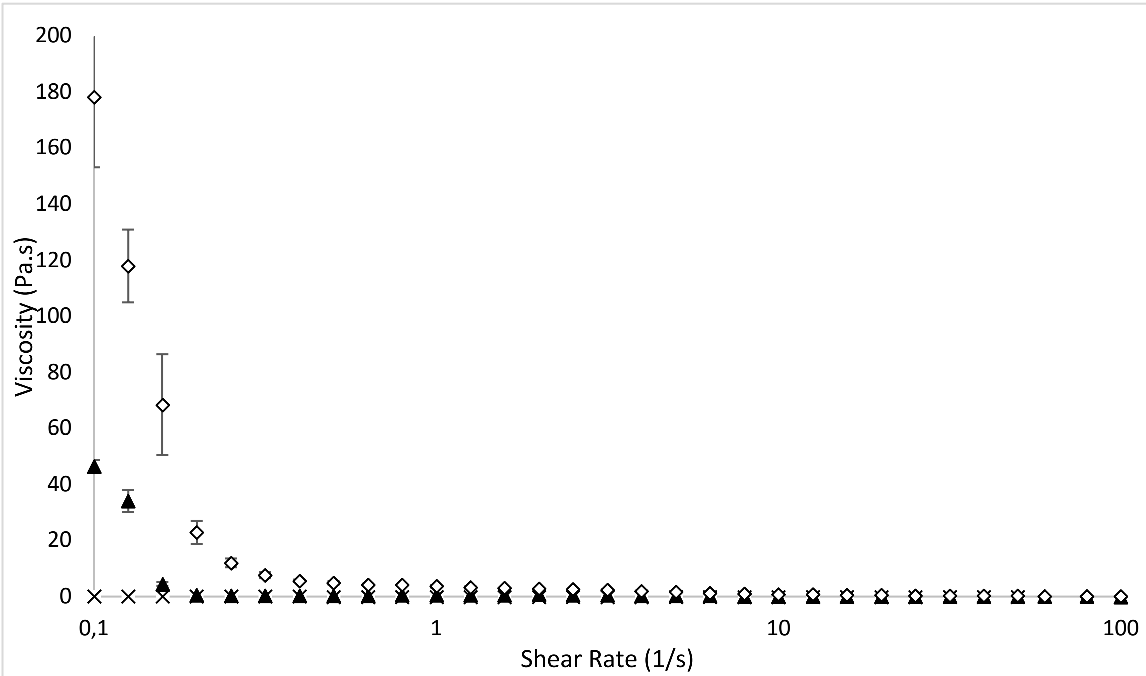
It was observed that there was considerably higher shear stress at lower shear rates, as supported in the study on the rheological properties of dough done by Petrofsky and Hoseney (1995). The authors results showed that at low strains, the viscosity is high, and the dough structure does not move or deform because at low applied stress and resulting strain, there is little impact of the inherent structure. At higher strain however, there is gradual structure destruction occurring with significant dis-orientation of the dough's complex matrix causing a reduction of the viscosity. This strain causing destruction of the structure is an indicator of the dough's strength.

Hershel Bulkley and Power-law models were the two models used to characterize the shear thinning behavior of fluid foods as previously discussed.
Regarding SBP samples, a considerably sharp shear stress fall was observed in Fig 3.1 after starting the tests. The rheological results were represented using an empirically derived model (Eq. 3.4)

$$\mu(\dot{\gamma}) = k + a \exp(-b.\dot{\gamma}) \qquad \text{Eq. 3.4}$$

where $\mu(\dot{\gamma})$ and $\dot{\gamma}$ represent the apparent viscosity (Pa.s) and shear rate (1/s), respectively, k is the yield stress, a is the consistency index factor and b represents the flow index. Parameters obtained experimentally are presented in Table 3.1.

a)



b)

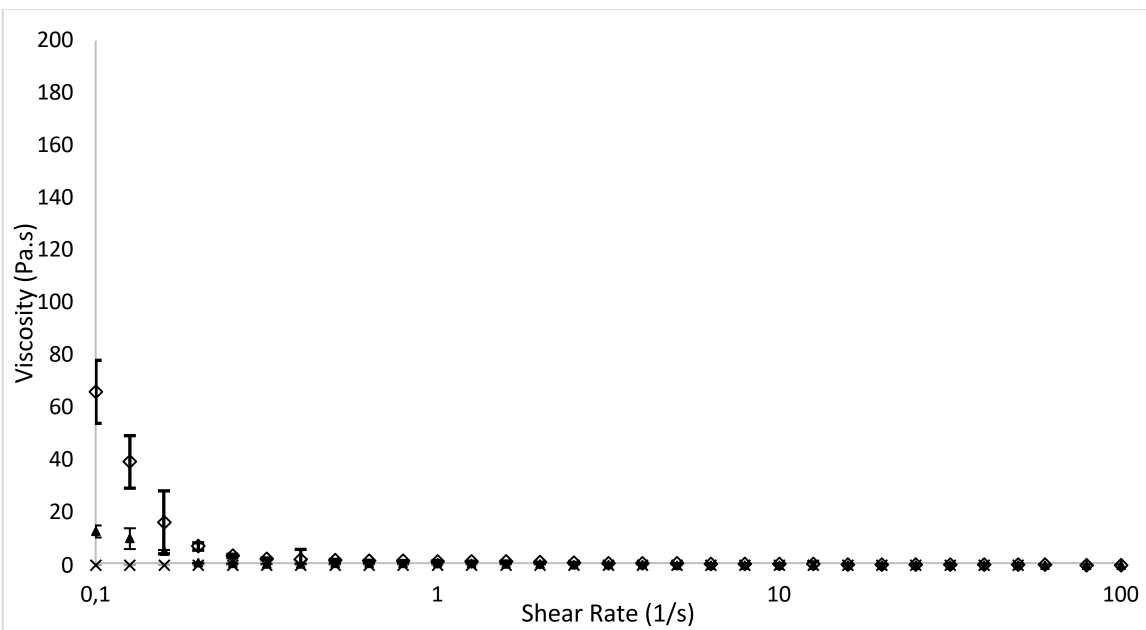


Figure 3.1. Viscosity (Pa.s) vs. shear rate (1/s) for SBP solutions containing a) white bread concentrations of 5% (×), 10% (▲)and 20% (◊), and b) whole wheat bread concentrations of 5% (×), 10% (▲), and 20% (◊).

Based on initial evaluation of thickened properties of dried powders it was decided to study 5%, 10% and 20% level of dried powder and compare it common dosage of LBG used in food applications. As can be seen in Figure 3.1 the viscosity was higher first and reduced by a sudden drop with increasing shear rate. This phenomenon is likely due to the weak molecular bonding that is initially created within SBP aqueous solutions. The networks rearrangements in the flow direction with the SBP solutions are much more rapid due to less friction between the molecules of SBP in the solution than for hydrocolloid gums (as seen with LBG in Figure 3.2). It can be demonstrated that with gums there is a more resistance to the alignments within the molecules, thus it takes greater shear rates to rearrange the molecular networks affecting flow. In the latter, the homogeneity of response is due to a gradual response to the shear rate ramp. This difference is due to the structure of the molecules of the staled crumb and their inner resistance to flow being able to be altered with increased shear rate. In other words, the resistance of shear rate comes from two main friction forces; the molecular expansion and the intermolecular resistance of the molecules to shear rate and alignments. In fact, SBP contains bonds from the gluten complex with starch, as well as amylose complexed with lipids, other leached amylopectin, and fibers such as wheat bran. The molecules and their interactions differ in SBP from the hydrocolloidal LGB solution which mainly contains hydrogen bonds and long chains polysaccharides.

The factors existent in the shear thinning behavior of thickening agents typically used for soups and salad dressings are due to the molecular rearrangements and orientation of the particles of the samples along the flow lines. As explained in Juszczak and other (2013), generally, also can be due to the viscosity in the presence of some of the partially gelatinized starch during the SBP dissolution in aqueous solution (Juszczak, et al., 2013). The partially gelatinized starch granules found in the SBP solution are the starch that have not completely been gelatinized during the bread making process and have undergone the retrogradation process. These pre-gelatinized starch granules can swell in the presence of water. Generally, gelatinized starch granules are swollen during cooking and processing, and retrograded during storage time and, when dissolve in water, their presence can lead to a viscosity build up which could be seen in the flow test result.

The model parameters fitting to Eq. 3.4 are shown in Table 3.1. The model fitness showed acceptable results due to the R-square values showing values relatively closer to 1 ranging from 0.85 to 0.99.

Table 3.1 Rheological empirical model parameters of Eq. 3.4, for the SBP samples containing white and whole bread powders.

Sample	a	b	k	SSE	R-square	RMSE
SBP-5% whole wheat[a]	0.08±0.0	2.11±0.1	0.01±0.0	0.01	0.85	0.00
SBP-10% whole wheat[b,d]	79.92±3.2	17.71±1.3	0.25±0.0	7.64	0.97	0.52
SBP-20% whole wheat[b]	635.80±21.4	22.67±3.1	0.93±0.1	20.92	0.99	0.86
SBP-5% white[c]	0.14±0.0	3.38±0.2	0.01±0.0	0.01	0.97	0.00
SBP-10% white[a,c,d]	637.80±49.5	25.69±3.8	0.34±0.1	140.60	0.95	2.24
SBP-20% white[f]	2973.00±103.2	27.43±1.7	3.81±0.1	1596.00	0.96	7.42

Different superscript letters indicate statistical difference at 0.05.

In the case of the “a” parameter, it ranged between 0.077 to 635.8 in the case of the whole wheat bread while this value was higher for the white bread with increasing concentration of SBP. A similar increasing trend was observed for b and k and for both bread types. However, the increase in each parameter followed a non-linear trend. The increase in model parameters showed an increase in viscosity as a function of increasing SBP concentration. Flow test results were compared using paired t-test to evaluate null hypothesis at the significant level of 0.05. the results confirmed that the flow data at 5% whole wheat was significantly different with 10% and 20%. While the results for white bread were slightly different. It was seen that white SBP at 5% and 10% were not significantly different while both were different when compared with a 20% concentration. The 20% white SBP was not the same as any of the other samples tested. According to the data, whole wheat SBP at concentration levels of 10% and 20% were not significantly different with10% white SBP.

The Carreau model was used to illustrate the flow behavior of locust bean gum (presented in Figure 3.2) at different concentrations in Table 3.2. To choose a reference shear rate for apparent viscosity comparisons, a shear rate equal to 1 was chosen.

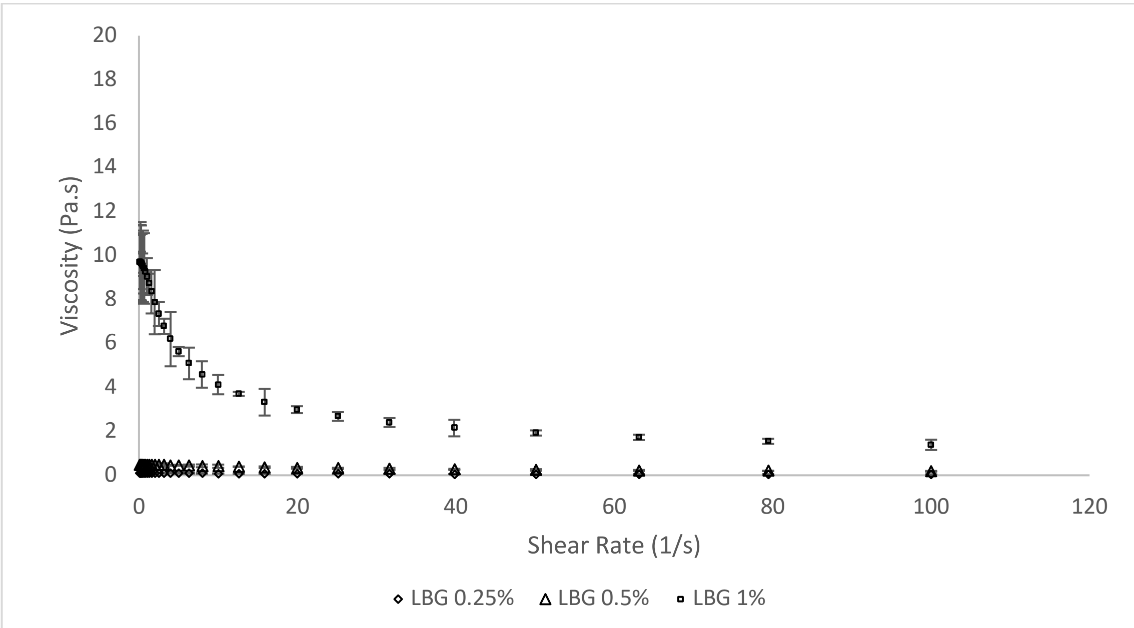


Figure 3.2. Illustration of viscosity (Pa.s) vs. shear rate (1/s) for LBG solutions containing locust bean gum 0.25%, 0.5% and 1%.

It was seen, at a shear rate of 1 s^{-1}, that viscosities of 0.11 Pa.s, 0.47 Pa.s and 8.73 Pa.s were experienced for 0.25%, 0.5% and 1% LBG, respectively. On the other hand, for 5, 10, and 20% whole wheat SBP, viscosities of 0.0078, 0.95, 4.73 Pa.s, were experienced, respectively. Comparatively, solutions of white bread SBP had viscosities of 0.019, 0.65, 3.77 Pa.s for 5, 10 and 20% concentrations.

Table 3.2 Carreau model parameters for the LBG samples.

%concentration	η	ʎ	N
0.25	0.11±0.0	0.24±0.0	0.17±0.0
0.5	0.47±0.0	0.09±0.0	0.21±0.0
1	9.71±0.4	0.59±0.1	0.23±0.0

Overall, bread powder samples were considered effective in increasing the apparent viscosity of solutions; however, the viscosities of bread powder solutions were lower than those obtained with locust bean gum. Also, between brown and white bread powders, the white bread showed a slightly higher viscosity. As Seyer and Gélinas (2009) concluded in their study on whole wheat bread characteristics, the presence of a certain amount of bran in whole wheat can reduce the water absorption capacity of the system, since bran is an insoluble fiber (Seyer & Gelinas, 2009). Therefore, white SBP is likely to increase water absorption leading to more pronounced increase in viscosity over that of whole wheat SBP. Locust bean gum's viscosity increased with an increase in concentration (Figure 3.2). at all concentration levels, a non-Newtonian behavior was observed. This phenomenon can be explained by the fact that a lower shear rate is not as destructive to created networks therefore the molecular entanglements may be balanced out and reformed, however at the higher shear rate, the entanglements cannot readily reform and maintain the same level of viscosity (Barak & Mudgil, 2014).

3.3.2 Oscillation test

The steady shear measurements provided information about the character and rheological behavior of the material. Dynamic shear measurements inform about the textural and structural behavior of the substance. This useful information can aid food processors to predict the behavior of food formulations undergoing processing.

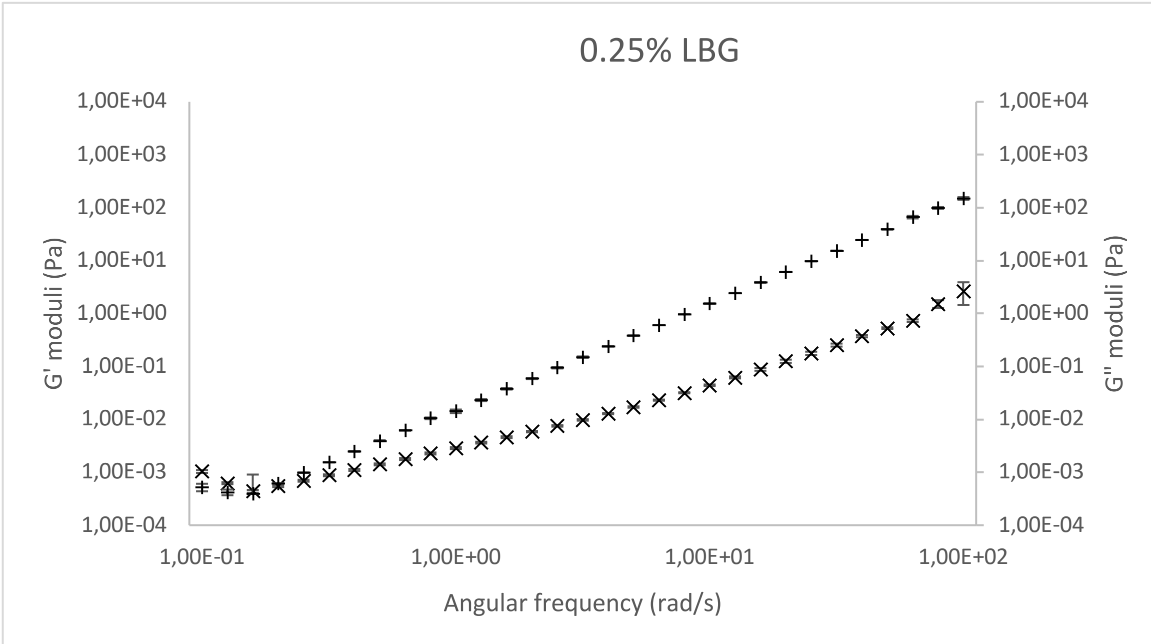
The viscoelastic properties of LBG and SBP samples are presented in Figures 3.3. to 3.5. As can be seen for whole wheat bread samples (Figure 3.5), initially, the G'' was higher that G'. It showed the viscous behavior of all samples at lower frequencies. In general, the dominant viscous modulus is a representative of a fluid-like behaviour while a dominant elastic behavior is indicative of a stronger solid-like characteristic.

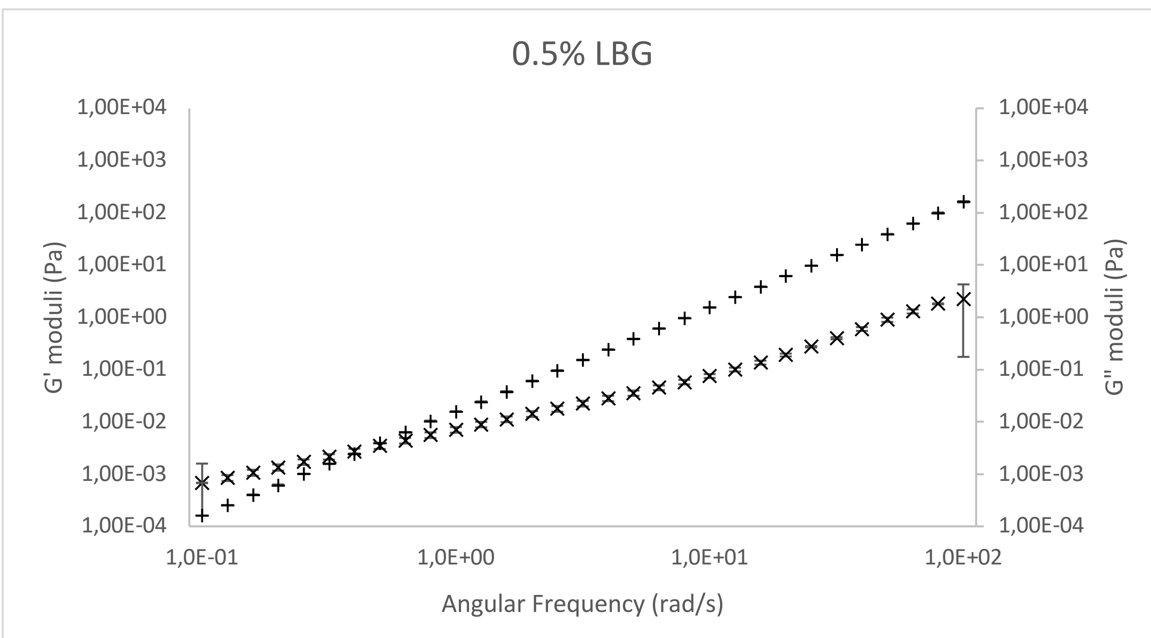
According to Figure 3.4, the G'' was also initially higher for all white bread samples. However, increasing the frequency resulted in a crossover point in which G' becomes higher than G''. This point is usually referred to as the gelling point. The gelling point is a turning point in the rheological characteristics of a liquid in which the elastic behavior of the fluid shows high gel-like properties. The crossover point was also observed for all LBG samples (Figure 3.3). Thus, the similar trend in viscoelastic behaviour of the bread powder samples suggested a similar rheological property with other commonly used food thickeners, such as locust bean gum.

The G' and G'' graphs of LBG presented in Figure 3.3 show a homogeneous texture of the solution, while the non-linearities in the viscoelastic curves of bread samples indicated a multiphase and more complex structures of their solutions. The crossover point was seen to be directly related to the concentration level of the bread samples. In other words, higher concentrations on bread powder lead to higher crossover points. The crossover point was seen at 1, 1.59 and 10 for 5%, 10% and 20% of white bread powder in solution. Finally, the crossover point was seen at 0.40, 1.59 and 10 for 5%, 10% and 20% for whole wheat bread, respectively.

The results for the whole wheat bread were also very close to the ones for the white bread. This indicated minimal effects of the contained fiber on the viscoelastic properties. It might be due to the insolubility of this phase which means it will not participate in the colloidal structure of each solution, although it may actually hinder flow.

As can be seen, the crossover points for the LBG samples were 0.16, 0.50, and 2.5 for 0.25%, 0.5%, and 1% solutions, respectively. The results show a lower range of concentrations at which LBG turns into a gel. This indicates higher gelling properties for the LBG over that of the bread samples. However, the thickening properties of bread powders remain a point of interest due to their clean-label and their ability to easily dissolve in water for increasing the viscosity of a solution (Yoon & Yoo, 2017).


0.25% LBG
G' moduli (Pa)
G'' moduli (Pa)
1,00E+04
1,00E+03
1,00E+02
1,00E+01
1,00E+00
1,00E-01
1,00E-02
1,00E-03
1,00E-04
1,00E-01
1,00E+00
1,00E+01
1,00E+02
Angular frequency (rad/s)


0.5% LBG
G' moduli (Pa)
G'' moduli (Pa)
1,00E+04
1,00E+03
1,00E+02
1,00E+01
1,00E+00
1,00E-01
1,00E-02
1,00E-03
1,00E-04
1,0E-01
1,0E+00
1,0E+01
1,0E+02
Angular Frequency (rad/s)

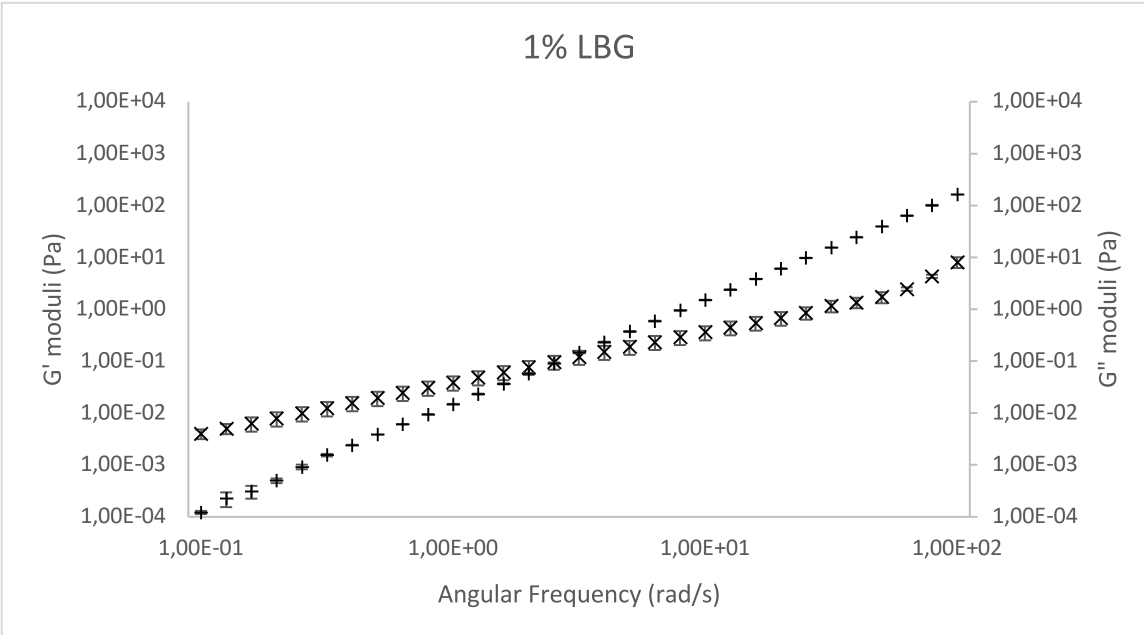
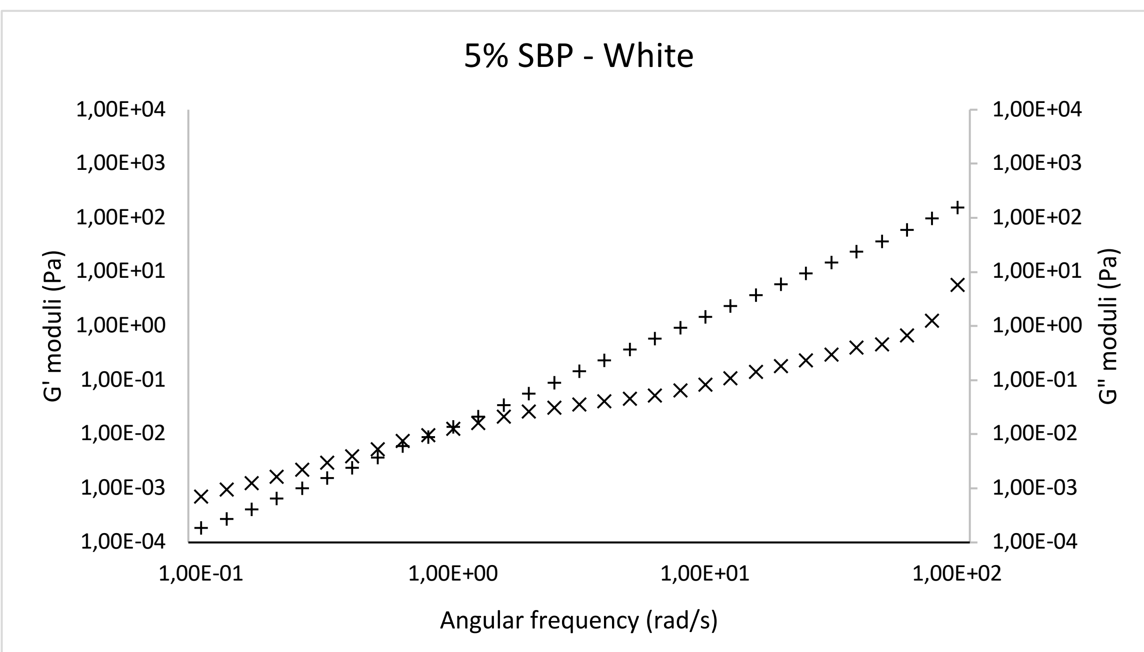
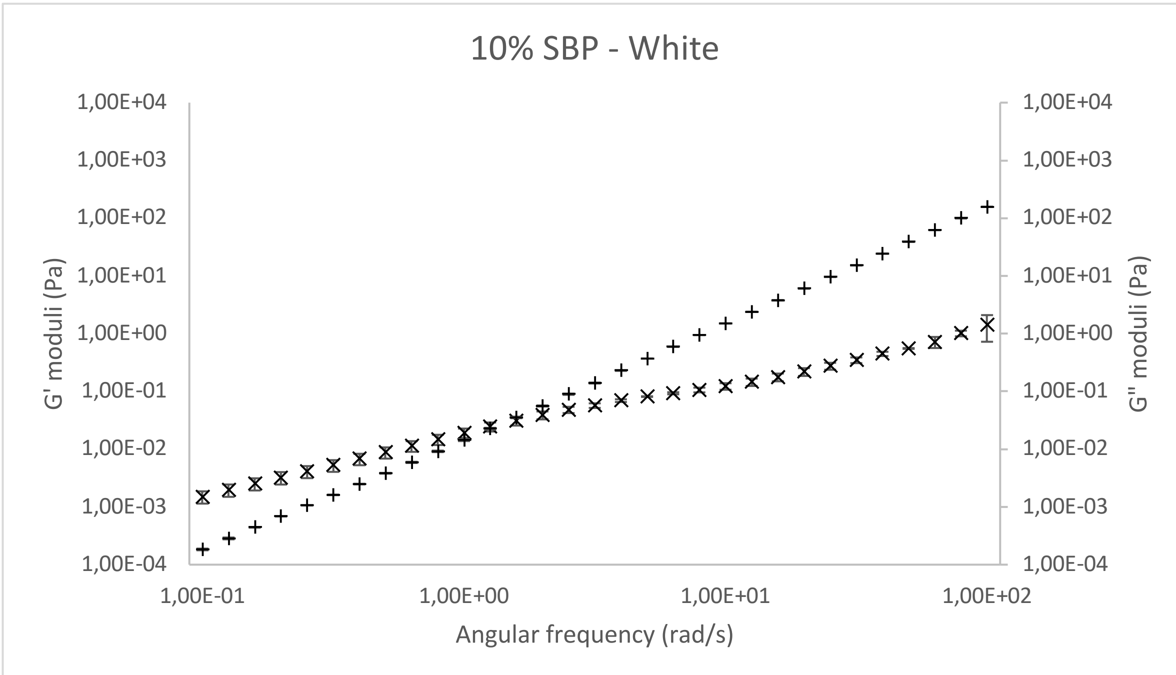


Figure 3.3. Storage (G') (+), and loss (G'') (×) moduli of aqueous solutions of locust bean gum (LBG) at 0.25 %, 0.5%, and 1% concentration levels. The angular frequency sweep is done at 0.1 to 100 (rad/s).





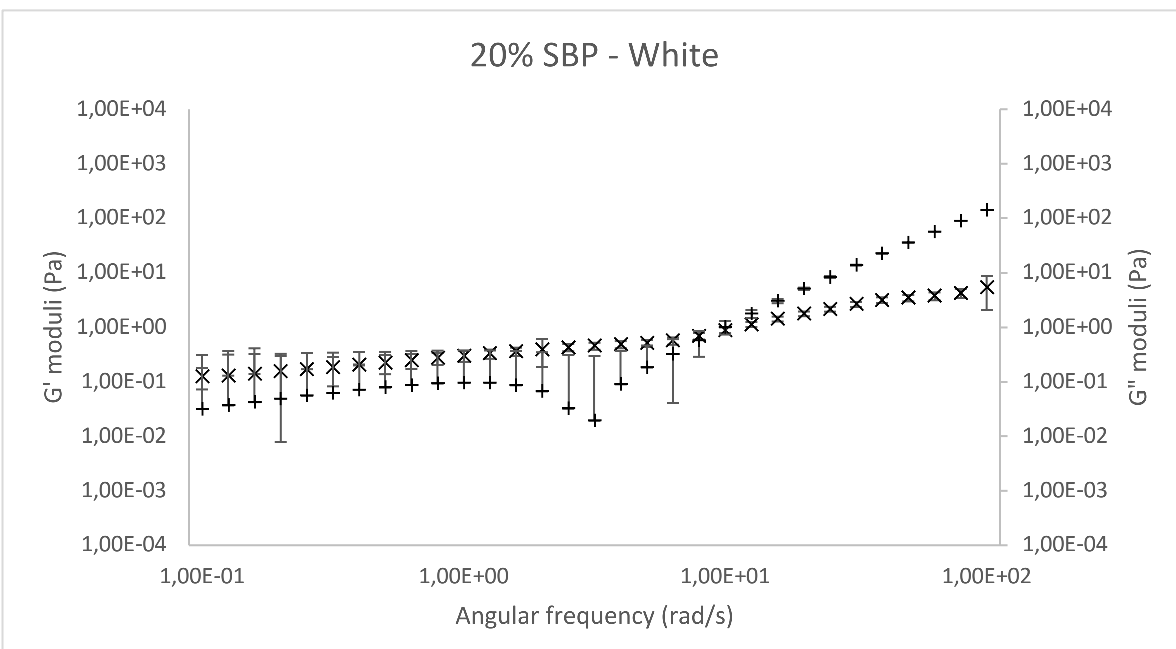
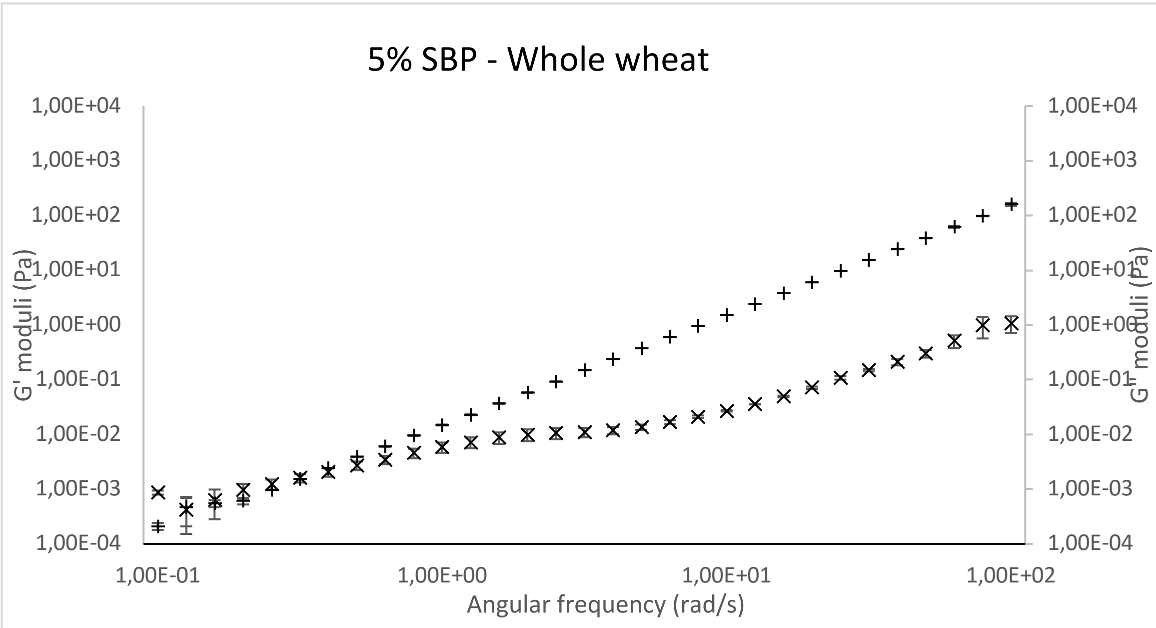
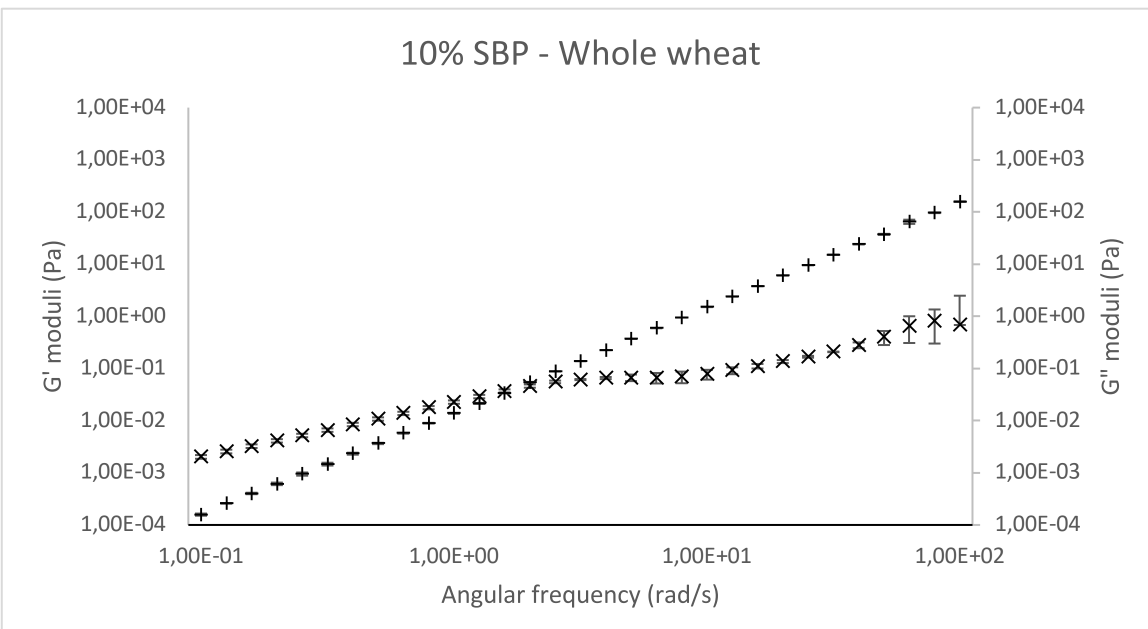


Figure 3.4. Storage (G') (+), and loss (G'') (×) moduli of aqueous solutions of white staled

bread powder (SBP) at 5%, 10%, and 20% concentration levels. The angular frequency sweep is done at 0.1 to 100 (rad/s).





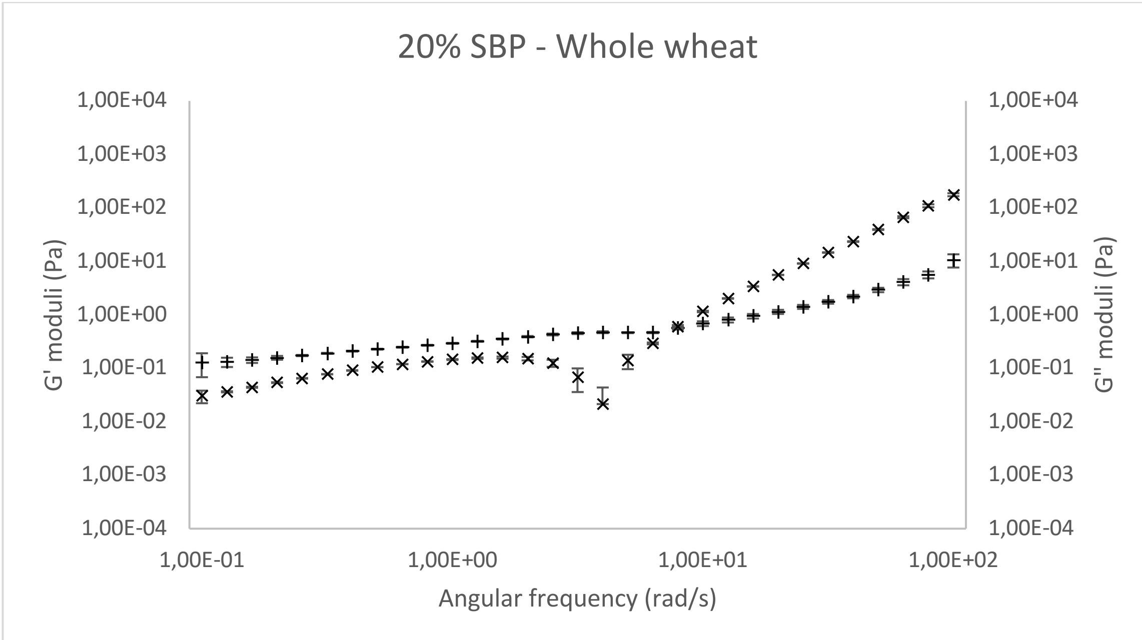
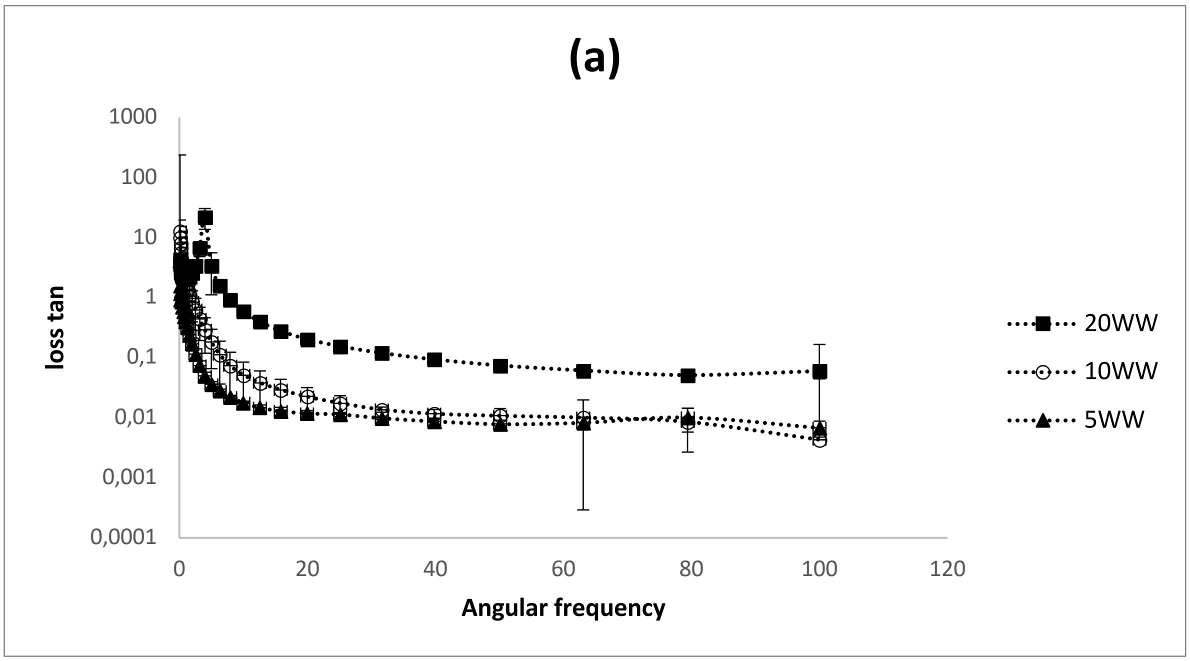


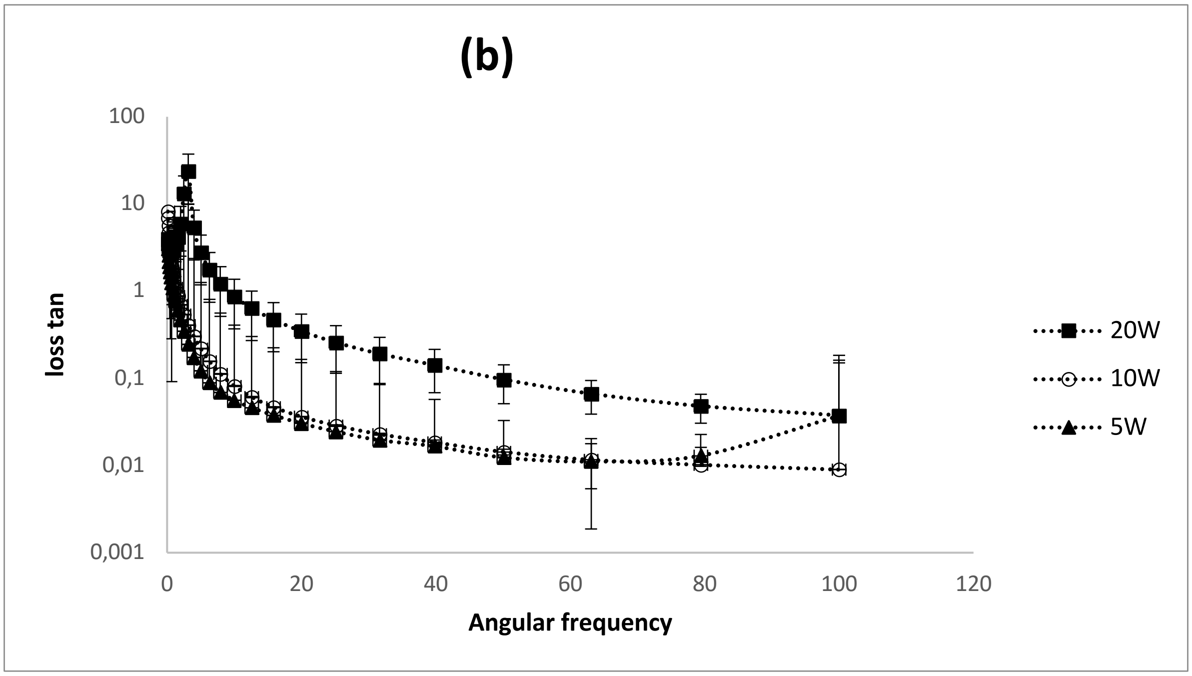
Figure 3.5. Storage (G') (+), and loss (G'') (×) moduli for aqueous solutions of whole wheat staled bread powder (SBP) at 5 %, 10%, and 20% concentration levels. The angular frequency sweep is done at 0.1 to 100 (rad/s).

In a study conducted by Mandala and others in 2004, a model-sauce was created adding gums such as locust bean gum followed by storage. After the storage period, dynamic and static rheological testing was performed to observe the behavior. Results showed that when a small amount of locust bean gum was added, the viscosity of the sauce was reduced, however, the stability of the sauce was greater than for the emulsion by its own (Mandala, et al., 2004). On the other hand, if larger amounts of LBG were added, an increased in viscosity occurred. LBG addition reduced the sauce consistency, however, the effect was less pronounced than when xanthan gum was used. In all cases, the G' values were greater than G'' modulus. In their case, the G'' to G' ratio was greater than 0.1 meaning that the samples were not true gels and rather were described as weak gels which are typical of the behavior of salad dressings and emulsions as demonstrated by the authors (Mandala, et al., 2004).

Generally, the greater the G', the more rigid and gel-like the sample would be. In the study by Mandala et al. (2004), the samples with LBG showed lower syneresis in comparison to samples having a higher amount of xanthan gum, because LBG has more available sites which are responsible for hydrogen bonding with water molecules. These hydrogen bonds caused a reduction or inhibition of the syneresis process from occurring. LBG decreases the retrogradation of starch occurring in starch samples and separation of water from the matrix formed.

Figure 3.6 presents the obtained loss tangent values, denoted as tan δ, for white, whole wheat bread powders and LBG solutions. As shown in Figure 3.6, the plastic behavior of the samples was more distinct at lower angular frequencies and transformed to a more predominantly solid or gel at higher frequencies. For both bread powders and LBG samples, a higher loss tangent was observed at more concentrated solutions. The loss tangent of both types of bread samples had similar decreasing trendline to LBG.





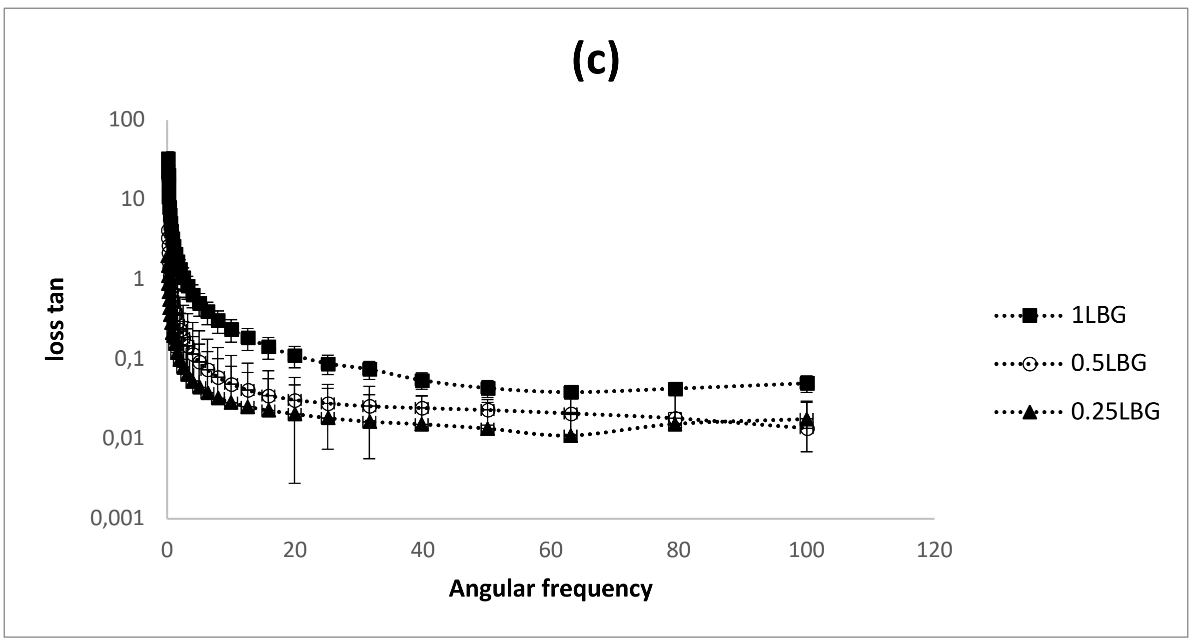


Figure 3.6. Calculated loss tangent for a) whole wheat "WW" (5% (▲),10% (○) and 20% (■) solutions) b) white SBP "W" (5% (▲),10% (○) and 20% (■) solutions) and c) Locust bean gum "LBG" samples (0.25% (▲), 0.5% (○) and 1% (■)).

3.4 Conclusion

In the presence of water, SBP from white and whole wheat breads increase the viscosity of aqueous mixtures. Thus, SBP can be an excellent alternative ingredient for its thickening properties when added to paste-like food products in aqueous mixtures. Contrarily to commercial gums used as thickening agents, this powder can form a paste at cold, ambient or hot temperatures. When SBP is dissolved in an aqueous solution, it is expected to show a shear-thinning behavior like the majority of the commercially available thickening agents.

The SBP solution showed a non-Newtonian flow which followed a shear thinning behavior characterized by an exponential model. Results showed that the flow behavior depended on the homogeneity of the components and particles of the samples and their alignment causing resistance to flow in the fluid. The investigation of the flow behavior leads to conclude that SBP is a potential thickener with a slightly higher viscosity experienced for white SBP rather than whole wheat bread powder. The potential of using SBP can also be highlighted since bread flour can be considered clean-label and nutritious due to its complex carbohydrate composition, and the potential to decrease the waste production from the bakery industry. The dynamic oscillatory testing of the staled bread samples found that a gelling point existed in both sample types of SBP and with LBG. Thus, there was a similar trend in the viscoelastic behavior of staled bread samples and LBG samples.

Connecting text

Chapter 3 discussed the rheological properties of different levels of staled whole wheat and white bread SBP samples in aqueous solutions. There is a potential of SBP samples to be used as additives in food formulations as a thickening agent.

Chapter 4 discusses the physico-chemical properties of SBP aqueous samples of white and whole wheat bread. The thermal properties were monitored using Differential Scanning Calorimetry (DSC). The microstructural differences of whole wheat and white staled bread powders were observed under Scanning Electron Microscope (SEM), while their dissolution capacity and cooking properties were tested to establish the potential use of SBP as an ingredient in food formulations.

Chapter 4
Physicochemical Properties of Staled Bread Powder (SBP)

Abstract

In this study, selected physical and thermal properties of white and whole wheat staled bread powders (SBP) at different concentrations (5%, 10%, and 20%) were evaluated. The dissolution capacity of both types of SBP was measured. Water retention is a crucial element to monitor since it has a direct impact on the shelf-life of foods. A variation in dissolution capacity was found between the different concentration of SBP ranging between 22.3 g and 75.5g for white and 16g and 75g for the whole SBP for a 100g of solution. With its low concentration of bran, as the insoluble fiber content, white staled bread powder (SBP) produced from staled bread crumb had a better WHC than whole wheat SBP samples. Cooking properties of samples were also measured in terms of the syneresis after a heat treatment followed by a cold storage cycle. With a storage period of 14 days at 4 °C, an increase in syneresis of maximum of 9% and 11.73% was seen in the separation phases between water and the sample solutions of 5% SBP concentration level for white and whole wheat, respectively. The higher syneresis observed are due to decreased cooking properties of thickening for both types of bread. A zero-order kinetics model was proposed to study the syneresis and concentration at all three levels of both SBP types. The microstructural texture of SBP powder was observed using a scanning electron microscope (SEM). The microstructural differences were principally seen due to the existence of bran in the whole wheat bread samples which lead to a less smooth surface with relatively more porous structure. Thermal properties of SBP from whole and white bread powders were monitored by Differential Scanning Calorimetry, where the heat capacity was determined using two different models and the white SBP showed a greater melting value compared to the whole wheat SBP curve due to its more abrupt endothermic curve.

4.1 Introduction

The functional properties of thickeners are affected by their ability to absorb and hold water within the food matrix they are incorporated in. A good understanding of the dissolution capacity is important to limit water loss after extensive storage time as a result of syneresis (Mao, et al., 2001). Dissolution capacity measurements are important determinants of quality deterioration in food pastes and gels as affected by external forces.

Often, the dissolution capacity predicts the quality of the food products not only due to storage conditions but also due to other transformations during processing and packaging. Food processing operations aim to avoid water loss from the product while ensuring textural quality and consumer acceptance. In the case of bread, the baking conditions can affect the bread retrogradation process and slow down water evaporation therefore, lowering the staling process (Rosell & Santos, 2010).

Generally, dissolution capacity in baked goods affects the starch granules and changes their order from glassy to rubbery state and thus preserving desirable attributes. Here, hydrocolloids come into play to form cross links hydrogen bonds with the water molecules thus forming thicker solutions, increasing viscosity, but most importantly retaining moisture, thus slowing down the process of staling. This advantage of water adsorption can enhance shelf-life of foods by slowing down the release of water from the food matrix (Mir, et al., 2016). As a result, it is needed to consider the stability of moisture content in food and food ingredients. The simplest way of measuring dissolution capacity is using a method known as centrifugation where centrifugal forces are exerted on the sample to observe the amount of water that was retained in the solid sample, measured after the process of centrifugal separation.

At the molecular level, the bread starch made of amylose and amylopectin, mixed with commercial food thickeners can highly influence and impact the dissolution capacity of the food formulation. Zhu and others (2012), reported that starch with longer length chains such as amylopectin and lower amylose content have tendency to increase gelatinization of granules, improve pasting and reduce the retrogradation process.

It has been highlighted in the literature that the shorter length chains of starch, like amylose, affect the retrogradation of bread (Kilcast and Subramaniam, 2011), causing staling. Amylose and amylopectin gelatinization process and retrogradation are not the only phenomena that can affect baked foods like bread but also other parameters, such as the dietary fiber (DF) content play an important role. In the case of staled bread powder (SBP), the DF content is slightly higher in the staled whole wheat bread due to its bran fiber (Siljeström, et al., 1986). The DF influences the textural properties of bread, impacting shelf life due to its ability to hold more water content for a longer period of storage.

An important physical character studied, in the case of the water retaining properties of ingredients during cooking, is known as syneresis. In fact, syneresis is the process that can be observed when the water found in the interstitial cavities of the food structure is expelled due to external forces. Moreover, the syneresis process leaves the product undesirable to consume and alters its textural properties. When syneresis occurs during cold storage, the molecules of gelatinized starch tend to re-associate. The process of reassociation which expels water molecules and causes syneresis needs to be slowed down and this can be achieved with the application of food thickeners within the food formulation.

Therefore, it is known that the thermal processing of food can affect textural and other quality criteria of foods. Heating treatments, such as cooking, can affect the food matrix in a way that it would release its water from the final product during cold storage.

In addition, the formulations used, including the type of thickening agent, influence the physical properties and texture of the formulated food products. The texturing properties of SBP from whole wheat and white breads can be monitored under Scanning Electron Microscopy (SEM) where important characteristics such as apparent porosity and smoothness can be evaluated. The mentioned physical characteristics are important to note since it may influence the extent of the thickening properties of SBP during cooking related to the viscosity of the paste formed.

In a study carried out by Reddy and others, (2013) where they studied the extent of retrograded starch, they found that the retrogradation of starch is inversely proportional to the viscosity of the starch. The higher the extent of retrogradation the lower the thickening capacity the sample would experience (Reddy, et al., 2015). Although retrogradation of starch in the staled bread cannot be evaluated under SEM, the images can provide valuable information on void cell elongation and porosity, which can be measured to predict the end-product quality of the food that SBP is added to (Hager, et al., 2012; Sidhu, et al., 1997). The starch crystallization during aging of bread appears to be significant, and amylose leaches out of the granules due to the baking conditions (Hug-Iten, 2003). Reheating pre-gelatinized starch cannot fully render the starch containing amylopectin and amylose to an amorphous state, however, it will still form a desirable paste which could be potentially used in food formulations. Therefore, studying the micro-structural properties of the SBP using SEM can help to characterize differences in the microstructure of SBP upon aging of white and whole wheat dry crumb.

SEM observations of wheat doughs have been shown to illustrate a bi-continuous gluten system with an embedded starch in which the protein creates a web-like or fibrous-like structure in the gluten dough and the bread (Ahlborn, et al., 2005). Thus, the baked bread upon aging is expected to show a random structure with less clarity. However, there is indeed a web-like structure seen where gas cells are evident within SEM images. Those gas cells are cavities also known as voids and are due to the dried staled breadcrumbs upon storage, and they can be evaluated in both white and whole wheat bread.

When a starch-based product is heated with water, there is a phenomenon that causes an irreversible disruption of starch granules, this phenomenon is known as gelatinization, as previously mentioned. At that point, the amorphous part of the starch will go through the glass transition phase which is the starting of the melting of the hard phase to transform into a rubber-like form (Ong, et al., 1998). The gelatinization temperature is determined using a Differential Scanning Calorimeter (DSC). During storage, due to retrogradation, the crystalline starch can re-associate at a certain temperature at which this reassociation can be monitored using DSC.

At the molecular level, as moisture content of the sample increases, it also experiences an increase in molecular mobility of the components. Therefore, the lower the water activity in amorphous material would cause more crystallization and need of a higher melting temperature (T_m) than T_g. Crystallization and melting of system components are described by a first-order phase transition between the liquid and the solid states. Hence, the crystallization's latent heat that is released from the sample is equal to the amount of heat gained for melting at the same temperature (Telis and Tonon, 2017).

Semi-crystalline amorphous polymers have a glass transition temperature, however, the crystalline regions of such materials remain hard at temperatures between the melting temperature and glass transition temperatures. As the semi crystalline polymer melts above the melting temperature, a rapid drop in modulus is observed mainly occurring in partially crystalline carbohydrates polymers such as cereal foods, most specifically in starches. It should be noted, as reported by Roos and Drusch (2015) in their findings on the phase transitions of food, that semi crystalline polymers such as starch from wheat products have a T_g at about 100-150°C below T_m. Therefore, at approximately 100°C above the glass transition temperatures, the amorphous materials should approach the equilibrium of liquid state (Fandhui, 2017). When the starch granules are heated up to gelatinize with high moisture content, granules swell because of the water absorption. The longer heating time allows more starch granules to swell. The heating of the retrograded starch of staled bread powder makes starch gelatinization difficult to occur resulting in higher gelatinization transition temperatures (Morris, 1990).

Studies have shown that by using DSC, the measured thermal values are affected by the sample preparation and the DSC method of operation. The parameters that affect the DSCs' final data are the moisture content, degree of gelatinization of the granules of starch, enthalpy changes, particle size and solubility (Tea, et al., 2000; Wang et al., 2002).

Noda and others (1996) postulated that the glass transition temperature and heat capacity are influenced by the molecular architecture of the crystalline region of starch which is due to the amylopectin's distribution of short chains but not by the proportion of the crystalline region of amylose (Yagi, et al., 1996). Zhou and others (2002) reported that amylose is responsible for short-period changes during retrogradation, however, the amylopectin is responsible for the longer-period of crystallization due to its larger molecular structure compared to amylose (Zhou, et al., 2002a; 2002b). Slade and Levine (1988), in their study on the non-equilibrium melting of native granular starch stated that water acts as a plasticizer of the amorphous regions in the native granules at the glass transition temperature.

As a result, the objectives of this study were to report on selected physical properties of SBP. This characterization will help in obtaining a deeper understanding of the effects of heat on the functional properties of SBP. In this regard, the capacity of thickeners described by their ability to prevent syneresis during prolonged storage time is evaluated. Also, selected concentrations of SBP in solutions, made of whole and white wheat bread crumb, were compared and monitored for their potential ability to slow down the process of syneresis. Then porosity of the physical structure of SBP was studied through SEM to evaluate the surface morphology (homogeneity of porosity) and compare the white and whole wheat SBP to correlate with their quality as a thickener. Finally, a DSC study effectively characterized the thermal properties of SBP.

4.2 Materials and Methods

4.2.1 Evaluation of hydration and dissolution capacity

Selected concentrations of 5g of SBP, 10g of SBP, 20g of SBP for whole wheat and white bread were prepared and 95g, 90g, and 80g of water were respectively added to the different concentrations of SBP (w/w) into centrifuge bottles. The bottles were agitated for 1 h using a magnetic stirring plate at approximately 600 rpm, then rested for 10 min. After manually shaking for 1 min, the tubes were rested for 5 min and then centrifuged for 10 min at 3000 x g. The supernatant (liquid) was then discarded and each tube was weighed, and the dissolution capacity (g of water/g flour) was calculated using Eq. 4.1 for each sample. The procedure was conducted in triplicate to minimize experimental errors.

Dissolution capacity= [(wt of bottle after decanting- wt of dry bottle)- (total flour wt (g)]/ total flour wt (g) Eq. 4.1

4.2.2 Cooking properties measurement (syneresis)

5 g, 10 g, and 15 g, of whole and white wheat bread SBP were each time added to boiling water in a cooking pan. The amount of boiling water was adjusted to make a sum of 100 g solution for each sample. The solutions were mechanically agitated until forming a paste for 3 min and were let to rest in the pan for 1 h at room temperature. The samples were then poured into centrifugal tubes, sealed properly and placed in cold storage (4 °C). All experiments were done in three replicates. The cooking properties were measured after 4,

7 and 14 days of storage and the results were reported as expressed in the following equation (Eq. 4.2) as a percent of water released after gravimetric separation of water following cold storage (Charoenrein et al., 2008). Each experiment was done in duplicate.

% syneresis = (mass of the liquid separated from paste)/(total mass paste)*100 Eq. 4.2

4.2.3 Differential scanning calorimetry (DSC)

To perform the DSC analysis, 10 mg of SBP from whole wheat and white wheat bread was weighed and placed in hermetically sealed aluminum pans (TA Q2000, TA Instruments, Newcastle, DE, USA). Nitrogen gas was purged at a rate of approximately 50 mL/min. The thermal scanning calorimetry was performed with a temperature sweep test at a rate of 5 °C/min from -25°C to 170°C. The reference was an empty aluminum pan. The outcome results were collected as the heat flux J/g as a function of temperature (°C). All outcomes results were done in duplicate and analyzed using the Universal Analysis Software (version 3.6C, provided by TA instruments, Newcastle, NJ).

4.2.4 Scanning Electron Microscopy (SEM) analysis

Scanning Electron Microscopy (SEM) images of SBP from white and whole wheat bread were obtained after 14 days of storage at room temperature (22 °C). The dried powdered samples were mounted on aluminum stubs with conductive adhesive for SEM (HHT, Hitachi TM3000, USA). The images were captured (at x50, x150, x180, x200, x500, x600, x800, x1.0k, x2.5k) to observe the structure of white SBP and whole wheat SBP. The imaging condition was 5kV Accelerating voltage and 6 mm working distance.

4.2.5 statistical analysis

Statistical analysis was carried out using Microsoft Excel software. Significance of trends were confirmed if comparison of means of sets differed $P<0.05$ (student's t-test).

4.3 Results & Discussion

4.3.1 Dissolution capacity

Dissolution capacity is an important factor to determine the potential applications of thickening agents in food products (Khemakhem, et al., 2019). With a low dissolution capacity, the more adverse effects are seen such as retrogradation and crystallization that occur, affecting yield and quality attributes of the product in which the thickening agent is used. A potential thickening agent is considered functional when it has the ability to increase the viscosity while minimizing the syneresis as well as having good dissolution capacity (Gujral, et al., 2002).

Therefore, the capacity of dissolution of white and whole wheat staled bread powders were tested using a low-speed centrifugation method where the unabsorbed water will slowly expel and separate from the sample. The only force causing the water to separate from the samples of SBP is due to the applied centrifugal force and gravity.

Dissolution capacity is affected by a number of variables during sample preparation, such as concentration, agitation degree, the centrifugal force and the type of staled bread. The total moisture content for treatments after 10 min rest was measured and is reported in Table 4.1. Results demonstrated a lower dissolution capacity regarding the 95g of water added to 5g of SBP samples for both types of bread. The more water expelled demonstrates the lower ability for holding water within the structural network of SBP.

Table 4.1 Dissolution Capacity (% per 100g samples by centrifugation method at 1000×g for 10 minutes)

	SBP-WW20%	SBP-WW10%	SBP-WW5%	SBP-W20%	SBP-W10%	SBP-W5%
Dissolution Capacity	75.0%± 5.2%^{a}	51.0%±3.6^{b}	16.0%±1.9^{c}	75.5%±6.7^{a}	52.0%±5.0^{b}	22.3%±1.8^{d}

WW: Whole Wheat, W: White

Different superscript letters indicate statistical difference at 0.05.

As can be seen in Table 4.1, the white SBP expelled less water than whole wheat SBP at all concentration levels. The results showed a significant difference between all concentrations of each group. In addition, at 20% and 10%, the dissolution capacity of whole wheat SBP and white SBP did not show a meaningful difference (<0.5). Overall, at higher concentration levels, less water was separated throughout the centrifugation and the dissolution capacity was not related to the type of bread at higher concentrations. However, the dissolution capacity was considerably higher for the white SBP at 5% than that of whole wheat bread. Seyer and Gélinas (2009), in a study on the bran characteristics of wheat in whole wheat bread, concluded that there is a correlation between water absorption of bran and the insoluble fiber in the whole wheat SBP. Thus, it could be concluded that the ability for dissolution of whole wheat bread powder is affected due to the bran content when compared with white bread.

Considering the higher nutritive value of whole wheat bread due to its bran content, wheat bran is converted to a source of insoluble fiber in the human body. Fiber intake is generally appreciated for its health benefits and may provide prevention of diseases such as colon and breast cancers, cardiovascular disease, obesity and gastrointestinal diseases (Stevenson & Phillips, 2012). However, the bran can have a negative effect on the bread volume and its ability for absorbing water (Boita et al., 2016), especially when processed into SBP.

The dissolution capacity was concentration dependent at higher concentrations and was influenced by the ability of the SBP to hold water. In this regard, it was found that the dissolution capacity decreased with increasing amount of SBP as illustrated in Table 4.1. The results suggest that there is a direct relationship between moisture held after centrifugation, to the inherent binding property of the powder staled bread. The dissolution capacity of SBP could be highly affected by the high absorption of water due to the weak association of amylose-amylopectin compounds in the already gelatinized granules. However, lower dissolution capacity could be due to a stronger association of the starch polymers in the aged granules and could result in expelling the water molecules out of their matrix (Ali, 2016).

4.3.2 Cooking properties (syneresis)

Evaluating the degree of syneresis of SBP implies monitoring the percentage of water released per 100 g of cooked, thickened samples as a function of the subsequent period of storage under cold temperatures (4 °C), (Correa, et al., 2013). The experimental data are shown in Table 4.2. According to the data, Syneresis increased for all samples as a function of storage time. The syneresis level decreased with increase in the concentration. The lowest and highest values belonged to 5% and 20% whole wheat bread samples.

According to a study on rice-locust bean gum gels by Correa et al. (2013), application of food thickeners, such as locust bean gum, could enhance the cooking characteristics of the starchy-products. Their approach to measure the mentioned parameter was to measure the syneresis after several freezing and thawing cycles and they finally concluded that syneresis was reduced upon addition of the thickener whereas syneresis increased without the use of a thickening agent.

Table 4.2 The experimental data obtained from cookin properties tests based on % syneresis of liquid phase from 5%, 10% and 20% hydrated SBP powders from whole wheat and white breads during cold storage at 4˚C up to 14 days.

	% Syneresis of white SBP solutions		
Storage (days)	**5%^{a}**	**10%^{bd}**	**20%^{c}**
4	6.56 ± 0.8	2.38 ± 0.1	0
7	8.09 ± 1.1	3.16 ± 1.3	0.43 ± 0.3
14	9.00 ± 2.1	4.85 ± 0.8	1.83 ± 1.2
	% Syneresis of whole wheat SBP solutions		
Storage (days)	**5%^{a}**	**10%^{b}**	**20%^{cd}**
4	8.01 ± 0.7	2.21 ± 1.4	0 ± 0.0
7	10.25 ± 1.6	2.58 ± 0.8	0.31 ± 0.2
14	11.73 ± 1.4	3.19 ± 1.7	1.00 ± 0.8

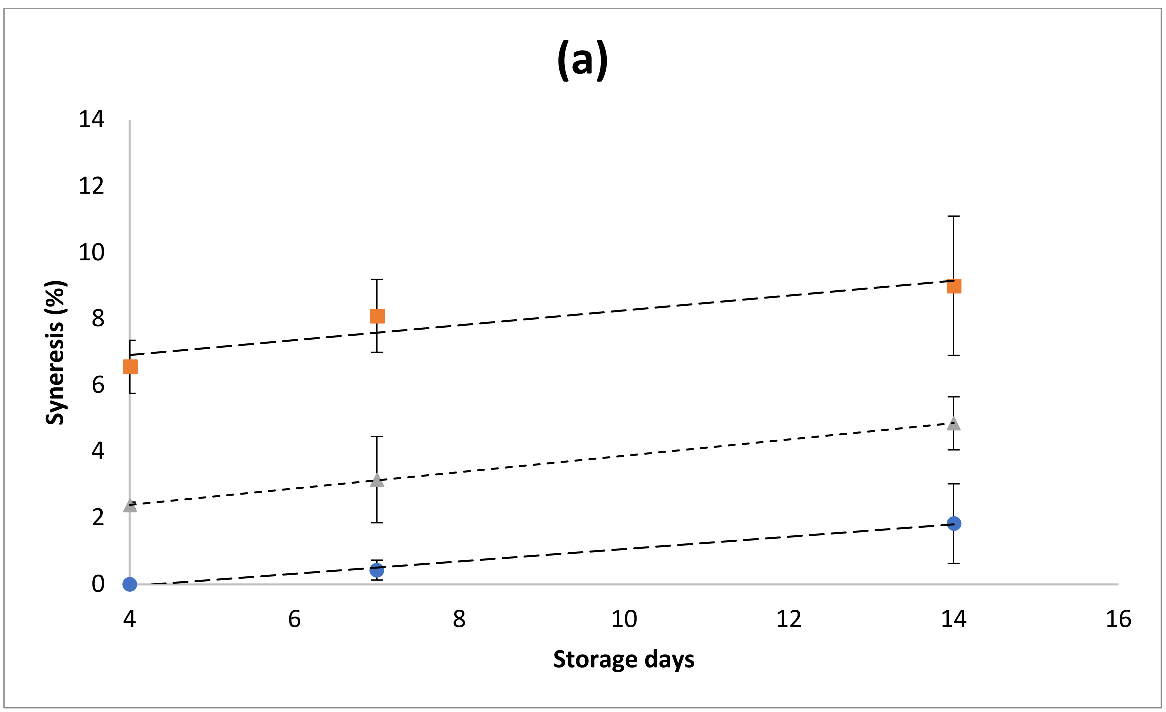
Different superscript letters indicate statistical difference at 0.05.

Modeling the syneresis (cooking properties)

As can be seen in Figure 4.1, the measured syneresis from all samples fits a zero-order kinetic model (Eq. 4.3). The model parameters are shown in Table 4.3. The obtained slope ranged between 0.1 to 0.34 for whole wheat SBP solutions and the slope for white SBP solutions ranged from 0.18 to 0.25. A steeper slope for whole wheat SBP was seen. It could be inferred that the steeper slopes result in a greater concentration dependency of the cooking properties.

$$S = kt + b \qquad \text{Eq. 4.3}$$

Where S, k, t, and b represent Syneresis percentage, reaction rate (1/d), time (d), and line intercept, respectively.



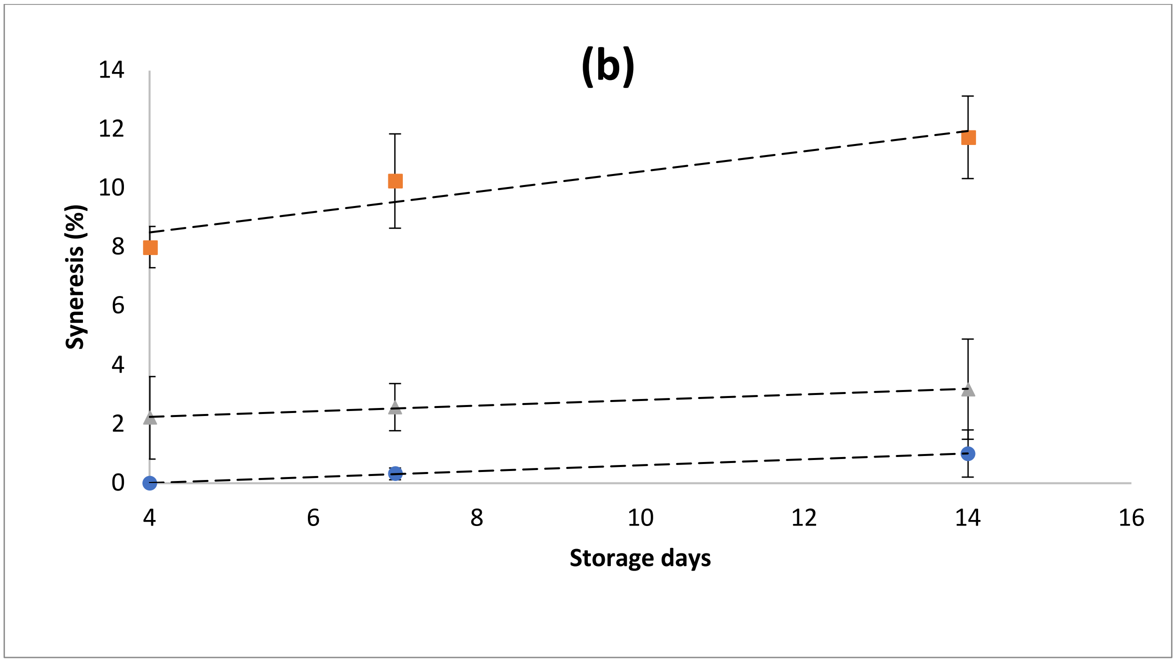


Figure 4.1. Measured water syneresis of a) white and b) whole wheat SBP at three different concentrations of 5% (■), 10% (▲), and 20% (●) as a function of different storage days of 4,7, and 14 days at cold storage (4 °C) with their fitted models.

For both types of SBP solutions, a reduction of syneresis, with an increase of concentration was apparent which is likely due to the ability of the increasing starch granules to absorb more water, swell, and turn into much bigger sized granules.

Table 4.3 The obtained zero-order kinetics model parameter syneresis of whole and white wheat SBP as a function of storage time.

	5%SBP -White	*5%SBP-Whole wheat*	*10%SBP -White*	*10%SBP-Whole wheat*	*20%SBP -White*	*20%SBP-Whole wheat*
k	0.22	0.34	0.2466	0.09	0.19	0.10
b	6.02	7.13	1.4126	1.87	-0.79	-0.39
R^2	0.99	0.99	0.99	0.98	0.87	0.89

Generally, thick pastes from SBP solutions or food gels are susceptible to syneresis during cold storage. The more elastic the SBP solution, the less syneresis is shown after cold storage because of the increased dissolution capacity of the added thickening agent. On the other hand, when there is less thickening agent added, the more brittle the gel is and more syneresis is to be expected during cold storage. Thus, the concentration of SBP highly affects the extent of syneresis. As stated in the study by Banerjee and Bhattacharya (2011), there is a relationship between the increase in the concentration of thickening agent and the decrease of the syneresis in food gels. Decreasing syneresis for food gels can provide better cooking properties, thus rendering a better quality and texture during subsequent cold storage.

It has been reported by Nguyen and others (2017) that a stronger correlation between the syneresis and the concentration of the thickening additives exists at only a certain range of concentration of hydrocolloids. The authors suggested that only within this range the increase in the concentration can lead to an increase in the firmness of food gels thus a reduced syneresis (Nguyen, et al., 2017).

The existence of a correlation between syneresis and concentration exist only when the sample has an elastic character (Kontogiorgos, et al., 2006). It is observed that with an increase of concentration, the elastic modulus of the food thickener was predominant over the viscous modulus. Their study mainly focused on the effects of gums on dough rheology and bread quality parameters in gluten-free products using gelatin. However, when the authors presented other hydrocolloidal gums like xanthan gum and carrageenan at lower concentrations, syneresis did not correlate with the concentration and did not offer a direct dependency between syneresis and concentration. The previous results showed difference of behavior that was explained due to do the ability of gelatin to not settle and flocculate in the protein network formed in the food matrix compared to other hydrocolloid gums; for example, they used dough and gluten network to explain their findings.

As can be seen in Figure 4.1, the intercept for white SBP solutions is 6.56 for 5% concentration, 2.38 for 10% concentration and 0 for 20% concentration. Intercept for whole wheat SBP solution is 8.01 for 5% concentration, 2.22 for 10% concentration, finally 0 for 20% concentration of the samples. It was seen that the intercept parameter had a higher value for whole wheat at 5% concentration than for white SBP. The meaning behind it is that after 4 days of storage the syneresis for whole wheat at 5% is more significant than in the white bread samples.

The syneresis results were characterized using two variables (slope and intercept). To combine the effect of variation of both variables at each concentration, the area under the curve was determined by integration as presented in Eq. 4.4 for each line shown in Figure 4.1. The absolute values of the area under the line or in other words the integrals for the boundary conditions tested are illustrated in Table 4.4.

$$I = \int_{4}^{14} (kt + b)\, dt \qquad \text{Eq. 4.4}$$

Table 4.4 The calculated integral under the line of syneresis vs. storage time obtained from Figure 4.1. (W,white wheat bread; WW whole wheat bread).

Sample	**5SBP-W**	**5SBP-WW**	**10SBP-W**	**10-SBP-WW**	**20SBP-W**	**20SBP-WW**
Integral	**80.39±19.5**	**102.31±17.67**	**36.32±10.32**	**27.27±4.67**	**8.79±2.12**	**5.09±1.1**

As can be seen, the area under the curves ranged between 5.09 to 102.31 for whole wheat bread powder and between 8.79 and 80.39 for white bread powder. The cooking properties of the SBP samples were evaluated for further analysis. The data failed to fit a model based on the Arrhenius equation to achieve the activation energy parameter. However, when plotted as a function of concentration, the integral values showed a power law relationship (Eq. 4.5) with the concentration levels as can be seen in Figure 4.2.

$$I = mc^{n} \qquad \text{Eq. 4.5}$$

Where “I” is the graphical integral values presented in Table 4.4, and m is the constant factor, c is the concentration and n is the exponent. The fitted plots are shown in Figure 4.2, while the constant factor (m) and exponent (n) are presented in Table 4.5.

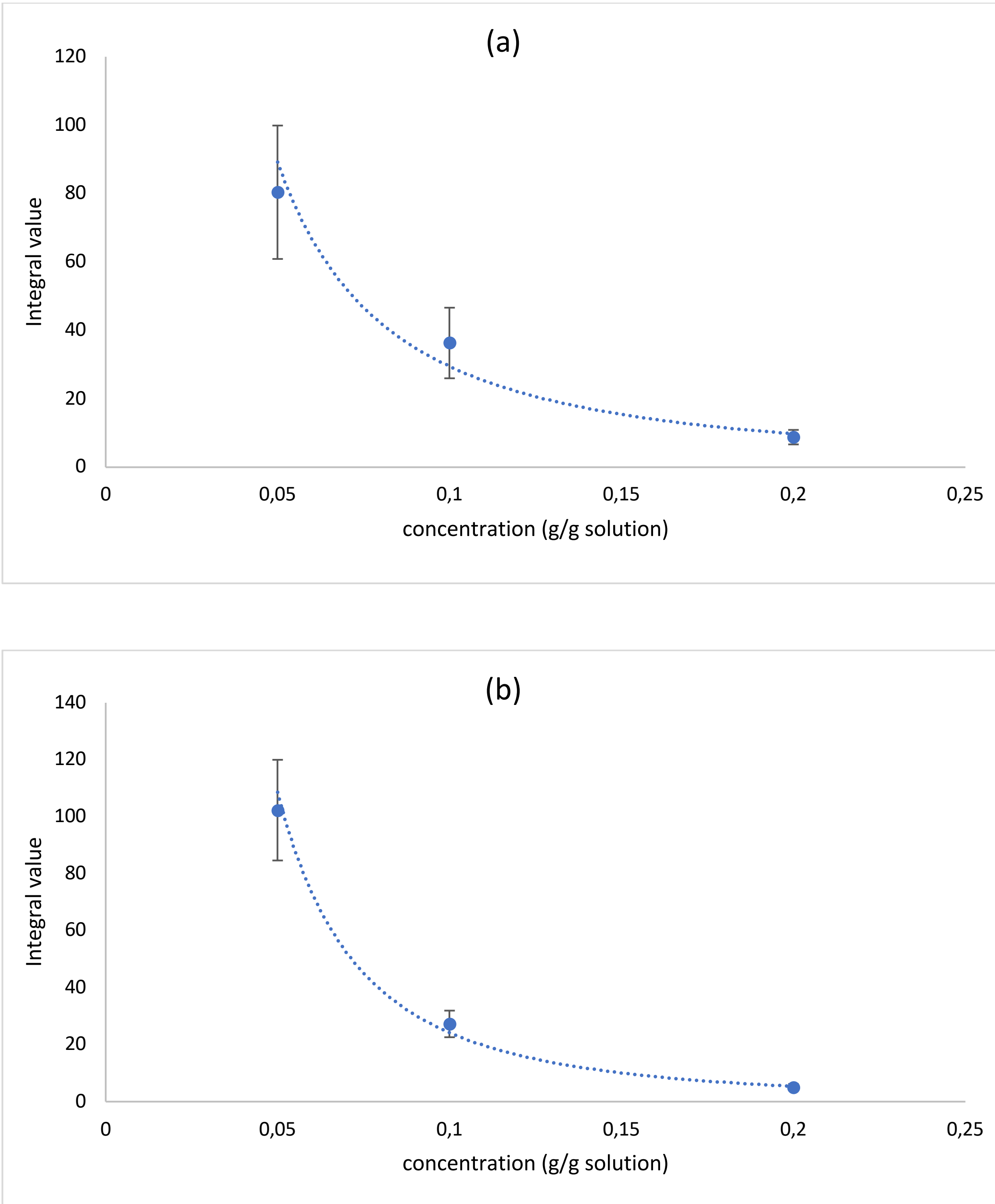


Figure 4.2. Plot of I vs. 1/c; where I is the area under the line of syneresis % vs. storage day for three different concentrations (c) of 0.05, 0.10 and 0.20 (w/w) of a) White SBP and b) whole wheat SBP.

The model suggested that the cooking properties were improved with an increase in the concentration. Syneresis was reduced with increased concentrations while syneresis increased with an increase in storage period over the tested period of 2 weeks. The obtained values of the power law model (Eq. 4.5) are presented in Table 4.5. The constant value for the whole wheat SBP was lower than for the white SBP, however, the overall cooking properties were more enhanced by an increase of the concentration for the whole wheat SBP samples since the absolute values of the n parameter was greater for this sample.

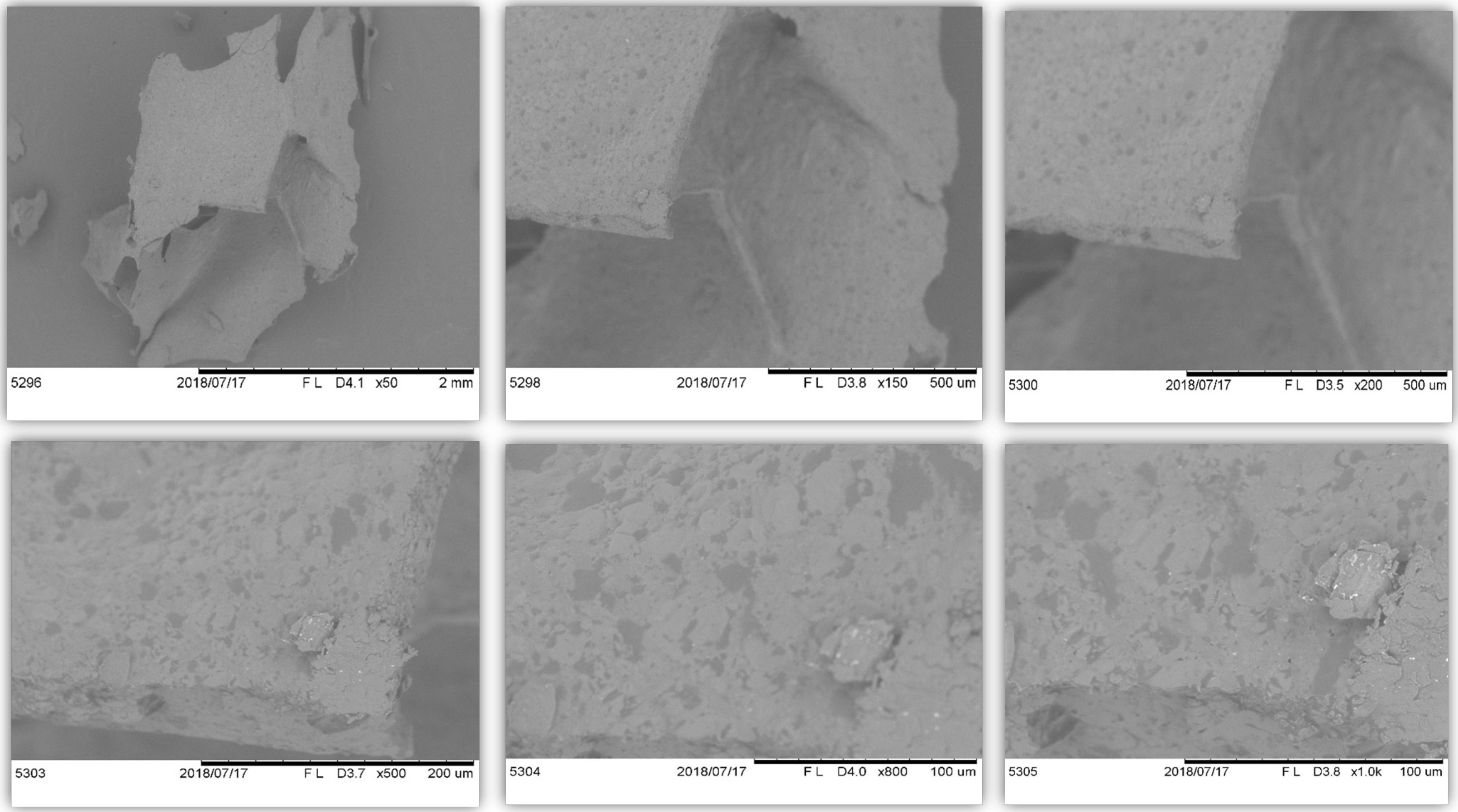
Table 4.5 The obtained parameters of the power law model for the cooking properties of whole and white wheat bread SBP solutions as a function of concentration.

Sample	m	n	R^2	RMSE
Whole SBP	0.29	-1.95	0.99	1.93
White SBP	1.61	-1.30	0.97	5.73

4.3.3 Microstructural properties

Scanning electron microscopy (SEM) was used to monitor and compare the microstructure of staled white and whole wheat bread powders. In the following SEM images (Figure 4.3.) the surface morphology of bread for 6 different magnifications is illustrated; x50, x150, x180, x200, x500, x600, x800, x1.0k, x2.5k. The crumb staled powder exhibited larger cavities for whole wheat bread than for white bread (as can be seen by comparing Figure 4.3 a) with Figure 4.3 b). The cavity are not homogenously distributed and were not of a uniform size, as also presented in a study done by Giannone and others (2016) in which it was explained that the in-homogeneity of the pores found in both types of aged crumb powder is due to the extended storage period and accelerated bread staling at lower moisture content levels. The lower water activity after staling of crumb increases the shrinkage of pores giving a slightly more oval shape to the pore such as in Figure 4.3 a) for whole wheat SBP. The morphology evaluations showed more homogeneous air-filled structures in white staled bread crumb. In fact, the microstructure of whole wheat bread showed a more complex structure with many cavities due to the fiber content from whole wheat compared to white SBP, as the shape of pores and the irregular size is affected by the bran content.

a)


5296 2018/07/17 F L D4.1 x50 2 mm
5298 2018/07/17 F L D3.8 x150 500 um
5300 2018/07/17 F L D3.5 x200 500 um
5303 2018/07/17 F L D3.7 x500 200 um
5304 2018/07/17 F L D4.0 x800 100 um
5305 2018/07/17 F L D3.8 x1.0k 100 um

b)

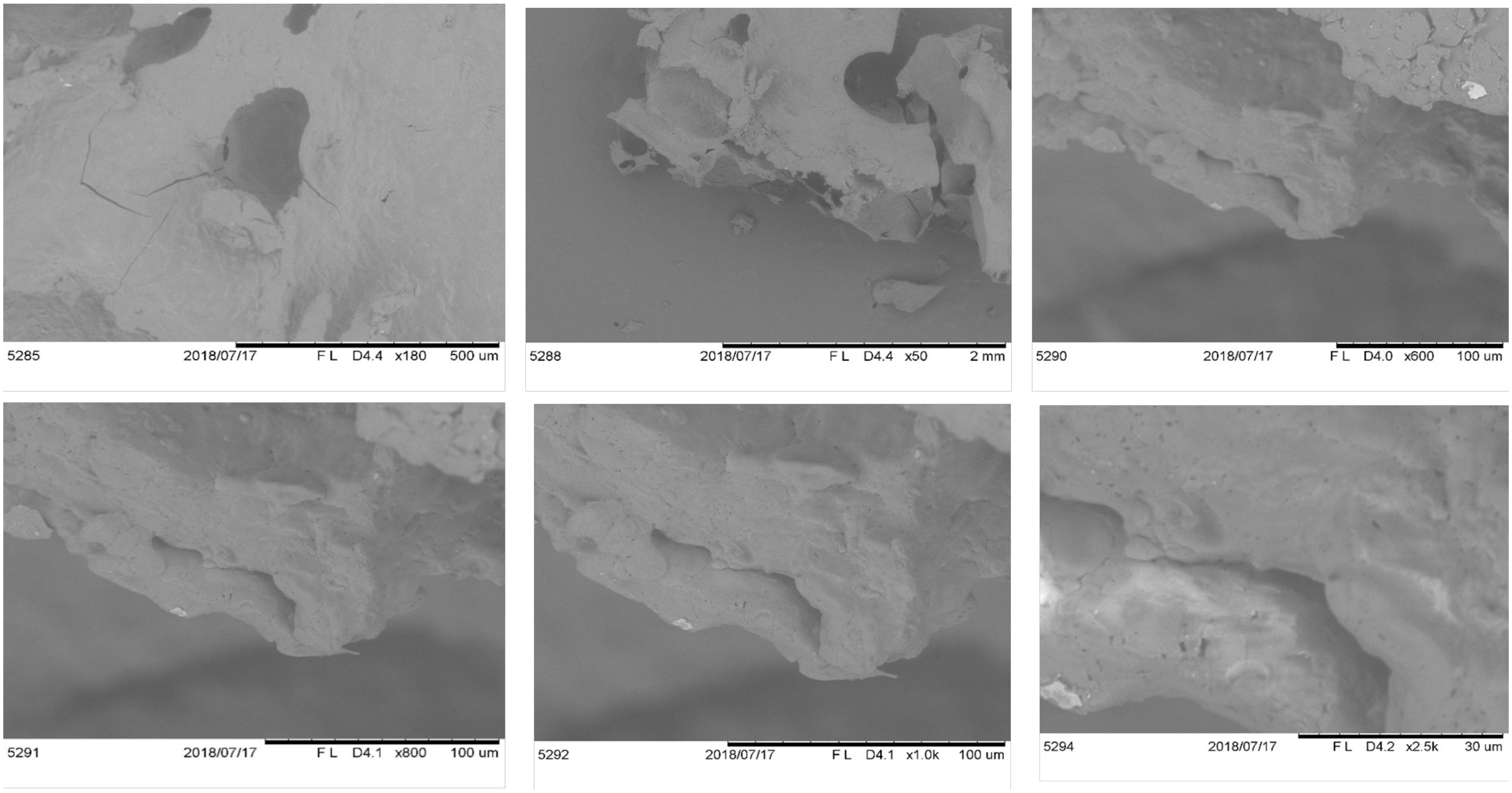


Figure 4.3. Scanning Electron Microscopy (SEM) of staled a) whole wheat bread powders and b) white bread powders after 14 days of storage at room temperature (22 °C).

White bread seemed to have less cavities than whole wheat bread and in comparison, the white SBP had a smoother structure due to its lower fiber content.

4.3.4 Differential Scanning Calorimetry (DSC)

A thermal analysis was conducted using Differential Scanning Calorimetry (DSC). Several authors have used DSC analysis as a strong tool for the evaluation of the bread staling phenomenon. The chemical composition of each type of flour is important in the extent of staling. Mainly, the starch part undergoes various physical changes during both baking and storage which could affect the staling phenomenon.

In general, starch is known to be the main reason of staling development. The amylose fraction of starch is the first component that starts the staling process within hours after baking. However, the amylopectin fraction of starch is claimed to be the main reason of the development of the firmness of bread during storage (Ribotta and Le Bail, 2007).

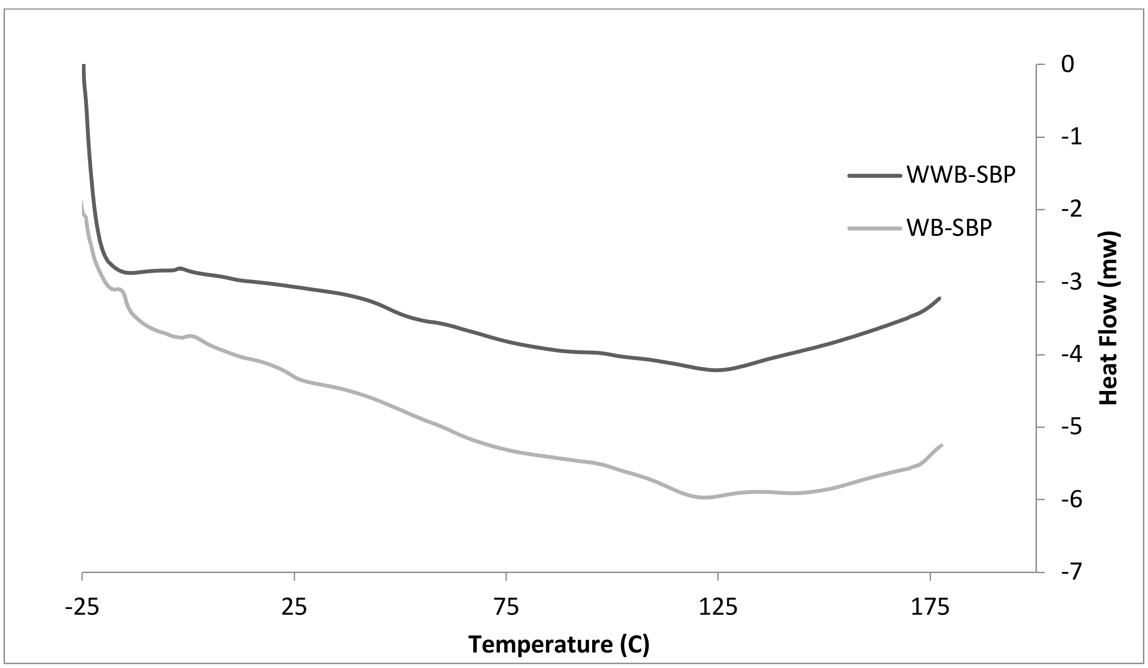


Figure 4.4. The differential calorimetry scanning (DSC) thermograms of staled breadcrumbs after 7 days of storage at 25°C. The measurements were done from -25°C to 170 °C running a temperature sweep of 5°C/min.

The results (Figure 4.4) for both samples showed gradual drop in the heat flow graphs. This indicates an endothermic behavior of SBP during heating. In other words, both samples absorbed the heat energy provided by the calorimeter. This energy is used as a source to provide different reactions within the material such as denaturation, phase change, etc. As can be seen in Figure 4.4 the thermograms of both whole wheat and white samples followed the same pattern. In other words, the thermal fingerprint of both samples was almost the same. This could be because of the similar starch composition of both types of breads. However, the white bread powder showed higher degree of endothermic behavior compared to the whole wheat bread powder samples since the falling trend was more visible (Fadda, et al., 2014).

Ribotta and Le Bail, (2007) stated that the degree of staling is in a direct relationship with the endothermic fall observed on DSC curves. Thus, it could be suggested, from the differences in DSC curves, that white bread powder showed a higher degree of staling. Van Hung et al. (2007) studied the staling behavior of white waxy wheat flour breads made by removing germs and bran from the flour. They concluded that removing the germ and bran resulted in a delay in the staling phenomenon. This was claimed to be as a result of increasing the waxy starch percentage relatively within the formulation after removing the germ and bran components. Based on this assumption, regarding our research, it can be concluded that the difference between the white bread and the whole wheat bread was principally caused by the presence of the bran.

4.3.5 Heat capacity

The heat capacity is a measure of the energy needed to increase the temperature of a given mass of material. It is an important physical thermophysical property during the heating and cooling of foods. This property is usually a function of temperature and can be calculated by processing the DSC data. In this regard, the apparent heat capacity was calculated using Eq. 4.6 (Morîntale, et al., 2013):

$$\frac{dq}{dt} = mC_p\frac{dT}{dt} \quad \text{Eq. 4.6}$$

where $\frac{dq}{dt}$ (J/s), m(g), C_p(J.°C^{-1}. g^{-1}), and $\frac{dT}{dt}$ (°C/s) represent heating rate, mass, heat capacity, and rate of temperature change.

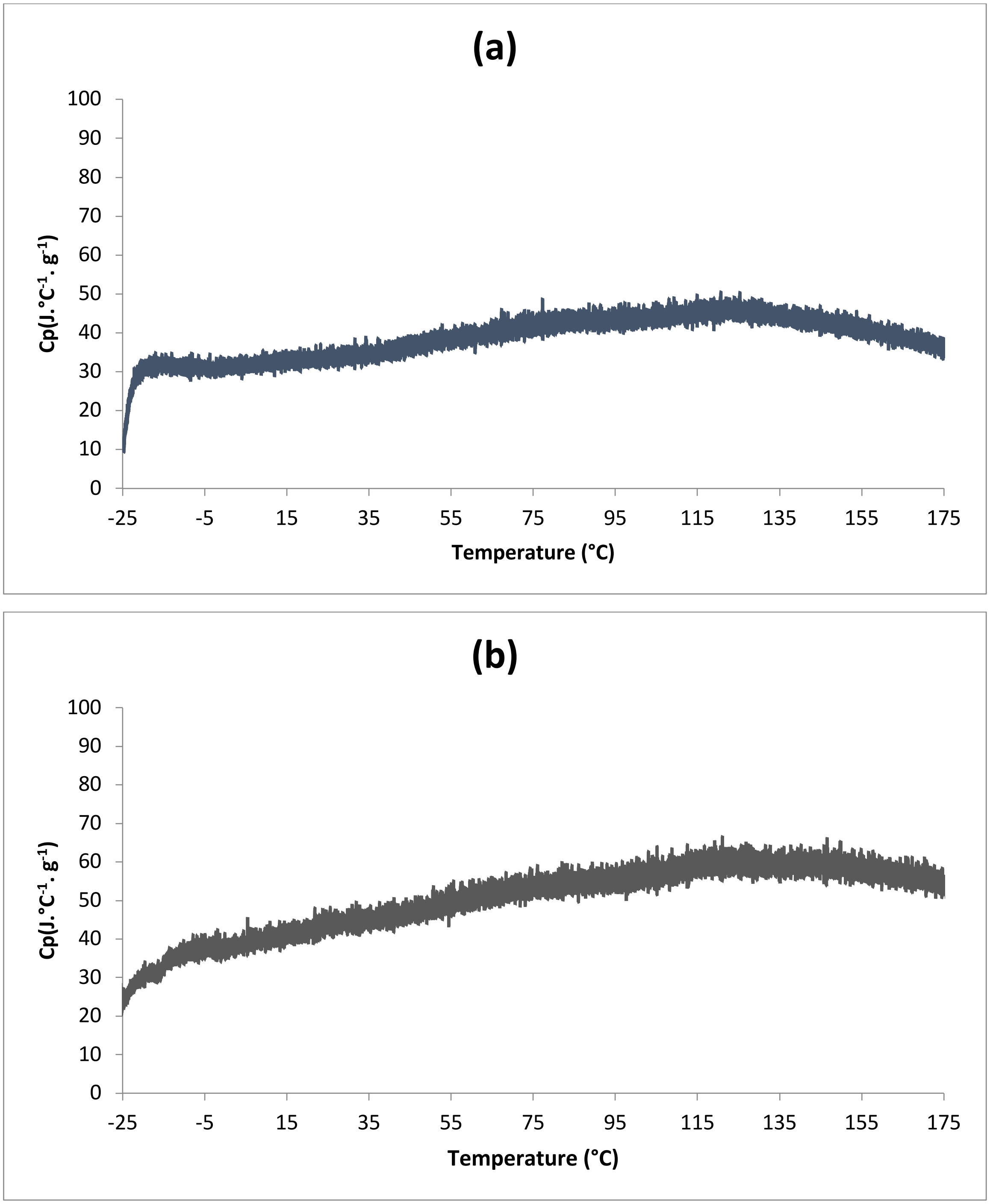


Fig 4.5. The calculated heat capacity using Eq. 4.6 based on the DSC values presented in Figure 4.4. (a) and (b) show the calculated values for whole bread and white bread, respectively

The heat capacity values presented in Figure 4.5 were modeled using a third order polynomial function of temperature. The maximum heat capacity values for whole bread and white bread were 55.5 and 65 ($J.C^{-1}.g^{-1}$) observed at 100 and 135 (°C), respectively.
To characterize the heat capacity data, the obtained values fitted a cubic polynomial function which demonstrated the heat capacity as a function of temperature (Table 4.6). A similar trend and approach were also proposed by Mohapatra and Bal, (2003) in which they obtained similar trends regarding the DSC analysis of brown rice.

Table 4.6 The obtained cubic models of heat capacity C_p ($J°C^{-1}.g^{-1}$) as a function of temperature (°C).

Sample	**Model for C_p**	**R^2**
White bread	$-4.0 \times 10^{-6}T^3 - 3.0 \times 10^{-4}T^2 + 2.7 \times 10^{-1}T + 3.7 \times 10^1$	0.95
Whole wheat bread	$-1.0 \times 10^{-5}T^3 + 1.2 \times 10^{-3}T^2 + 1.1 \times 10^{-1}T + 3.0 \times 10^1$	0.89

The cubic trend in the heat capacity measurements followed a similar pattern to the ones presented for aqueous starch solutions by Tan et al. (2004), obtained for maize starch solutions. It could indicate that the heat capacity of SBP was strongly affected by the thermal behavior of its starch phase.

4.4 Conclusion

In conclusion, the physicochemical properties were measured and evaluated for whole wheat and white staled bread crumb. In this regard, it can be concluded that the overall physicochemical properties of white bread, for the purpose of thickening paste food products, were more desirable as a potential additive to consider. White SBP showed a higher dissolution capacity and less syneresis after cooking and storing.
Further research is required in order for the food industry to benefit from this sustainable application of wasted bread. Specifically, more work should be done to monitor the difference in flavor and sensory attributes of dried white and dried whole wheat when added into soups and other paste products.

Chapter 5
General Conclusion

Sustainable solutions to food waste are a critical issue of the 21st century. In this study, the potential use of staled bread as a potential food thickener was studied. The pseudoplastic behaviour of SBP was a promising feature which could make SBP usable in a variety of food formulations as a thickener/filler. Also, the increase in the concentration of SBP in water solutions showed a direct relationship with the obtained viscosity.

The SBP solution at higher concentrations showed better dissolution capacity and cooking properties. This parameter could show a potential use of such powders in soup, or other powder forms for food pre-mixes in substitution or complementarity to starch and hydrocolloid gums. The relationship between the syneresis and the concentration of SBP was non-linear indicating a higher order of kinetics reaction involved. However, the syneresis after the cold storage of SBP followed a linear relationship.

Considering all measured physical parameters, SBP can be potentially added to several paste-based foods such as ready-to-eat soups, sauces, purees or beverage-based additives such as smoothies. The microstructural images obtained from both types of SBP showed a porous structure, particularly homogeneous for the white bread powder. With respect to the whole wheat SBP, its higher composition of bran prevented a purely homogeneous texture. The thermal behaviour of SBP obtained from DSC measurements was also discussed. The data confirmed a higher endothermic fall in the White SBP probably because of a greater extent of melting of amylose crystals. In addition, the heat capacity profile of both white and whole wheat bread followed cubic trend as a function of temperature.

5.1 Recommendations for future studies

This research focused on the characterization of staled bread powder from white and whole wheat flour breads. The experimental part of this research work emphasized on properties that affect the rheological and physicochemical behaviour of SBP added into aqueous solutions.

The following recommendations are proposed for future research studies such as;

- Exploring the different applications of SBP in ready-to-eat soups.
- Further functional properties must be studied such as nutritional benefits of white SBP and whole wheat SBP as notable additive to food products.
- Evaluation of the sensory attributes of SBP used in food products.

REFERENCES

Abdulagatov, I. M., Abdulagatova, Z. Z., Kallaev, S. N., Bakmaev, A.G., Ranjith P.G. (2015). Thermal-diffusivity and heat-capacity measurements of sandstone at high temperatures using laser flash and DSC methods. International Journal of Thermophysics, vol. 36, no 4, p. 658-691.

Aguirre, J.F, Osella, C.A., Carrara, C.R., Sanchez, H.D., del Pilar Burea, M. (2011). Effect of storage temperature on starch retrogradation of bread staling. Starch-Stärke, vol. 63, no 9, p. 587-593.

Ahlborn, G. J., Pike, O. A., Hendrix, S. B., Hess, W. M., & Huber, C. S. (2005). Sensory, mechanical, and microscopic evaluation of staling in low-protein and gluten-free breads. *Cereal chemistry*, *82*(3), 328-335.

Akhtar, M., Murray, B. S., Dickinson, E. (2006). Perception of creaminess of model oil-in-water dairy emulsions: Influence of the shear-thinning nature of a viscosity-controlling hydrocolloid. Food hydrocolloids, vol. 20, no 6, p. 839-847.

Baik, M. and Chinachoti, P. (2000). Moisture redistribution and phase transitions during bread staling. Cereal chemistry, vol. 77, no 4, p. 484-488.

Baker, A. E., Dibben, R. A., and Ponte, J. G. (1987). Comparison of bread firmness measurements by 4 instruments. Cereal Foods World, vol. 32, no 7, p. 486-489.

Banerjee, S. and Bhattacharya, S. (2011). Compressive textural attributes, opacity and syneresis of gels prepared from gellan, agar and their mixtures. Journal of Food Engineering. **102**(3): p. 287-292.

Barak, S. and D. Mudgil, Locust bean gum: processing, properties and food applications—a review. International Journal of Biological Macromolecules, 2014. **66**: p. 74-80.

Barcenas, M.E. and C.M. (2005). Rosell, Effect of HPMC addition on the microstructure, quality and aging of wheat bread. Food hydrocolloids. **19**(6): p. 1037-1043.

Berendsen, H.J. (1975). Specific interactions of water with biopolymers, in Water in Disperse Systems. Springer. P. 293-330.

Bellido, G., Gazzola, G. and Matveeva, I. Method of producing a baked product with alpha-amylase, lipase and phospholipase. U.S. Patent Application No 14/781,164, 19 mai 2016

Biliaderis, C. (2009). Structural transitions and related physical properties of starch. Starch: Chemistry and technology. **3**: p. 293-372.

Boita, E. R., Oro, T., Bressiani, J., Santetti, G. S., Bertolin, T. E., & Gutkoski, L. C. (2016). Rheological properties of wheat flour dough and pan bread with wheat bran. Journal of Cereal Science, 71, 177-182.

Boutboul, A., Giampaoli, P., Feigenbaum, A., Ducruet, V. (2002).Influence of the nature and treatment of starch on aroma retention. Carbohydrate polymers. **47**(1): p. 73-82.

Bourne, M. (2002) .Food texture and viscosity: concept and measurement. Elsevier.

Carini, E., Curti, E., Fattori, F., Paciulli, M., & Vittadini, E. (2017). Staling of gluten-free breads: physico-chemical properties and 1 H NMR mobility. *European Food Research and Technology*, *243*(5), 867-877.

Cauvain, S. P. (2007). Technology of breadmaking. Springer.

Cauvain, S. P. and Young, L.S. (2008).Baked products: science, technology and practice. John Wiley & Sons.

Cauvain, S.P. (2012). Breadmaking: improving quality. Elsevier.

Charoenrein, S., Tatirat, O., & Muadklay, J. (2008). Use of centrifugation–filtration for determination of syneresis in freeze–thaw starch gels. Carbohydrate Polymers, 73(1), 143-147.

Chaurasia, A., Sahoo, N.G., Wang, M., He, C., Mogal V.T. (2015). Fundamentals of Polymers and Polymer Composite, in Handbook of Manufacturing Engineering and Technology. Springer. p. 3-42.

Chinachoti, P. and Y. Vodovotz (2000). Bread staling. CRC Press.

Chhabra, R.P. and J.F. Richardson (1999). Non-Newtonian flow in the process industries: fundamentals and engineering applications. Butterworth-Heinemann.

Chung, M. S., Lee, J. K., Hur, N. Y., Kim, D. S., & Baik, M. Y. (2003). Textural analysis for bread staling. *Food Science and Biotechnology*, *12*(6), 727-736.

Collar, C., Jiménez, T., Conte, P., & Piga, A. (2015). Significance of thermal transitions on starch digestibility and firming kinetics of restricted water mixed flour bread matrices. *Carbohydrate polymers*, *122*, 169-179.

Colwell, K. H., Axford, D. W. E., Chamberlain, N., & Elton, G. A. H. (1969). Effect of storage temperature on the ageing of concentrated wheat starch gels. *Journal of the Science of Food and Agriculture*, *20*(9), 550-555.

Cornell, H. (2012). The chemistry and biochemistry of wheat. Breadmaking. Woodhead Publishing. p. 35-76.

Copetti, G., Grassi, M., Lapasin, R., & Pricl, S. (1997). Synergistic gelation of xanthan gum with locust bean gum: a rheological investigation. Glycoconjugate journal, 14(8), 951-961.

Correa, M. J., Ferrero, C., Puppo, C., & Brites, C. (2013). Rheological properties of rice–locust bean gum gels from different rice varieties. *Food hydrocolloids*, *31*(2), 383-391.

Curti, E., Carini, E., Tribuzio, G., & Vittadini, E. (2014). Bread staling: effect of gluten on physico-chemical properties and molecular mobility. *LWT-Food Science and Technology*, *59*(1), 418-425.

Day, D. F. (1998). Alginates. In Biopolymers from renewable resources (pp. 119-143). Springer, Berlin, Heidelberg.

Debet, M.R. and M.J. Gidley (2007), Why do gelatinized starch granules not dissolve completely? Roles for amylose, protein, and lipid in granule "ghost" integrity. Journal of Agricultural and Food Chemistry. **55**(12): p. 4752-4760.

Demirkesen, I., Mert, B., Sumnu, G., & Sahin, S. (2010). Rheological properties of gluten-free bread formulations. Journal of food Engineering, 96(2), 295-303.

Dolz, M., Hernandez, M. J., Delegido, J., Alfaro, M. C., & Munoz, J. (2007). Influence of xanthan gum and locust bean gum upon flow and thixotropic behaviour of food emulsions containing modified starch. *Journal of Food Engineering*, *81*(1), 179-186.

Dincer, I. and M. Rosen (2002), Thermal energy storage: systems and applications. John Wiley & Sons.

Eliasson, A. and M. Gudmundsson (1996), Starch: physicochemical and functional aspects. Food Science and Technology-New York-Marcel Dekker-, p. 431-504.

Ellison, C.J. and J.M. Torkelson (2003), The distribution of glass-transition temperatures in nanoscopically confined glass formers. Nature materials. **2**(10): p. 695-700.

Erbaş, M., Ertugay, M.F., Certel M. (2005). Moisture adsorption behaviour of semolina and farina. Journal of Food Engineering, 2005. **69**(2): p. 191-198.

Fadda, C., Sanguinetti, A. M., Del Caro, A., Collar, C., & Piga, A. (2014). Bread staling: updating the view. Comprehensive Reviews in Food Science and Food Safety, 13(4), 473-492.

Fanghui, F. (2018). Structural relaxations and crystallization in amorphous food model formulations. 2017. FAO . Website: http://www.fao.org/3/ca0995en/CA0995EN.pdf

Fu, Z. Q., Wang, L. J., Li, D., Zhou, Y. G., & Adhikari, B. (2013). The effect of partial gelatinization of corn starch on its retrogradation. *Carbohydrate polymers*, *97*(2), 512-517.

Ghannam, M.T. and Esmail, M. N. (1997). Rheological properties of carboxymethyl cellulose. Journal of applied polymer science, vol. 64, no 2, p. 289-301.

Giannone, V., Lauro, M. R., Spina, A., Pasqualone, A., Auditore, L., Puglisi, I., & Puglisi, G. (2016). A novel α-amylase-lipase formulation as anti-staling agent in durum wheat bread. *LWT-Food Science and Technology*, *65*, 381-389.

Government of Canada, issued October 2012: Website http://www.agr.gc.ca/resources/prod/Internet-Internet/MISB-DGSIM/ATS-SEA/PDF/6257-eng.pdf

Government of Canada, last modified 2017-10-26: Website https://www.ic.gc.ca/app/scr/app/cis/performance/rev/31181;jsessionid=0001pt-s2m9EoTJ4skjszVtloyz:-24P7QV

Goubet, I., Le Quere J.-L., and Voille. A. (1998). Retention of aroma compounds by carbohydrates: influence of their physicochemical characteristics and of their physical state. A review. Journal of Agricultural and Food Chemistry. **46**(5): p. 1981-1990.

Gray, J. and Bemiller, J. (2003). Bread staling: molecular basis and control. Comprehensive reviews in food science and food safety.**2**(1): p. 1-21.

Gujral, H.S., Sharma, A. and Singh, N. (2002). Effect of hydrocolloids, storage temperature, and duration on the consistency of tomato ketchup. International Journal of food properties. **5**(1): p. 179-191.

Hager, A. S., Wolter, A., Czerny, M., Bez, J., Zannini, E., Arendt, E. K., & Czerny, M. (2012). Investigation of product quality, sensory profile and ultrastructure of breads made from a range of commercial gluten-free flours compared to their wheat counterparts. *European Food Research and Technology*, *235*(2), 333-344.

Hamdami, N., J.-Y. Monteau, and Le Bail, A. (2004).Thermophysical properties evolution of French partly baked bread during freezing. Food Research International. **37**(7): p. 703-713.

Hamdami, N., Pham, Q. T., Le-Bail, A., & Monteau, J. Y. (2007). Two-stage freezing of part baked breads: application and optimization. *Journal of food engineering*, *82*(4), 418-426.

Höhne, G. and Glöggler, E. (1989). Some peculiarities of the DSC-2/-7 (Perkin-Elmer) and their influence on accuracy and precision of the measurements. Thermochimica Acta. **151**: p. 295-304.

Holdsworth, S. (1971). Applicability of rheological models to the interpretation of flow and processing behaviour of fluid food products. Journal of Texture Studies. **2**(4): p. 393-418.

Hug-Iten, S., Escher, F., and Conde-Petit, B. (2003). Staling of bread: Role of amylose and amylopectin and influence of starch-degrading enzymes. Cereal Chemistry. vol. 80, no 6, p. 654-661.

Imeson, A. P. (2012). Thickening and gelling agents for food. Springer Science & Business Media.

Juszczak, L., Z. Oczadły, and Gałkowska, D. (2013).Effect of modified starches on rheological properties of ketchup. Food and Bioprocess Technology. **6**(5): p. 1251-1260.

Katzbauer, B. (1998). Properties and applications of xanthan gum. Polymer degradation and Stability. **59**(1-3): p. 81-84.

Kerch, G., J. Zicans, and Meri, R.M. (2010). The effect of chitosan oligosaccharides on bread staling. Journal of cereal science. **52**(3): p. 491-495.

Koletta, P., Irakli, M., Papageorgiou, M., & Skendi, A. (2014). Physicochemical and technological properties of highly enriched wheat breads with wholegrain non wheat flours. *Journal of Cereal science*, *60*(3), 561-568.

Kilcast, D. and Subramaniam, P. (2011). Food and beverage stability and shelf life. Elsevier.

Khemakhem, M., H. Attia, and Ayadi, M.A. (2019). The effect of pH, sucrose, salt and hydrocolloid gums on the gelling properties and water holding capacity of egg white gel. Food Hydrocolloids. **87**: p. 11-19.

Kontogiorgos, V., Vaikousi, H., Lazaridou, A., & Biliaderis, C. G. (2006). A fractal analysis approach to viscoelasticity of physically cross-linked barley β-glucan gel networks. *Colloids and Surfaces B: Biointerfaces*, *49*(2), 145-152.

Lai, H.-M. and Lin, T.-C. (2006). Bakery Products. Handbook of Food Science, Technology, and Engineering. **149**(1).

Lee, S. K., & Klostermeyer, H. The effect of pH on the rheological properties of reduced-fat model processed cheese spreads. LWT-Food Science and Technology, 34(5), 288-292. 2001.

Levine, H. and Slade, L. (1990). Influences of the glassy and rubbery states on the thermal, mechanical, and structural properties of doughs and baked products, in Dough rheology and baked product texture. Springer. p. 157-330.

Liu, P., Yu, L., Liu, H., Chen, L., & Li, L. (2009). Glass transition temperature of starch studied by a high-speed DSC. *Carbohydrate polymers*, *77*(2), 250-253.

Maga, J.A. and Ponte, J.G. (1975). Bread staling. Critical Reviews in Food Science & Nutrition. **5**(4): p. 443-486.

Monteau, J. Y., Purlis, E., Besbes, E., Jury, V., & Le-Bail, A. (2017). Water transfer in bread during staling: Physical phenomena and modelling. *Journal of Food Engineering*, *211*, 95-103.

Mandala, I., T. Savvas, and Kostaropoulos, A. (2004). Xanthan and locust bean gum influence on the rheology and structure of a white model-sauce. Journal of Food Engineering. **64**(3): p. 335-342.

Mao, R., J. Tang, and Swanson, B. (2001). Water holding capacity and microstructure of gellan gels. Carbohydrate polymers. **46**(4): p. 365-371.

Mir, S. A., Shah, M. A., Naik, H. R., & Zargar, I. A. (2016). Influence of hydrocolloids on dough handling and technological properties of gluten-free breads. *Trends in Food Science & Technology*, *51*, 49-57.

Mohapatra, D., & Bal, S. Determination of Specific Heat and Gelatinization Temperature of Rice using Differential Scanning Calorimetry. I2003 ASAE Annual Meeting (p. 1). American Society of Agricultural and Biological Engineers.

Morîntale, E., Harabor, A., Constantinescu, C., & Rotaru, P. Use of heat flows from DSC curve for calculation of specific heat of the solid materials. Physics AUC, 23, 89-94. 2013.

Menjivar, J. A. (1990). Fundamental aspects of dough rheology. In Dough rheology and baked product texture (pp. 1-28). Springer, Boston, MA.

Moreira, R., Chenlo, F., and Torres, M. D. (2011). Rheology of commercial chestnut flour doughs incorporated with gelling agents. Food Hydrocolloids. 25(5), 1361-1371.

Morris, V. J. (1990). Starch gelation and retrogradation. Trends in Food Science & Technology, 1, 2-6.

Mudgil, D., Barak, S., & Khatkar, B. S. (2014). Guar gum: processing, properties and food applications—a review. Journal of food science and technology. 51(3), 409-418.

Nussinovitch, A., M. Steffens, and Chinachoti, P. (1992). Elastic properties of bread crumb. Cereal chemistry, 1992. **69**: p. 678-678.

Najafabadi, L. I., Le-Bail, A., Hamdami, N., Monteau, J. Y., & Keramat, J. (2014). Impact of baking conditions and storage temperature on staling of fully and part-baked Sangak bread. *Journal of cereal science*, *60*(1), 151-156.

National Zero Waste Council, issued 2017: Website http://www.nzwc.ca/Pages/default.aspx.

Nguyen, P. T., Kravchuk, O., Bhandari, B., & Prakash, S. (2017). Effect of different hydrocolloids on texture, rheology, tribology and sensory perception of texture and mouthfeel of low-fat pot-set yoghurt. *Food hydrocolloids*, *72*, 90-104.

Ong, M. H., Whitehouse, A. S., Abeysekera, R., Al-Ruqaie, I. M., & Kasapis, S. (1998). Glass transition-related or crystalline forms in the structural properties of gelatin/oxidised starch/glucose syrup mixtures. Food Hydrocolloids. 12(3), 273-281.

Onsøyen, E. (1997). Alginates. In Thickening and gelling agents for food (pp. 22-44). Springer, Boston, MA.

Pareyt, B., Finnie, S. M., Putseys, J. A., & Delcour, J. A. (2011). Lipids in bread making: Sources, interactions, and impact on bread quality. *Journal of Cereal Science*, *54*(3), 266-279.

Pourfarzad, A., Khodaparast, M. H. H., Karimi, M., Mortazavi, S. A., Davoodi, M. G., Sourki, A. H., and Razavizadegan Jahromi, S. H. (2011). Effect of polyols on shelf-life and quality of flat bread fortified with soy flour. *Journal of Food Process Engineering*, *34*(5), 1435-1448.

Ronda, F., Caballero, P. A., Quilez, J., & Roos, Y. H. (2011). Staling of frozen partly and fully baked breads. Study of the combined effect of amylopectin recrystallization and water content on bread firmness. *Journal of cereal science*, *53*(1), 97-103.

Reddy, C.K., S. Pramila, and Haripriya, S. (2015).Pasting, textural and thermal properties of resistant starch prepared from potato (Solanum tuberosum) starch using pullulanase enzyme. Journal of food science and technology. **52**(3): p. 1594-1601.

Ribotta, P.D., A.E. León, and Añón, M.C. (2001). Effect of freezing and frozen storage of doughs on bread quality. Journal of Agricultural and Food Chemistry. **49**(2): p. 913-918.

Ribotta, P. D., and Le Bail, A. (2007)Thermo-physical assessment of bread during staling. LWT-Food Science and Technology. 40(5), 879-884.

Román, L., Santos, I., Martínez, M. M., & Gómez, M. (2015). Effect of extruded wheat flour as a fat replacer on batter characteristics and cake quality. Journal of food science and technology. 52(12), 8188-8195.

Roos, Y.H. and Drusch, S.(2015). Phase transitions in foods. Academic Press.

Rojas, J. A., Rosell, C. M., De Barber, C. B., Perez-Munuera, I., & Lluch, M. A. (2000). The baking process of wheat rolls followed by cryo scanning electron microscopy. *European Food Research and Technology*, *212*(1), 57-63.

Rosell, C. M., and Santos, E. (2010). Impact of fibers on physical characteristics of fresh and staled bake off bread. Journal of Food Engineering, 98(2), 273-281.

Stevenson, L., Phillips, F., O'sullivan, K., & Walton, J. (2012). Wheat bran: its composition and benefits to health, a European perspective. *International journal of food sciences and nutrition*, *63*(8), 1001-1013.

Svegmark, K., & Hermansson, A. M. (1993). Microstructure and rheological properties of composites of potato starch granules and amylose: a comparison of observed and predicted structures. Food Structure, 12(2), 6.

Stevens, D. and Elton, G. (1971). Thermal properties of the starch/water system Part I. measurement of heat of gelatinisation by differential scanning calorimetry. Starch-Stärke. **23**(1): p. 8-11.

Salehifar, M. (2011). Effects of protein variation on starch cystallinity and bread staling. in International Conference on Food Engineering and Biotechnology.

Saha, D. and Bhattacharya, S. (2010). Hydrocolloids as thickening and gelling agents in food: a critical review. Journal of food science and technology. **47**(6): p. 587-597.

Steffe, J.F., Rheological methods in food process engineering. 1996: Freeman press.

Siljeström, M., Westerlund, E., Björck, I., Holm, J., Asp, N. G., & Theander, O. (1986). The effects of various thermal processes on dietary fibre and starch content of whole grain wheat and white flour. *Journal of Cereal Science*, *4*(4), 315-323.

Sidhu, J.S., P. Caceres, and Behbehani, M. (1997). Measurement of starch properties during staling of Arabic bread. Starch-Stärke. **49**(5): p. 180-186.

Slade, L. and Levine, H. (1988). Non-equilibrium melting of native granular starch: Part I. Temperature location of the glass transition associated with gelatinization of A-type cereal starches. Carbohydrate Polymers. **8**(3): p. 183-208.

Telis, V.R. and Tonon, R.V. (2017). The Effects of Non-Equilibrium States and Storage Conditions on Glass Transitions in Food, in Non-Equilibrium States and Glass Transitions in Foods. Elsevier. p. 379-403.

Teo, C. H., Karim, A. A., Cheah, P. B., Norziah, M. H., & Seow, C. C. (2000). On the roles of protein and starch in the aging of non-waxy rice flour. *Food Chemistry*, *69*(3), 229-236.

TAN, C. Physical Chemistry in Flavor Products Preparation: An Overview.

Tan, I., Wee, C. C., Sopade, P. A., & Halley, P. J. (2004).Estimating the specific heat capacity of starch-water-glycerol systems as a function of temperature and compositions. Starch-Stärke. 56(1), 6-12.

Vieira, M. G. A., da Silva, M. A., dos Santos, L. O., & Beppu, M. M. (2011). Natural-based plasticizers and biopolymer films: A review. *European Polymer Journal*, *47*(3), 254-263.

Van Hung, P., Maeda, T., & Morita, N. (2007). Dough and bread qualities of flours with whole waxy wheat flour substitution. Food Research International, 40(2), 273-279.

Vitali, A. and Rao, M. (1984). Flow properties of low-pulp concentrated orange juice: effect of temperature and concentration. Journal of Food Science. **49**(3): p. 882-888.

Wieser, H. (2007). Chemistry of gluten proteins. Food microbiology.**24**(2): p. 115-119.

Würsch, P. and Gumy, D. (1994). Inhibition of amylopectin retrogradation by partial beta-amylolysis. Carbohydrate research. **256**(1): p. 129-137.

Wei, Y., C. Wang, and Wu, J. (2001). Flow properties of fruit fillings. Food Research International. **34**(5): p. 377-381.

Wang, J., M.K. Cheung, and Y. Mi, Miscibility and morphology in crystalline/amorphous blends of poly (caprolactone)/poly (4-vinylphenol) as studied by DSC, FTIR, and 13C solid state NMR. Polymer, 2002. **43**(4): p. 1357-1364.

Wang, S., Li, C., Copeland, L., Niu, Q., & Wang, S. (2015). Starch retrogradation: A comprehensive review. *Comprehensive Reviews in Food Science and Food Safety*, *14*(5), 568-585.

Yagi, K., Umeki, T., Terauchi, H., & Noda, Y. (1996). Glass transition in K1− x (NH4) xI mixed crystals. Physica B: Condensed Matter, 219, 281-283.

Yoon, S.-N. and Yoo, B. (2017). Rheological behaviors of thickened infant formula prepared with xanthan gum-based food thickeners for dysphagic infants. Dysphagia. **32**(3): p. 454-462.

Yi, J. and Kerr, W.L. (2009). Combined effects of freezing rate, storage temperature and time on bread dough and baking properties. LWT-Food Science and Technology. **42**(9): p. 1474-1483.

Zhou, Z., Robards, K., Helliwell, S., & Blanchard, C. (2002a). Ageing of stored rice: changes in chemical and physical attributes. Journal of Cereal Science, 35(1), 65-78.

Zhou, Z., Robards, K., Helliwell, S., & Blanchard, C. (2002b). Composition and functional properties of rice. International journal of food science & technology, 37(8), 849-868.

Zhu, F. (2016). Staling of Chinese steamed bread: Quantification and control. Trends in Food Science & Technology. **55**: p. 118-127.