Rheological and textural characterization of sauces

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DEDICATION

To my mother, and my father, this thesis is most affectionately dedicated.

ABSTRACT

Due to their ability to enhance flavor and texture, sauces have become essential part of many local and international cuisines. This study investigated quality parameters of sauces that influence consumer acceptability using rheometry and textural analysis. Firstly, the steady state and oscillatory rheology of some selected commercial meat sauces were characterized at different process temperatures. The sauces exhibited shear thinning flow behavior that was well described by the Hershel-Bulkley model ($R^2 \geq 0.975$). Temperature was seen to significantly affect ($p < 0.05$) the model parameters. Additionally, temperature dependency of oral shear viscosity followed an Arrhenius-type model ($R^2 \geq 0.952$). Results from dynamic rheological measurements revealed that the sauces had a weak gel structure. Storage modulus greater than loss modulus over the frequency range and temperatures investigated, signifying that meat sauces possessed predominant elastic behavior over viscous properties. Viscoelastic properties were modelled by a power law function of oscillatory frequency ($R^2 \geq 0.958$). Moreover, linear, and non-linear modified forms of Cox-Merz rule were used to correlate steady state and oscillatory rheological properties ($R^2 \geq 0.784$).

The thermal, swelling, and fat/water absorption properties of rice starch as influenced by high intensity ultrasonication were also evaluated. This was aimed at assessing its suitability in the formulation of starch-based sauces. Severe ultrasound treatment was seen to completely gelatinize rice starch and improve its swelling and fat/water absorption capacity, indicating its suitability for application in white sauce formulation. The rheological, textural, and freeze/thaw stability of the ultrasound-treated starch-based sauces were further investigated. Viscoelastic behavior of white sauces also proved the existence of a weak gel-like structure; with dominant solid-like properties over viscous behavior. They had a pseudoplastic and thixotropic flow behavior, which was well modeled by the Ostwald de Waele model ($R^2 \geq 0.870$). The area of hysteresis significantly reduced

($p < 0.05$) with increased ultrasound treatment and after a freeze/thaw cycle, signifying a more stable molecular structure. Textural attributes (stickiness, stringiness, and work of adhesion) of starch-based sauces were significantly enhanced ($p < 0.05$) with increasing ultrasound treatment. Moreover, ultrasound treated starch-based sauces showed reduced syneresis after a freeze/thaw cycle, further indicating its freeze/thaw stability. Overall, the data obtained are potentially useful for product development and process design and optimizations.

RÉSUMÉ

En raison de leur capacité à améliorer la saveur et la texture, les sauces sont devenues une partie essentielle de nombreuses cuisines locales et internationales. Cette étude a examiné les paramètres de qualité des sauces qui influencent sur l'acceptabilité par les consommateurs, à l'aide d'une analyse rhéométrique et texturale. Tout d'abord, l'état stationnaire et la rhéologie oscillatoire de certaines sauces commerciales à base de viande ont été caractérisés à différentes températures de traitement. Les sauces présentaient un comportement d'amincissement par cisaillement bien décrit par le modèle Hershel-Bulkley ($R^2 \geq 0{,}975$). On a constaté que la température avait une influence considérable ($p < 0{,}05$) sur les paramètres du modèle. De plus, la dépendance de la température à la viscosité de cisaillement par voie orale a suivi un modèle de type Arrhenius ($R^{2\ \geq}$ 0,952). Les résultats de mesures rhéologiques dynamiques ont révélé que les sauces avaient la structure d'un gel faible. Le module de stockage était supérieur au module de perte sur la gamme de fréquence et les températures étudiées, ce qui signifie que les sauces de viande possédaient un comportement élastique prédominant sur les propriétés visqueuses. Les propriétés viscoélastiques ont été modélisées par une fonction de la loi de puissance de la fréquence oscillatoire ($R^2 \geq 0{,}958$). De plus, des formes modifiées linéaires et non linéaires de la règle de Cox-Merz ont été utilisées pour corréler les propriétés rhéologiques stationnaires et oscillatoires ($R^2 \geq 0{,}784$).

Les propriétés d'absorption thermique, de gonflement et de graisse/eau de l'amidon de riz, influencées par des ultrasons de haute intensité, ont également été évaluées. Il s'agissait d'évaluer leur pertinence à la formulation de sauces à base d'amidon. Un traitement aux ultrasons sévère a été observé pour gélatiniser complètement l'amidon de riz et améliorer son gonflement et sa capacité d'absorption de graisse/eau, indiquant son aptitude à être appliqué dans une formulation de sauce blanche. La stabilité rhéologique, texturale et de congélation/dégel des sauces à base d'amidon traitées par ultrasons a fait l'objet d'une étude plus approfondie. Le comportement

viscoélastique des sauces blanches a également prouvé l'existence d'un gel faible, avec des propriétés solides dominantes sur le comportement visqueux. Ils avaient un comportement d'écoulement pseudoplastique et thixotropique, qui était bien modélisé par le modèle d'Ostwald de Waele ($R^2 \geq 0.870$). La zone d'hystérésis a considérablement diminué ($p > 0,05$) avec un traitement par ultrasons accru et après un cycle de gel/dégel, ce qui signifie une structure moléculaire plus stable. Les propriétés texturales (adhérence, rigidité et travail d'adhérence) des sauces à base d'amidon ont été considérablement améliorées ($p < 0,05$) avec l'augmentation du traitement par ultrasons. De plus, les sauces à base d'amidon traitées par ultrasons ont montré une réduction de la synérèse après un cycle de gel/dégel, ce qui indique en outre sa stabilité au gel/dégel.

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Valentine Chiemezie Cyprian Okonkwo
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CONTRIBUTION OF AUTHORS

All the manuscripts in the thesis were authored by **Valentine C. Okonkwo** (principal author). He is the MSc candidate who was responsible for the design of experiments, experimental setup, analytical work in the laboratory, data analysis, and preparation of manuscripts. All experiments reported herein were conducted in the Food and Bioprocess Engineering Laboratory, Department of Bioresource Engineering, Macdonald Campus of McGill University. **Dr. Michael O. Ngadi**, James McGill Professor at the Department of Bioresources Engineering, McGill University, Macdonald Campus, is the thesis supervisor. Dr. Ngadi provided scientific advice, research funds, and technical supervision during the entire program. **Dr. Ogan I. Mba** is a Research Associate at the Food and Bioprocess Engineering Laboratory, McGill University, Macdonald Campus. With his wealth of experience in the field of food science and technology, he provided guidance during conceptualization and ensured the manuscripts met standards by posing several technical questions and suggestions. **Dr. Ebenezer M. Kwofie** is a Research Associate at the Food and Bioprocess Engineering Laboratory, McGill University, Macdonald Campus. He provided technical guidance during conceptualization and manuscript development.

The manuscripts listed below are either under review in reputable academic journals, accepted for publication in a journal, presentation in scientific conferences or ready for submission.

- ***Valentine C. Okonkwo***, Ogan I. Mba, Ebenezer M. Kwofie, Michael O. Ngadi. "Rheological, textural, and antioxidant properties of sauces: a review" (Manuscript submitted for publication – *Food Engineering Reviews*).

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- ***Valentine C. Okonkwo***, Ogan I. Mba, Ebenezer M. Kwofie, Michael O. Ngadi. "Rheological properties of meat sauce as influenced by temperature" (Prepared for submission).
- ***Valentine C. Okonkwo***, Ebenezer M. Kwofie, Ogan I. Mba, Michael O. Ngadi. (Accepted – In press) "Impact of thermo-sonication on quality indices of starch-based sauces" *Ultrasonics Sonochemistry*.

Signed: Valentine Chiemezie Cyprian Okonkwo

Date: August 2020

[1] This paper will be presented next year because the conference was postponed to May 2021 due to the outbreak of COVID-19 pandemic.

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NOMENCLATURE

Abbreviation/acronym	Full form
C	Multiplicative constant
FAC	Fat absorption capacity
ln	Natural logarithm
LVE	Linear viscoelastic
p	Probability value
PCA	Principal component analysis
PRH	Percentage relative hysteresis
PROC GLM	Generalized linear model procedure
psi	Pound per square inch
R^2	Coefficient of determination
RMSE	Root mean square error
SAS	Statistical analysis software
WAC	Water absorption capacity

Symbols

Symbols	*Quantity*	*Unit*
$\dot{\gamma}$	Shear rate	s^{-1}
E_a	Activation energy	kJ/mol
T_0	Onset temperature	°C
T_K	Absolute temperature	K
T_c	Conclusion temperature	°C
T_p	Peak temperature	°C
k_c	Casson constant	$(Pa.s)^{0.5}$
α_2	Power index	
η_{50}	Oral shear viscosity	Pa.s
η_a	Apparent viscosity	Pa.s
σ_0	Yield stress	Pa
σ_{0c}	Casson yield stress	$Pa^{0.5}$
τ_c	Dynamic yield stress	Pa
ΔH	Enthalpy of gelatinization	J/g
A	Pre-exponential factor	Dimensionless
G'	Storage modulus	Pa
G''	Loss modulus	Pa
G^*	Complex modulus	Pa
k	Consistency index	$Pa.s^{n}$
k'	Consistency coefficient for storage modulus	$Pa.s^{n'}$
k''	Consistency coefficient for loss modulus	$Pa.s^{n''}$
n'	Flow behavior index for storage modulus	Dimensionless
n''	Flow behavior index for loss modulus	Dimensionless

R	Universal gas constant	kJ/K.mol
tan δ	Loss/damping factor	Dimensionless
α	Linear shift factor	
η*	Complex viscosity	Pa.s
ω	Angular frequency	rad/sec
σ	Shear rate	Pa

THESIS FORMAT

This thesis is submitted in the format of papers suitable for journal publication. This thesis format has been approved by the Faculty of Graduate and Postdoctoral Studies, McGill University, and follows the conditions outlined in the Guidelines: Concerning Thesis Preparation, which are as follows:

"As an alternative to the traditional thesis format, the dissertation can consist of a collection of papers of which the student is an author or co-author. These papers must have a cohesive, unitary character making them a report of a single program of research". The structure for the manuscript-based thesis must conform to the following:

1. Candidates have the option of including, as part of the thesis, the text of one or more papers submitted, or to be submitted, for publication, or the clearly duplicated text (not the reprints) of one or more published papers. These texts must conform to the "Guidelines for Thesis Preparation" with respect to font size, line spacing and margin sizes and must be bound together as an integral part of the thesis. (Reprints of published papers can be included in the appendices at the end of the thesis).

2. The thesis must be more than a collection of manuscripts. All components must be integrated into a cohesive unit with a logical progression from one chapter to the next. In order to ensure that the thesis has continuity, connecting texts that provide logical bridges between the different papers are mandatory.

3. The thesis must conform to all other requirements of the "Guidelines for Thesis Preparation" in addition to the manuscripts. The thesis must include the following:

(a) A table of contents;

(b) An abstract in English and French;

(c) An introduction which clearly states the rational and objectives of the research;

(d) A comprehensive review of the literature (in addition to that covered in the introduction to each paper);

(e) A final conclusion and summary;

4. As manuscripts for publication are frequently very concise documents, where appropriate, additional material must be provided (e.g., in appendices) in sufficient detail to allow a clear and precise judgment to be made of the importance and originality of the research reported in the thesis.

5. In general, when co-authored papers are included in a thesis, the candidate must have made a substantial contribution to all papers included in the thesis. In addition, the candidate is required to make an explicit statement in the thesis as to who contributed to such work and to what extent. This statement should appear in a single section entitled "Contributions of Authors" as a preface to the thesis. The supervisor must attest to the accuracy of this statement. Since the task of the examiners is made more difficult in these cases, it is in the candidate's interest to clearly specify the responsibilities of all the authors of the co-authored papers".

THESIS ORGANIZATION

Chapter one: General introduction to the research work, including the scope and research objectives.

Chapter two: Review of relevant literature pertaining the rheological, textural, and antioxidant properties of sauces.

Chapter three: Rheological properties of meat sauces as influenced by temperature.

Chapter four: Impact of temperature on rheological properties of gluten-free white sauces.

Chapter five: Assessing the impact of high-intensity ultrasonication on quality indices of starch-based sauces.

Chapter six: General summary and conclusions.

Chapter seven: References.

CHAPTER ONE

1. GENERAL INTRODUCTION

1.1 Background

Nowadays, convenience foods supply much of the nutrient requirements in the general population of most industrialized countries. Globally, the consumption of convenience foods has continued to rise, possibly as a result of urbanization and evolving consumer preference, where the consumption of processed or imported foods is seen as an "evidence" of modern living (Yan, 1997). These foods are characterized by their ease of preparation, wide availability, and relative low cost. Majority of these foods are usually sold frozen and are accompanied by assortment of sauces, dressings, or dips (Arocas et al., 2009b). Sauces may be in liquid or semi-solid form and are typically served with other products. They can also be applied to foods such as pancakes, egg dishes, vegetables dishes, as well as fish and meat dishes. Sauces are increasingly becoming part of modern-day culinary delight. Worldwide, coating food products with sauces has continued to increase because of the enhanced flavor, color, texture and sometimes nutrients they offer. The top ten countries actively driving the import value of sauces and condiments around the world is shown in Fig. 1.1. The trend shows significant increase in trade within the last five years. As cities become more diverse and consumers' taste preferences keep evolving, the food industry is continuously faced with the challenge of finding the right combination of ingredients to meet the changing customer preferences, while maintaining food quality attributes, such as desired rheological and textural properties.

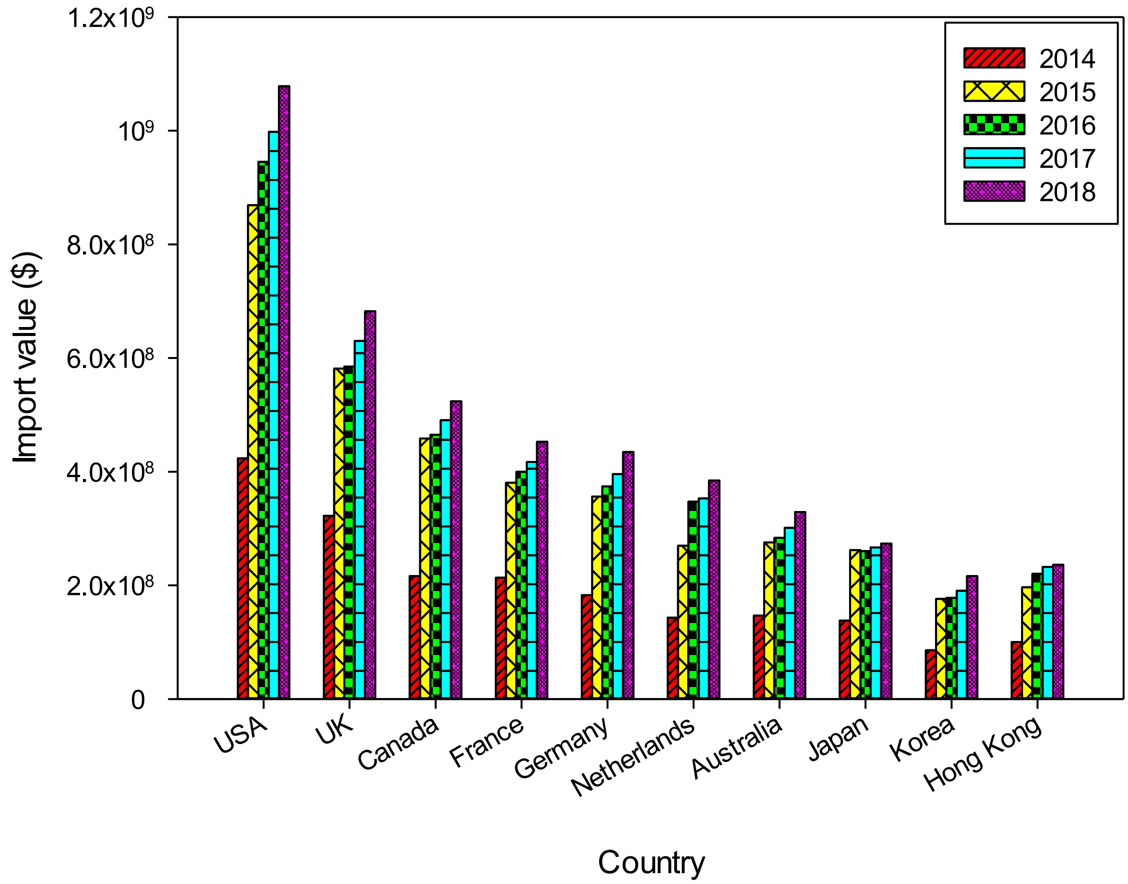


Fig. 1.1: Import value for sauces and condiments from July 2014 – July 2018 (Global Trade Tracker, 2019)

A recent report published by Mordor Intelligence (2019) estimates that the annual growth rate of the global market for sauces, condiments and dressings will increase by 4.9% between 2016 and 2024. The global market for sauces, dressings and other condiments valued at 30.09 billion US dollars in 2018 has been projected to generate about 45 billion US dollars by 2026 (Zion Market Research, 2018). The United States is the largest consumer of sauces, dressings and condiments in the world, accounting for 20% of the global retail consumption and 13% of global import. Other major players supply market are Vietnam, India, Mexico, and Canada. In Canada, the sauce supply market is valued at 258.6 million US dollars (Agriculture and Agri-Food Canada, 2018). Some of the leading industries in the global sauce and condiments market are Kraft Heinz Co., McCormick & Co Inc., ConAgra Foods Inc., Nestlé S.A., General Mills Inc., Campbell Soup Co., Unilever group, Hellmann's and Best Foods, and Kikkoman Corporation.

There are numerous types of sauces and equally unlimited ways of using or consuming them. According to Escoffier’s classification, the five mother sauces are: béchamel, velouté, espagnole, hollandaise, and tomato sauces (Peterson, 2017). These serve as base for other secondary sauces, such as meat sauce derived from tomato sauce. Among the different ingredients used in the formulation of sauces, the role of starch is crucial in determining consumer acceptance. This is because it is used as a gelling and thickening agent and provides a variety of textures and mouthfeel (Sanz et al., 2016). Based on labelling perspective, starches are classified as either native or modified (McDonagh, 2012). Native starch is extracted from naturally existing cereals, roots, and tubers, such as rice, cassava, and potato. However, the application of native starch in the industrial production of sauces and indeed other foods is limited due to retrogradation, syneresis, loss of viscosity, poor shear, and thermal stability. To overcome these limitations of native starches, different starch modification methods have been developed and applied. These methods are aimed at improving the functional properties of starch which is desired in food processing. Modification techniques reported in literature include physical, chemical, enzymatic, and genetic manipulations. Arocas et al. (2009b) reported that white sauces formulated with native starch showed syneresis after a freeze/thaw cycle in contrast to their modified starch counterparts. The phenomenon of syneresis happens when water leaches out from the food matrix after thawing and portends negative quality. White sauces formulated with modified starches have also been shown to possess enhanced rheological properties (Sanz et al., 2016). Though desired qualities are achieved through starch modification, there seems to be a conflict with the recent consumer interest in clean label foods. Clean label foods are foods that are organic, natural, and free from artificial additives (Asioli et al., 2017). With this definition, sauces and other food products formulated with starches modified through chemical, enzymatic, and genetic means do not meet the description of clean label foods, and have to be specified on the product label (Alting & Van De Velde, 2012); necessitating the need for sauces formulated using physically methods of starch modification, such as ultrasonication.

Ultrasonication has been applied as a physical, non-thermal, simple, inexpensive, and environmentally benign method of starch modification and have been demonstrated to have reduced processing time (Falsafi et al., 2019) and increased enzyme and microbial inactivation capacity (Dolas et al., 2019). Increasingly, low, and high intensity ultrasound are being employed in the food industry. Low-intensity ultrasound uses acoustic vibrations at very high frequencies (> 1 MHz). In contrast, high-intensity ultrasound uses lower frequency (20 – 100 kHz) and higher amplitude (Zhu & Li, 2019). Overall, ultrasound generates acoustic waves whose frequency is usually beyond the threshold of human hearing. Ultrasonication has been reported to affect the water solubility, gelatinization, morphological, retrogradation, and pasting properties of starch (Punia 2020). Ultrasonication effect is dependent on a variety of factors, such as duration of application, temperature, amplitude, starch source and concentration. In corn starch, the most effective factors were temperature and duration of application (Amini et al., 2015). The consequence of ultrasonic treatment is an outcome of acoustic cavitation, which is due to generation, growth, and eventual implosive collapse of bubbles, which causes the generation of heat and pressure (Monroy et al., 2018). Despite these advantages, there appears to be no study, reported in the literature, that has detailed the effect of ultrasound-treated starches on quality parameters of starch-based sauces.

Food quality parameters, such as rheology and texture, strongly influence consumer acceptance. The science of rheology examines the flow and deformation/stress-strain relationship of materials.

Sauces, as is the case with many foods, are considered complex structured or multiphase dispersed systems because they exist in the transient area between solids and liquids, hence, they are termed viscoelastic fluids (Tabilo-Munizaga & Barbosa-Cánovas, 2005). Rheological investigations seek to characterize the functional relationship between stresses, deformation, and flow, resulting to material properties, such as viscosity and viscoelasticity (Fischer et al., 2009). From an industrial standpoint, sauce production heavily relies on complex flow processes, hence knowledge of its rheological behavior is crucial in optimizing pumping efficiency, handling, quality control, storage stability, and general process design (Ngadi & Yu, 2004). Starch and gums have been used to improve the rheological properties of chili sauce (Gamonpilas et al., 2011), mustard sauce (Wang et al., 2016), and strawberry sauce (Sikora et al., 2007). Overall, the rheological properties of sauces are characterized by a shear thinning flow behavior and a viscoelastic property of a weak gel, signifying dominant behavior over viscous properties. The rheological properties of sauces are not only dependent on formulation ingredients, but they are also affected by processing conditions such as temperature, as reported by Bortnowska et al. (2016). It is also important to find a relationship between the properties obtained from different rheological measurements. This is useful because the limitation of a measurement can be greatly overcome when another type of measurement is used and then correlating the properties obtained from both measurements (Gunasekaran & Ak, 2000). For instance, steady state viscosity is difficult to measure, especially at high shear, due to instabilities, such as secondary flows, sample fracture, and slip. Hence, measurements obtained through small-amplitude oscillation are more reliable (Snijkers & Vlassopoulos, 2014). Important relationships, such as that described by Cox and Merz (1958), has been reported for many foods.

Although studies have been conducted on a variety of sauces, reports that have focused on meat sauces appear to be scares. Moreover, the impact of process conditions, such as temperature, on the rheological properties of meat sauce has not been properly elucidated. Additionally, studies that have utilized starches modified by non-thermal and environmentally friendly modification technologies, such as ultrasonication, in the formulation of sauces have not been reported.

1.2 Hypothesis

Quality parameters of sauces are directly influenced by the nature of starch used in its formulation. Rheological properties, textural attributes, and freeze/thaw stability of sauces can be improved by the utilization of modified starches during sauce production. Since there are increasing consumer concern regarding sauces formulated with chemically modified starches, it important to adopt the use of clean label starches. In this regard, starches produced using physical modification techniques, such as ultrasonication, can be used in the formulation of sauces. Characterizing the rheological and textural properties, including finding an interrelationship between different types of rheological characteristics of sauces can provide useful information necessary for continuous process improvement.

1.3 Research Objectives

The overall objective of this research is rheological characterization of sauces in that could be useful in designing flow processes and quality control. This entails the following specific objectives:

1. Evaluate steady shear and oscillatory rheological properties of meat sauces over a range of temperatures; and assess the applicability of the Cox-Merz rule.
2. Characterize the impact of temperature treatment on the rheological response of starch-based sauces.
3. Assess the impact of high-intensity ultrasonic treatment on quality indices of white sauces.

CHAPTER TWO

2. LITERATURE REVIEW

2.1 Classification of Sauces

It is quite difficult to classify sauces because there are endless opportunities through which a chef can combine a variety of stock and condiments to formulate sauces. This difficulty is intensified by tradition and aesthetics associated with the art of sauce making. Antonin Carême is credited to have sorted French sauces into four classes in the nineteenth century, which he called the mother or grand sauces (Peterson, 2017); espagnole, velouté, allemande, and béchamel. In the twentieth century Auguste Escoffier revised Carême's classification, demoting allemande to a subclass of velouté, and adding holladiase, and tomato sauce (Peterson, 2017; Rognså et al., 2014). Hence, in Escoffier's classification, the five mother sauces are: béchamel, velouté, espagnole, hollandaise, and tomato sauce. Typically, béchamel sauce is white, velouté sauce is blond, espagnole sauce is brown, hollandaise sauce is buttery, and tomato sauce is red. All other sauces that are derived from these mother sauces are called secondary sauces. This categorization of sauces is referred to as the "French sauce system" (Larousse, 1993). Generally, sauces offer consumers the advantage of food that is readily available, inexpensive, easy to prepare, and tasty.

2.1.1 Béchamel Sauce

This category of sauces is also referred to as white sauce, Béchamel sauce is possibly the simplest mother sauce since it does not require a stock. In classical French cuisine, Béchamel sauce is mainly composed of "roux", milk, and seasonings. The recipe usually starts with the preparation of roux, which is a cooked mixture of butter and flour, generally used to thicken sauces and soups (Heyman et al., 2010). This is followed by the addition of milk while stirring continuously. Onions and nutmeg could also be added and the whole mixture is simmered until it becomes creamy

(Peterson, 2017). Examples of secondary sauces of béchamel include mornay, mustard, and cheese sauces. White sauce can be used as base for macaroni cheese, fish pie, and casseroles.

2.1.2 Velouté Sauce

Velouté is another simple mother sauce made by light or chicken stock thickened by roux and then simmering the whole mixture for a while. Common derivatives of velouté are allemande, poulette, and supreme sauces. While allemande sauce is prepared by finishing basic velouté with egg yolk and mushroom cooking liquids, supreme sauce is prepared by finishing velouté with mushroom cooking liquid, cream, and butter (Peterson, 2017). Velouté sauce is usually served on poultry and seafood dishes.

2.1.3 Espagnole Sauce

Espagnole sauce is a French translation for Spanish sauce. It is formulated by thickening brown stock with roux, fresh tomato, and tomato paste. Other vegetable such as onions, clove garlic, mushroom, carrot, and bouquet garni could be added to improve the flavor (French Cooking Academy, 2018). Espagnole is typically brown in colour. In many commercial kitchens, a demi-glace is prepared by reducing espangnole sauce to a deeply flavorful syrup with light consistency (Peterson, 2017). Common secondary derivatives of espagnole sauce include chasseur, madeira, lyonnaise, and bercy sauces. Espagnole sauce is traditionally served with red meat.

2.1.4 Hollandaise Sauce

Hollandaise is basically an egg yolk stabilized butter sauce. The major components of hollandaise sauce are egg yolk, wine reduction, clarified butter, lemon juice, and salt. Whereas other mother sauces can be held for extended periods by using appropriate package and preservation methods, such as bottles and freezing, respectively, hollandaise sauce has poor storage stability due to the separation of the components into an oil and water phase (Schell & Schell, 2003). However, there is indication that storage stability can be improved by pasteurization, homogenization, and cooling

(Kroening, 2003). Hollandaise is mainly served with egg Benedict. Secondary sauces of hollandaise include dijon, béarnaise, and foyot (Rognså et al., 2014).

2.1.5 Tomato Sauce

Tomato sauce is an example of a puree providing the base for other derivatives, such as Creole and Portuguese sauces. Tomato sauce is formulated by simmering crushed tomatoes at 100 °C for 60 mins (Tomas et al., 2017). Improved flavor can be achieved by adding stock and vegetables, such as onions, carrot, celery, and clove garlic. Tomato sauce can be used in the preparation of mussel, pasta, and grilled cheese. The flavor of tomato sauce prepared with underripe tomatoes can be improved by the addition of sugar and vinegar, which serves to increase sweetness and acidity, respectively (Peterson, 2017).

2.2 Overview of Rheological Characterization

The science of rheology examines flow and deformation/stress-strain relationships of materials. Sauces, as is the case with many foods, are considered complex structured systems, because they exist in the transient area between solids and liquids, hence they are termed viscoelastic fluids (Tabilo-Munizaga & Barbosa-Cánovas, 2005). Most sauces have been characterized as exhibiting non-Newtonian, pseudoplastic, or time-dependent (thixotropic) flow behavior, indicating that minimal yield stress is often applied to initiate flow (García et al., 2016). On the other hand, caramel sauce, composed of syrup, water, and sugar, has been reported to display Newtonian behavior (Alvarez et al., 2004). The flow behavior of a material, such as shown for white sauce in Fig. 2.1, characterizes the functional relationship between shear stress and shear strain in the material. A general classification of flow behavior of fluids and semi-solids in presented in Fig. 2.2. Time independent fluids, sometimes called Boltzmann fluids, are those for which the shear rate is a function of the magnitude of the shear stress alone. Whereas time dependent fluids are characterized by a dependence on the magnitude and duration of the shear stress. Numerous flow models are used to describe the relationship between the rheological properties, such as shear stress and shear rate. Researchers have also recognized the importance of understanding how the model parameters are affected by factors, such as temperature and frequency. Rao (2014) classified such flow models as either empirical, theoretical, or structural. Hence, empirical models, like the power law model, were developed from observed experimental data. Theoretical models, such as that proposed by Labropoulos et al. (2002), were obtained from fundamental concepts. Theoretical models provide valuable guidelines to understand the role of the structure of the studied fluid. Structural models were developed to explain the kinetics driving the observed changes within the structure of the material. They are often used in combination with experimental data. In rheological measurements, it is a common practice to fit experimental data to established rheological models. Using statistical error quantifiers, such as standard error and root mean square error, the model with the least error is chosen as the model that best describes the relationship between shear stress and shear strain.

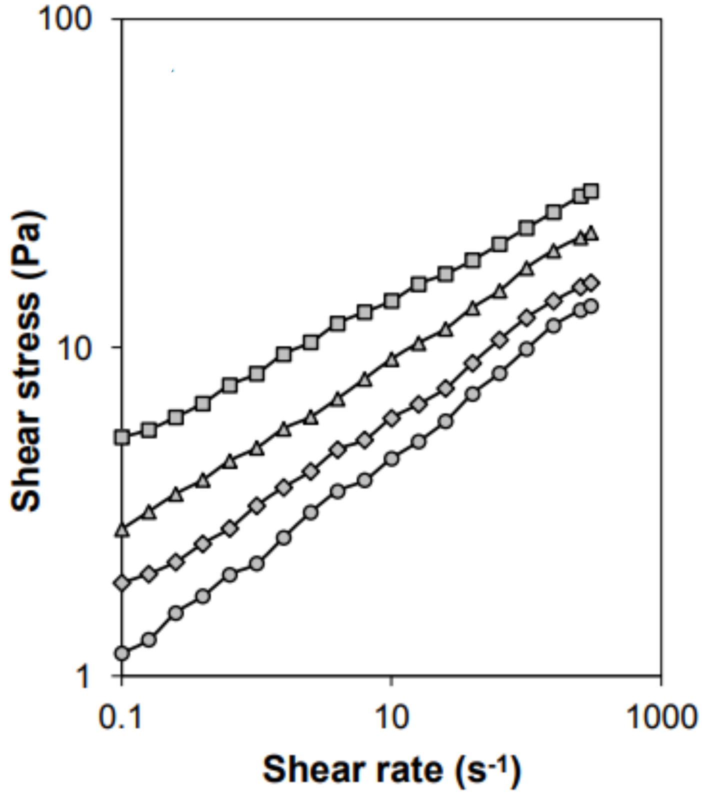


Fig. 2.1: Flow curves for waxy rice starch (WRS) sauce (circle: 2 wt% WRS; diamond: 2.5 wt% WRS; triangle: 3 wt% WRS; square: 3.5 wt% WRS) (Bortnowska et al., 2016)

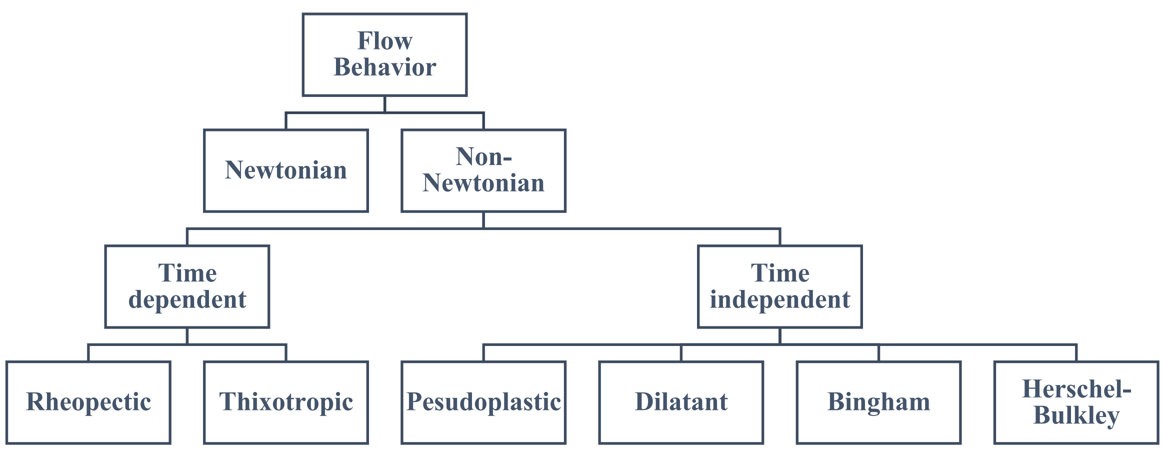


Fig. 2.2: Flow behavior of semi-solids

Viscoelasticity of sauces describes their ability to exist in the transient area between solids and liquids, both extremes obeying Hooke's law and Newton's law, respectively (Gunasekaran & Ak, 2000; Zhong & Daubert, 2013). This is related to the molecular structure and formulation differences. To precisely determine the relationship between molecular structure and viscoelastic behavior, it is often required that rheological measurements be conducted within a boundary where the properties of viscoelasticity are unaffected by the applied stress or strain. Such boundary is called the linear viscoelastic (LVE) region. Creep and dynamic oscillation (amplitude sweeps) have been used to determine the LVE region of polymers in controlled stress rheology (Papanicolaou & Zaoutsos, 2019; Wu et al., 2015). Amplitude sweep can be conducted either in strain or stress sweep modes. This involves ramping stress or strain linearly at constant frequency and temperature. The LVE of commercial chili sauces are shown in Fig. 2.3. The point at which viscoelastic functions, such as storage modulus (G') and loss modulus (G''), deviates from a constant plateau signifies departure from the linear viscoelastic region. This departure indicates an irrecoverable destruction of the sample structure. However, a 10% deviation from the constant plateau is still considered to be within the LVE region (Agirre-Olabide et al., 2015; Mezger, 2014). The curve starts off with $G' > G''$, depicting a superior solid-like behavior, followed by the crossover point, where both moduli are equal, generally termed "the gel point". Often, the crossover points and the maximum value of G'' are very close. Beyond the gel point, $G' < G''$ indicating the dominance of fluid-like/liquid-like properties. In determining the LVE range, more attention should be given to the G' curve since it is more vulnerable to structural deformation. Usually, the subsequent tests such as temperature and frequency sweeps, designed to further probe the viscoelastic properties of the sample are conducted using a value of the controlled variable (stress/strain) within the LVE region. Results from dynamic/oscillatory rheological experiments are usually illustrated on double logarithmic scales (Fig. 2.3 and Fig. 2.4). This is because the experimental data resulting from these tests span over several decades. More importantly, the part of the curve required for further analysis (frequency and temperature sweeps) are usually of low values. These values are not easily visualized on a linear scale. A robust rheological characterization involves both flow behavior and determination of viscoelastic properties (Adewale et al., 2014; Ma & Barbosa-Cánovas, 1995).

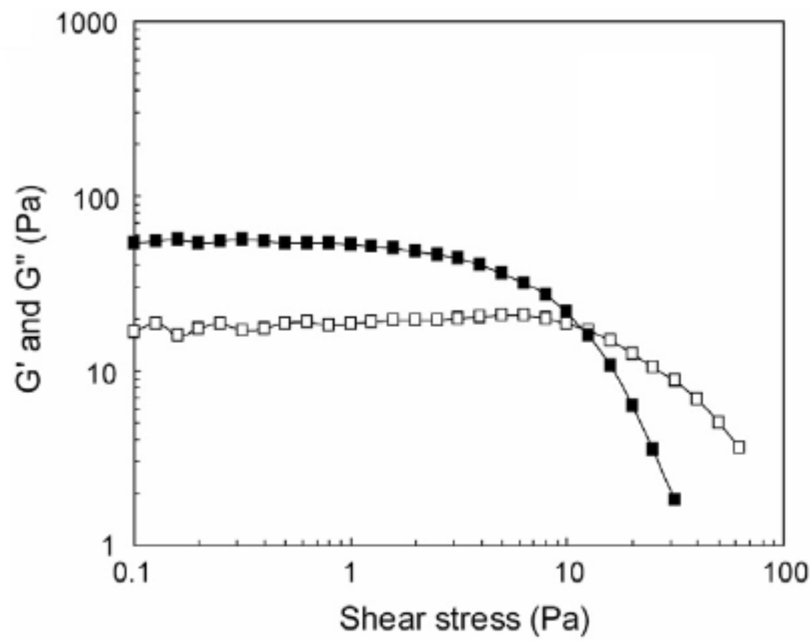


Fig. 2.3: Stress sweep profiles for chili sauce obtained at constant frequency of 1 Hz (G′: filled symbol, G″: unfilled symbol) (Gamonpilas et al., 2011)

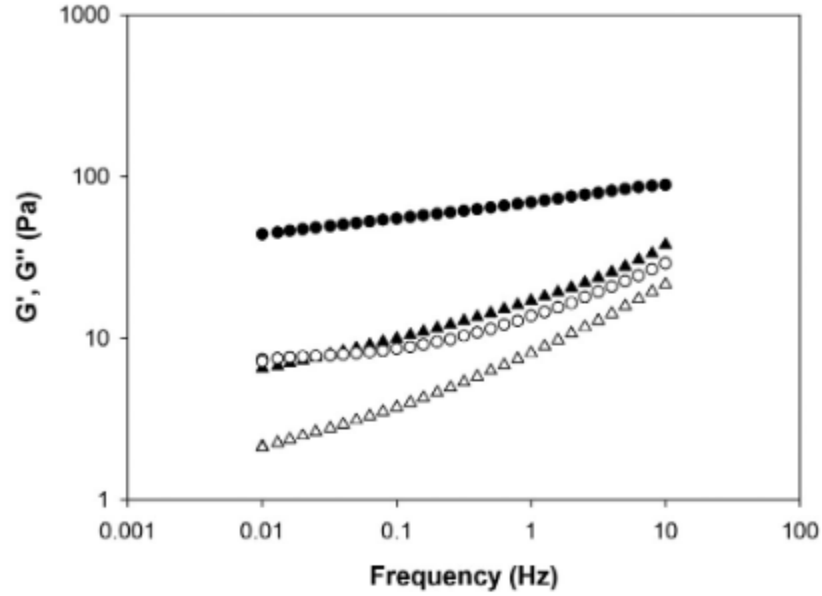


Fig. 2.4: Frequency sweep profiles for native starch white sauce (G′: filled symbol, G″: unfilled symbol; circle: fresh sample, triangle: thawed sample) (Sanz et al., 2016)

2.2.1 Hydrocolloids and Rheology of Sauces

Hydrocolloids generally represent a group of long-chain polymers, including polysaccharides and proteins that are easily dispersed, readily soluble, and prone to swell in water. They are known to have high affinity for water due to the presence of large numbers of hydroxyl group. They can form colloidal dispersions. Hence, they are known as 'hydrophilic colloids' or the more preferred 'hydrocolloids' (Saha & Bhattacharya, 2010). The application of hydrocolloids in food formulations helps to improve the rheology, texture, and customer acceptability of foods. They function as thickening, gelling, emulsifying and stabilizing agents. Hydrocolloids come in the form of plants extracts, exudates, seeds, microbial polysaccharides, modified polysaccharides, animal extracts, and cellulose-based polymers (Wüstenberg, 2015). Whey proteins are also categorized as hydrocolloids since they manifest similar aggregation and gelation behavior characteristic of other polysaccharide hydrocolloids (Li & Nie, 2016). Different types of hydrocolloids, including starchy, such as native corn and potato starches and acetylated distarch adipate (Arocas et al., 2011) and non-starchy hydrocolloids, such as guar gum, xanthan gum and carboxymethylcellulose

(Heyman et al., 2010) have been explored in sauce formulations. The hydrocolloids exert both individual and synergistic effects on the rheology of sauces.

2.2.1.1 Utilization of Starch in Formulation of Sauces

Starch is one of the most abundant polysaccharides and source of energy in food. In its polymeric form, it comprises many anhydrous glucose units joined by glycosidic bonds. Starch is composed of straight-chained amylose, essentially 99% (1-4) and (1-6)-α-linkages and branched amylopectin, which is 95% (1-4) and 5% (1-6)-α-linkages (Xie et al., 2013). Food grade starches are classified as either native or modified. Native starch is extracted from naturally existing cereals, roots, and tubers, such as rice, cassava, and yam. However, the application of native starch in the production of sauces is limited due to retrogradation, syneresis, poor shear and thermal stability (Królikowska et al., 2019). To overcome these limitations, different starch modification methods have been developed (Wang et al., 2016). These methods are aimed at improving the functional properties of starch which is desired in food processing. Common modification techniques include physical, chemical, enzymatic, and genetic manipulations. The merits and demerits of these starch modification techniques have been reviewed by different authors (Haq et al., 2019; Zia-ud-Din et al., 2017). Though desired qualities are achieved through starch modification, there seems to be a conflict with the recent consumer interest in clean label foods. Clean label foods are foods that are organic, natural, and free from artificial additives. With this definition, sauces and other food products formulated with starches modified through chemical, enzymatic, and genetic means do not meet the description of clean label foods and are usually identified on the product label (Alting & Van De Velde, 2012). This necessitates the adoption of physically modified starches in the formulation of sauces.

2.2.1.2 Synergistic Utilization of Starches and Gums in Formulation of Sauces

Over the past few decades, the food and pharmaceutical industries have increasingly been making use of edible gums. Edible gums provide stabilizing effect by increasing the viscosity of solutions at low concentration. They are inexpensive, odorless, chemically inert, and biocompatible. Edible gums also preserve the flavor of foods and are used as edible coatings to maintain freshness of fruits and vegetables and minimize oil uptake in fried products. However, the use of gums in sauce formulation is primarily due to its ability to improve rheological and textural properties. Gums, such as xanthan and guar gum have been used, either singly or in combination with various starches to achieve this purpose. Table 2.1 elucidates a summary of studies that investigated the single and synergistic effects of hydrocolloids on the rheological properties of various sauces.

Table 2.1: Summary of studies on rheological properties of sauces

Sauce	Hydrocolloid	Major findings on flow behavior and viscoelastic property	Additional comments	References
White sauce	Waxy corn starch (native, physically, and chemically modified)	Consistency index and flow behavior index increased in sauce formulated with modified starch compared to native starch.	Sauces formulated with modified starch had a more stable structure, indicated by their small thixotropic area.	(Sanz et al., 2016)
		Unlike the sauces formulated with native starch, the shape of the mechanical spectra of sauces formulated with modified starches remained unchanged. Moreover, the G′ and G″ values of native starch white sauce had a greater dependence of frequency.	The greater frequency dependence of native starch white sauces could have been an effect of retrogradation. Since the amylose component is unbranched, it is easier to realign itself forming a crystalline structure.	
Caramel sauce	Potato starch and xanthan gum	Increased xanthan gum concentration and storage caused an irregularity in flow parameters and the area of the hysteresis loop.	This may have been due to the competition for water molecules between the starch polysaccharides.	(Krystyjan et al., 2012)
		At a frequency of 1 Hz and increased xanthan gum concentration, the mechanical spectra of freshly prepared and stored caramel sauce revealed greater values of G″ compared to G′.	This is indicative of dominant liquid properties, leading to an undesirable reduced adhesiveness.	
White sauce	Rice starch, potato starch, corn starch (waxy and non-waxy)	Increased shearing speed led to a notable decrease in viscoelastic properties. At high shearing speeds, a crossover was observed in the mechanical spectra of potato and rice starch sauces.	The decrease in viscoelastic properties could have attributed to increased granular disintegration.	(Arocas et al., 2009a)
Chili sauce	Crosslinked tapioca starch and xanthan gum	The sauces exhibited a pseudoplastic flow behavior with very minimal yield stress. Viscoelastic properties also showed the existence of a soft gel, with weak frequency dependence.	Overall, the synergistic effect of xanthan gum and tapioca starch served to improve the rheological properties.	(Gamonpilas et al., 2011)
Sweet and sour sauce	Potato starch/xanthan gum, oat starch/xanthan gum, oat starch/oat hydrolysate, oat starch/oat hydrolysate/xanthan gum	It appears that the yield stress and thixotropic area increased with xanthan gum and oat hydrolysate concentration.	The increase in yield stress may be attributed to the greater thickening effect provided by the hydrocolloids. Higher values of yield stress signify improved structural integrity.	(Gibiński et al., 2006)

White sauce	Corn starch (native waxy, native non-waxy, hydroxyl distarch, acetylated adipate)	A freeze/thaw cycle was seen to significantly affect the viscoelastic properties of native starch sauces, especially at high temperatures. This was not the case with modified starch sauces.	This is an aftermath of retrogradation.	(Arocas et al., 2009b)
Mustard sauce	Cassava starch/xanthan gum, cassava starch/guar gum	Hysteresis loop and shear stress further increased with gum concentration.	A large hysteresis loop indicates a less stable structure and little resistance to shear.	(Wang et al., 2016)
		Evolution of G′ is more pronounced than that of G″. This was more evident in the formulation containing cassava starch/xanthan gum compared to cassava starch guar gum.	This is an indication of better conformational structure in xanthan gum molecules.	
Strawberry dessert sauce	Potato starch/xanthan gum, corn starch/xanthan gum, oat starch/xanthan gum	The flow profiles all showed a narrow hysteresis loop. However, there was no clear trend reported in the flow parameters for potato starch/xanthan gum and corn starch/xanthan gum combinations.	This could be a result of botanical differences in the origin of the starches.	(Sikora et al., 2007)
White sauce	Starch (native waxy rice, tapioca, high amylose maize)	Increased concentration led to a corresponding increase in viscosity of the resultant white sauce.	Increased viscosity was more visible in tapioca starch because it contained more amylose, which leached out during gelatinization.	(Bortnowska et al., 2016)
		Increased starch concentration gave higher values of viscoelastic functions. However, the difference between the mechanical spectra was remarkably greater in tapioca starch sauces.	This could have been due to the amylopectin composition which weakens the structural property.	
White sauce	Wheat and rice flour	In contrast to rice-based sauces, shear thinning behavior reduced with increasing particle size in wheat-based sauces.	Reduced shear thinning behavior is indicative of less molecular entanglements.	(Román et al., 2018)
		Dynamic spectra of rice-based sauce had smaller differences between the viscoelastic functions in comparison to wheat-based sauces. Increased particle size led to an increase in viscoelastic function of wheat-based sauces, as opposed to rice-based sauces.	Small differences between viscoelastic functions is an indication of a close gel point, beyond which liquid properties will gain dominance.	

2.2.2 Correlating Steady State and Dynamic Rheology of Sauces

Material functions, such as viscosity, obtained from steady state and oscillatory rheological measurements can be interrelated. In steady state rheology, apparent viscosity, η_a, is characterized by a dependence of shear stress on shear rate. However, in dynamic rheological measurements, complex viscosity, η^*, is a function of angular frequency. The most reliable correlation between steady state and dynamic rheology is described by the Cox-Merz rule, which is essentially the hypothesis that the functional dependence of the complex viscosity's magnitude is identical to the functional dependence of the apparent viscosity (Cox & Merz, 1958) as shown in Eqn. 2.1.

$$\eta_a(\dot{\gamma}) = \eta^*(\omega)\big|_{\dot{\gamma}=\omega} \tag{2.1}$$

where ω = angular frequency (rad/s) and $\dot{\gamma}$ = shear rate (s^{-1})

For polymer melts, Cox and Merz observed that a log plot of steady state viscosity versus shear rate appeared to overlay on the log plot of complex viscosity versus angular frequency. Hence, they postulated that the steady state viscosity is analogous to the absolute magnitude of complex viscosity. The Cox-Merz correlation is important because the limitation associated with one type of rheological measurement can be overcome when another type of measurement is used (Gunasekaran & Ak, 2000). Due to factors, such as secondary flows and slip, the steady state viscosity is quite difficult to measure, especially at high shear rates. Under a geometry operating at low shear rate, a food material experiences primary shear during steady state testing. High shear rates induce turbulence which causes secondary flows to overspread on the primary shear flow. It is important to note that in rheological testing, the applied shear stress on a material is calculated using the measured torque, while shear rate is calculated from the displacement. The turbulence and secondary flow cause an overestimation of the measured torque, ultimately leading to an incorrect increase in apparent viscosity (Ewoldt et al., 2015).

For fluids that obey this rule, their steady state rheological properties can be assessed through dynamic/oscillatory rheological measurements. However, most foods do not follow empirical Cox-Merz rule. At high angular frequency, it is noticed that apparent viscosity decreases more rapidly with increasing shear rate than complex viscosity does with angular frequency (Naji-Tabasi & Razavi, 2017). When this happens, the curve of complex viscosity against angular frequency is parallel to apparent viscosity against shear rate (Fig. 2.5), suggesting an approximate linear relationship (Rao & Cooley, 1992). Reasons adduced for the non-conformity of foods to the Cox-Merz rule are the presence of high-density entanglements and disruption of the network structure due to excessive stress (Alaeddini et al., 2018; Zhang et al., 2018). Hence, to correlate steady state and dynamic rheological properties, the empirical Cox-Merz rule can be modified by the addition of shift factors. The linear modification, called the extended Cox-Merz rule, can be achieved by multiplying either of η_a, γ, η^*, or ω by some shift factor or constant (Eqn. 2.2). Correlation could also be achieved using a non-linear modification. A power modified or generalized Cox-Merz rule is shown in Eqn. 2.3 (Augusto et al., 2012).

$$\alpha \cdot \eta_a(\dot{\gamma}) = \eta^*(\omega)\Big|_{\dot{\gamma}=\omega} \tag{2.2}$$

$$\left|\eta^*(\omega)\right| = \beta\eta(\dot{\gamma})^{\alpha_2}\Big|_{\dot{\gamma}=\omega} \tag{2.3}$$

where α, β = shift factors and α_2 = power index

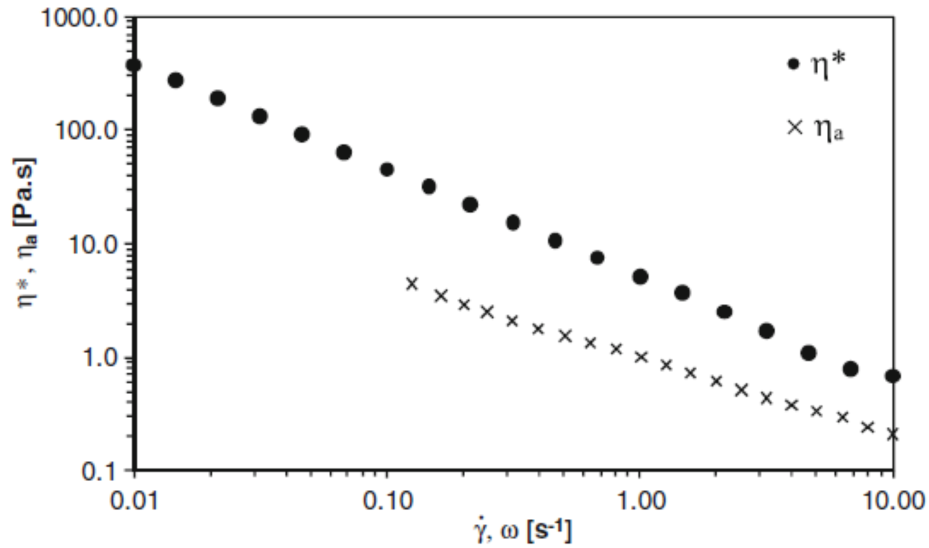


Fig. 2.5: Complex and apparent viscosities of tomato juice as functions of angular frequency and shear rate (Augusto et al., 2013)

The Cox-Merz rule is very important in rheological analyses. It can be used to characterize the shear/strain sensitivity of materials with network-like structures. However, the applicability of empirical or modified Cox-Merz rule in sauces is scarcely reported in the literature. Generalized Cox-Merz rule has been found to apply for white sauce prepared with waxy rice starch or tapioca starch (Bortnowska et al., 2016). The authors reported values of shift factors greater than one which increased with increasing starch concentration. This was attributed to the fact that the network structure of the sauce may have been less affected by dynamic/oscillatory test compared to steady state test. On the other hand, extended Cox-Merz rule did not apply to most commercial chili sauces thickened by modified starch and xanthan gum combinations (Gamonpilas et al., 2011). In this case, continuous flow, and differences in structure arrangement at small amplitude oscillation likely influenced the behavior of the chili sauces. More research efforts aimed at understanding the relationship between steady state and dynamic rheology of emulsion systems including sauces is still needed. An overview of studies published within the last five years, on different food systems that were found to obey various forms of modified Cox-Merz rule are presented in Table 2.2.

Table 2.2: Values of constant/shift factors of modified Cox-Merz rule for different products

Product	Shift Factor		References	Additional Comment
	α	β		
Meat emulsion	0.34 – 0.57	-	Ağar et al. (2016)	Meat emulsions prepared with sugar beet fiber showed increased adherence to Coz-Merz rule.
Batter and gluten-free cake (produced with extruded rice flour)	5.85 – 78.90	0.66 – 1.75	Das and Bhattacharya (2019)	Cox-Merz rule was successfully applied. No clear trend between shift factors and barrel temperature reported.
Yoghurt/molasses blends	0.21 – 0.25	-	Eroglu et al. (2016)	Increasing molasses concentration increased compliance to Cox-Merz rule.
Currant paste (formulated with different concentrations of water and glycerol)	0.722 – 1.272	0.456 – 333.396	Nikolidaki et al. (2019)	Conformity to modified Cox-Merz rule reported. No clear trend between treatments was observed.
Potato puree	0.3 – 0.61	-	Dankar et al. (2018)	Shift factor increased with additive concentration indicating enhanced structure.
Brazilian honey (80.89 – 83.57 °Brix)	0.913 – 0.998	0.970 – 1.082	Silva et al. (2017)	Temperature (T) affected compliance to the rule. T<30 °C did not follow the rule.
Meat emulsions	0.50 – 0.57	-	Genccelep et al. (2015)	Increasing modified starch concentration increased conformity to Cox-Merz rule.
Hazelnut milk (6.45 – 7.15 °Brix)	0.007 – 0.025	-	Gul et al. (2017)	Increase in shift factor led to increased adherence to Cox-Merz rule. Pressure somewhat affected behavior.
Salad dressing (prepared with pregelatinized potato starch)	0.29 – 1.17	0.18 – 5.98	Bortnowska et al. (2014)	Shift factors increased with increase in level of potato inclusion.
Rose hip marmalade	0.005 – 0.07	-	Sagdic et al. (2015)	Shift factor increased with increase in temperature.
Mechanically deboned chicken meat	0.194 – 0.623	-	Saricaoglu et al. (2017)	Shift factor decreased with increasing high-pressure homogenization. Deviation from Cox-Merz was pressure-dependent.
Sunflower oil-in-water emulsion prepared with tragacanth gum	0.27 – 0.74	-	Abdolmaleki et al. (2019)	Deviation from Cox-Merz rule reduced with increasing shift factor.

2.3 Textural Properties of Sauces

Texture is a critical quality attribute of foods that influences consumer acceptance. Texture profiling is an attempt to imitate human mouthfeel and mastication of foods. The complexity of defining the texture of foods is heightened by the fact that foods possess diverse textural properties, and consumers may not perceive the texture of a food in the same manner. A common definition of texture is as a sensory attribute of foods (Bourne, 2002; Brandt et al., 1963; Chen & Rosenthal, 2015; Lawless & Heymann, 2013; Szczesniak, 1963, 1987; Wilkinson et al., 2000). Among the well known definitions is that of Szczesniak (2002), which defines texture as "the sensory and functional manifestation of the structural, mechanical and surface tension properties of foods detected through the senses of vision, hearing and kinesthetic". In more recent times, this definition has been extended to include the new research areas of tribology (oral processing and mouthfeel). Proponents of this evolving area of texture studies argue that as food particles becomes much more smaller during oral processing/mastication, rheology alone is insufficient in describing the textural properties of the food (Prakash et al., 2013; van Stee et al., 2017; Wang et al., 2019). This complexity is brought about by the lubrication provided by saliva. Textural attributes of foods are either assessed through subjective (sensory analysis) or objective (instrumental analysis) means (Philipp et al., 2017; Saldaña et al., 2015; Scheuer et al., 2016). Instrumental analysis is further classified into destructive and non-destructive testing (Blanes et al., 2015; Li et al., 2016). Sensory evaluation is limited by its lack of objectivity. In addition, the time spent, and the high cost associated with mobilizing trained/untrained panelists are also of serious concern. In instrumental analyses, destructive testing leads to some economic losses to the food industry as tested foods are rendered inedible. To address these shortcomings, current food research efforts in instrumental texture measurement have seen the emergence of non-invasive, non-destructive and time-effective testing techniques, such as near infrared and visible near infrared spectroscopy, acoustic vibration, and hyperspectral imaging (Kucha et al., 2018). These techniques have been widely exploited in assessing textural properties in fruits (Goldberg et al., 2019) and meat (Zhao & Peng, 2015). However, it appears that reports on the application of non-destructive techniques to evaluate the important textural attributes of sauces, such as hardness, adhesiveness, cohesiveness, spreadability, gumminess, springiness, and stringiness have not been reported. A brief description of the terms used to describe the texture attributes of sauces is given in Table 2.3. It seems that textural measurement of sauces is still at the level of "destructive-instrumental analysis". In this regard, the force-deformation method is widely utilized in the objective assessment of textural properties of sauces. This measures the mechanical properties of sauces that are crucial to the sensory perception of texture by human hand and mouth and to resistance to mechanical damage during product handling. Other studies have found a correlation between sensory and instrumental data (Chen & Opara, 2013b; Paula & Conti-Silva, 2014; Półtorak et al., 2015). A method designed to simulate certain mechanical aspects of the tongue during mastication was developed by Chung et al. (2013). The method was used to determine textural properties, such as maximum peak force, residual force, and shear viscosity, in model turkey sauces. The authors observed a strong correlation between maximum peak force (related to viscosity) derived from the simulated mastication method and the viscosity from sensory analysis.

Table 2.3: Definition of textural properties

Property	Definition	Reference
Adhesiveness/stickiness	Force required to overcome the attractive forces between the sample and the probe	Szczesniak (2002)
Cohesiveness	Measure of the intermolecular forces binding the sample	Glibowski et al. (2008)
Firmness/hardness	Maximum force required to compress a sample or cause deformation	Chen and Opara (2013a)
Stringiness	A measure of how much a sample stretches, rather than breaks, when the fingers are separated, or probe is retracted	Civille and Dus (1991)
Springiness	Ability of a material to recover its original form upon removal of deformation force	Bourne (1978)
Gumminess	Energy needed to disintegrate a food material to a state where it is ready for swallowing (low degree of hardness × high degree of cohesiveness)	Civille and Szczesniak (1973); Kahyaoglu et al. (2005)
Spreadability	Quantifies the ease with which a product can be spread over a surface	Basu and Shivhare (2010)
Chewiness	Measure of energy required to masticate a solid food till it is safe for swallowing (hardness × cohesiveness × springiness)	Szczesniak (2002)

Though textural properties of sauces can be improved with the addition of different blends of hydrocolloids, the size distribution of the hydrocolloids is important for optimal results. It has been reported that dispersed particle size affected cohesiveness in mayonnaise (He Liu et al., 2007; Worrasinchai et al., 2006) and firmness and cohesiveness in chocolate (Afoakwa et al., 2008; Do et al., 2007). Mirzaei et al. (2018) reported an improvement in the textural properties of tomato sauce formulated with konjac-mannan, xanthan, and tragacanth gums. The synergistic interaction between konjac-mannan and xanthan gums yielded the sauce with optimal textural properties. The cohesiveness of tomato sauce improved with increased concentration of xanthan gum, representing the sauce with the finest particle size and monodispersity. Gumminess also improved with xanthan concentration, which was attributed to the formation of elastic gel as a result of interaction between konjac-mannan and xanthan gum. Similarly, an improvement in textural properties (hardness, gumminess, and spreadability) was observed in mustard sauce formulated with modified starch/xanthan gum and modified starch/guar gum (Wang et al., 2016) as well as sweet and sour sauce (Gibiński et al., 2006). However, it was observed that the improvement was more dominant in modified starch/xanthan gum sauce, indicating its superior textural properties to those of modified starch/guar gum.

Butter sauces, such as hollandaise sauce and béarnaise sauce (made from egg yolk, butter, white wine, and lemon juice), have also been studied (Nygren et al., 2001; Rognså et al., 2014). Although in commercial kitchens, hollandaise sauce is traditionally made using white wine, Rognså et al. (2017) studied the effect of the nature of the wine or wine reduction on the quality attributes of hollandaise sauce. Reducing white wine involves intensifying the flavor by simmering or boiling. Properties, such as firmness, consistency, cohesiveness, and index of viscosity were determined through textural analysis. They reported that the wine sauces gave higher values for these properties. The results signified that more force was required to push (positive extrusion force) and withdraw (negative extrusion force) the probe into/out of the wine sauces than the reduced wine sauces. This implied that the wine sauces were more viscous than the reduced wine sauces. This increase in viscosity could have been due to the high alcoholic content of the wine. Such correlation between alcoholic content and viscosity has been reported in red wine (Neto et al., 2015) and white wine (Nader et al., 2017; Yanniotis et al., 2007). In another study, Sikora et al. (2007) also reported that viscosity, positive- and negative- extrusion forces also increased with increase in xanthan gum concentration in both freshly prepared and stored dessert sauces formulated with combinations of potato starch/xanthan gum, corn starch/xanthan gum, and oat starch/xanthan gum.

In recent decades, the food and nutrition focus have been towards low-fat foods. This trend was necessitated by public health issues, such as obesity, cancer, and hypertension, which has been associated with the consumption of high-fat foods (Kurek et al., 2017; Mba et al., 2015). The food industry has responded by producing foods, and food ingredients, additives, and condiments with highly reduced total lipids content. The food industry sector that produces sauces and dressings have also followed this trend. In this regard, the applicability of various fat replacers and biopolymers has been evaluated. Hosseinvand and Sohrabvandi (2016) reported reduced fat content in mustard sauce with the addition of inulin, pectin, and β-glucan as fat replacers. The firmness, cohesiveness, and adhesiveness of these low-fat mustard sauces were observed to decrease with increasing concentration of the fat replacers, which implied decrease in their viscosity. Such correlation between viscosity and fat content has also been reported for other sauces (Chung et al., 2013). The synergistic interaction between various hydrocolloids, starch and fibre reportedly had a desirable effect on the textural properties and fat content of mayonnaise (Golchoobi et al., 2016; Maani et al., 2017). Firmness and cohesiveness decreased with the addition of fibrous materials. This can be correlated with decreasing viscosity and consistency values observed in the flow behavior test. This can be attributed to the antagonistic interaction between the cellulose and starch (Maani et al., 2017).

CONNECTING TEXT TO CHAPTER THREE

Chapter two of this thesis reviewed recent literature on the rheological and textural aspects of sauces. A wide range of opportunities exist for the formulation of different sauces with varying texture, flow behavior, and functional properties. Important rheological properties, such as viscosity, influence consumer acceptability. However, due to secondary flows and structural deformation, the steady state viscosity of sauces is quite difficult to measure, especially at high shear rates. Hence data obtained from oscillatory rheological measurements are usually more reliable. Yet, limitations, such as time and number of samples, may not permit both steady state and oscillatory rheological testing. The need exists to find a correlation between steady state and oscillatory rheological properties of sauces. This will permit obtaining steady state viscosity from oscillatory rheological measurements. This identified area is further investigated in Chapter three. Portions of chapter two has been submitted for publication. The review manuscript was co-authored by Dr. O. Mba, Dr. E. Kwofie, and Dr. M. O. Ngadi. All the literature cited in chapter two has been listed in the reference section at the end of this thesis.

Valentine C. Okonkwo, Ogan I. Mba, Ebenezer M. Kwofie, Michael O. Ngadi. “Rheological, Textural, and Antioxidant Peculiarities of Sauces: A Review” (Submitted for publication).

Chapter three of this thesis applied the modified Cox-Merz rule in finding a correlation between the steady state and oscillatory rheology of meat sauces. This correlation, performed over a range of temperatures, constitute the first objective of this dissertation. The format of the manuscript has been altered to be consistent with the thesis format. All the literatures cited in this chapter are listed in the reference section of this thesis.

CHAPTER THREE

RHEOLOGICAL PROPERTIES OF MEAT SAUCES AS INFLUENCED BY TEMPERATURE

Abstract

In this study, steady state and oscillatory rheology of seven commercial meat sauces were investigated in the temperature range of 0 – 75 °C using a controlled-stress rheometer, at shear rates between 0.1 – 100 s^{-1} and oscillatory frequency sweeps of 0.01 – 10 Hz. The sauces exhibited pseudoplastic behavior well described by the Hershel-Bulkley model ($R^2 \geq 0.975$). Estimates of model parameters showed that the yield stress and consistency index ranged from 0.027 – 33.958 Pa and 4.614 – 41.313 Pas^n, respectively. The flow behavior index, n, ($0.027 \leq n \leq 0.551$) confirmed the pseudoplastic behavior of the sauces. Temperature had a statistically significant effect on the estimated model parameters ($p < 0.05$). Furthermore, temperature dependency on oral shear viscosity followed an Arrhenius-type model ($R^2 \geq 0.952$). The oscillatory tests results revealed that all the sauces behaved like weak gels. Storage modulus (G') was greater than loss modulus (G") within the studied frequency range, indicating a dominant elastic structure over viscous properties. Viscoelastic properties were modelled by the power law function of oscillatory frequency ($R^2 \geq 0.958$). The related magnitude ranged from 23.998 – 2176.25 Pas^n and 0.114 – 0.277 for consistency index and flow behaviour index, respectively. Linear and non-linear/power modified Cox-Merz rule ($R^2 \geq 0.784$) were satisfactorily applied to correlate apparent and complex viscosity values at all the temperatures studied.

3.1 Introduction

Everyday food materials may be liquid or solid. However, the bulk of food products, such as sauces and dressings, are classified as soft condensed matter because they are composed of a range of hierarchical nano- and micro-structures (Mezzenga et al., 2005). Sauces are typically multiphase value-added food condiments either consumed by themselves or used to accompany other products. They are formulated to possess unique structure-property relationship that greatly influence oral perception and digestibility (Fischer & Windhab, 2011). From an industrial standpoint, sauce production heavily relies on complex flow processes, such as flow in pipes, hence knowledge of its rheological behavior is crucial in optimizing pumping efficiency, handling, quality control, storage stability, and general process design (Ngadi & Yu, 2004). In Canada and elsewhere around the world, accompanying food products with sauces has continued to increase because of the enhanced flavor, visual appeal, texture, and nutrients they offer. According to Escoffier's classification, the five mother French sauces are: béchamel, velouté, espagnole, hollandaise, and tomato sauce (Peterson, 2017). Sauces, such as meat sauces derived from tomato sauce, are called secondary sauces. Meat sauces, just like most foods, possess both liquid and solid properties, earning them the term viscoelastic fluids, accounting for their liquid and solid behaviors, respectively. Viscoelastic properties have been linked to textural quality attributes of foods that greatly influence customer acceptance (Amonsou et al., 2011). Rheological investigations seek to characterize the functional relationship between stresses, deformation, and flow, resulting to material properties, such as viscosity and viscoelasticity (Fischer et al., 2009).

Numerous rheological investigations have been conducted on different sauce varieties, such as white sauce (Arocas et al., 2009a; Román et al., 2018; Sanz et al., 2016), caramel sauce (Krystyjan et al., 2012), mustard sauce (Wang et al., 2016), and strawberry dessert sauces (Sikora et al., 2007). Overall, the flow behavior of most sauces is mostly characterized as shear thinning or thixotropic;

while their viscoelastic properties are strongly dependent on frequency, suggesting that sauces have structural molecular entanglements that have the behavior of a solid at higher frequencies and a liquid at lower frequencies. Rheological properties of sauces are not only dependent on formulation ingredients but also on processing conditions, such as temperature. The effect of temperature on rheological properties needs to be investigated, because a wide variation in temperature is encountered during food processing and storage (M. A. Rao, 2013).

It is important to find a relationship between the properties obtained from different rheological measurements. This is useful because the limitation of a measurement can be greatly overcome when another type of measurement is used and then correlating the properties obtained from both measurements (Gunasekaran & Ak, 2000). For instance, steady state viscosity is difficult to measure, especially at high shear, due to instabilities, such as secondary flows and slip; hence, measurements obtained through small-amplitude oscillation are more reliable (Snijkers & Vlassopoulos, 2014). The most reliable correlation between steady state and oscillatory rheological data is described by the Cox-Merz rule (Cox & Merz, 1958). Simply, it states that apparent viscosity is equal to complex viscosity at the same values of shear rate and angular frequency. For fluids, like polymer melts, that obey this rule, their steady state rheological properties can be assessed through oscillatory/dynamic rheological measurements.

Studies that have focused on the rheological properties of meat sauces appear to be scarcely reported. The study conducted by Martínez-Padilla and Rivera-Vargas (2006) evaluated the flow behavior of barbecue sauces, with special emphasis on validating a non-conventional way of assessing flow behavior but did not consider its viscoelastic properties. Both flow behavior and viscoelastic properties are necessary for a robust rheological characterization (Ahmed et al., 2007). Temperature treatment was reported to reduce the viscosity of white sauce (Bortnowska et al., 2016) and tomato ketchup (Koocheki et al., 2009), while increased starch concentration enhanced their viscosities. Moreover, there are no existing studies that have found a correlation between steady state and oscillatory rheological properties of meat sauces. This creates the need to elucidate the influence of temperature on rheological properties of meat sauces. Hence, the objectives of the current study are to evaluate the steady shear and oscillatory rheological characteristics of selected commercial meat sauces over a range of temperatures; and assess the applicability of the Cox-Merz rule for these sauces.

3.2 Materials and Methods

Seven commercial meat sauces were purchased from a local grocery store in Montréal and used in the study. The sauces are labelled as A (Bull's eye barbecue sauce, Ridg's Finer Foods, Don Mills, Ontario), B (Diana BBQ sauce, Diana Sauce, Toronto), C (HP sauce, Heinz Canada, North York, Ontario), D (Kraft BBQ sauce, Kraft Heinz Canada, Toronto, Ontario), E (Lagrille BBQ sauce, McCormick & Co., London, Canada), F (Le Steak sauce BBQ, Le Steak frites, St-Paul, Montreal), and G (St. Hubert Rib sauce, Meilleures Marques Ltd., Boisbriand, Québec). Table 3.1 summarizes the nutritional information as stated on the package label of these sauces.

Table 3.1: Nutritional composition of each commercial meat sauce

Sauce	Nutrients per 30 ml (g)					Other minerals (%)	
	Calories	Sodium	Carbohydrate	Sugar	Protein	Calcium	Iron
A	60	290	16	14	0.3	2	2
B	60	250	14	13	0.2	0	2
C	40	320	10	6	0.4	4	4
D	20	460	5	3	0.2	0	0
E	60	510	15	10	1	2	4
F	50	280	14	12	0.6	0	0
G	50	230	12	8	0.5	2	4

A (Bull's eye sauce), B (Daina sauce), C (HP sauce), D (Kraft sauce), E (Lagrille sauce), F (Le Steak sauce), G (St Hubert sauce)

3.2.1 Rheological Measurement

Rheological properties were measured using a controlled stress rheometer (AR2000, TA Instruments, New Castle, Delaware, USA). The instrument was equipped with a 40 mm parallel plate geometry using a gap of 2 mm. Laboratory grade compressed air (30 psi) was maintained throughout the experiment. Rheological properties were measured at four temperature levels (0, 25, 50, and 75 °C), regulated using a Peltier plate with an accuracy of ±0.1 °C. For each procedure, samples without mechanical history, i.e. fresh samples, were utilized. Before measurements were taken, five minutes was allowed for sample equilibration or structure recovery. An approximate sample volume of 2.50 mL was used in all the experiments. A silicon cone was used to cover the samples to prevent evaporation during testing. Data analysis was performed using TRIOS software v5.1.1 (TA Instruments, New Castle, Delaware, USA). Parameter estimates of the Hershel-Bulkley model were obtained by regression analysis.

3.2.1.1 Steady State Measurement

Flow test was conducted using the steady state flow algorithm, using the shear rate range of 0.1 – 100 s^{-1}, at the respective temperatures. Values for percentage tolerance, consecutive within tolerance, and maximum point time were programmed as 5, 3, and 1 min, respectively. The flow behavior of the sauces was modelled using the Hershel-Bulkley model (Eqn. 3.1).

$$\sigma = \sigma_0 + k\dot{\gamma}^n \qquad (3.1)$$

Where σ is shear stress (Pa), σ_0 is yield stress (Pa), k is consistency index (Pa.s^n), $\dot{\gamma}$ is shear rate (s^{-1}), n is flow behaviour index (dimensionless).

3.2.1.2 Viscoelastic Properties

3.2.1.2.1 Oscillatory Stress Sweep

Stress sweep experiments, from 0.01 – 100 Pa at a constant frequency of 1 Hz, were performed on the various sauces to determine their linear viscoelastic (LVE) regions (Parra et al., 2019).

3.2.1.2.2 Frequency Sweep

The sauces were next subjected to dynamic frequency sweep experiments between 0.01 – 10 Hz, using a controlled variable of 1 Pa within the LVE region. Values for storage modulus (G′), loss modulus (G″), and loss tangent (tan δ = G″/G′) were recorded as a function of frequency. Using non-linear regression, the viscoelastic moduli (G' and G'') were modelled as a power law function of angular frequency (ω) (Eqns. 3.2 and 3.3), using SAS software v9.4 (SAS Institute Inc., Cary, NC, USA).

$$G' = k' \cdot \omega^{n'} \tag{3.2}$$

$$G'' = k'' \cdot \omega^{n''} \tag{3.3}$$

Where k′ (Pa.s$^{n'}$) and k″ (Pa.s$^{n''}$) represent the consistency coefficients, while n′ and n″ (dimensionless) represents the flow behaviour index of the power law model in Eqns. 3.2 and 3.3. respectively.

3.2.1.3 Applicability of the Cox-Merz Rule

The data obtained from steady state and oscillatory rheological measurements were evaluated for its applicability to the Cox-Merz rule (Eqn. 3.4). This was achieved using least square regression in SAS software v9.4 (SAS Institute Inc., Cary, NC, USA).

$$\eta_a(\dot{\gamma}) = \eta^*(\omega)\Big|_{\dot{\gamma}=\omega} \tag{3.4}$$

η_a= apparent viscosity, η^*= complex viscosity, ω = angular frequency (rad/s) and $\dot{\gamma}$ = shear rate (s^{-1})

3.2.2 Statistical Analysis

All rheological measurements were carried out in triplicates. Regression (linear and non-linear) and analysis of variance (ANOVA) were performed using SAS software v9.4 (SAS Institute Inc., Cary, NC, USA). Statistical significance was determined at $p < 0.05$. Scheffé's adjustment was used to account for multiple comparison. Gauss-Newton iteration was used to achieve convergence during non-linear regression. Principal component analysis (PCA) was used to differentiate between sauce samples.

3.3 Results and Discussions

3.3.1 Steady Shear Properties

All the sauces exhibited shear thinning behaviour with a characteristic yield stress, σ_0, at all the temperatures evaluated. A typical steady state shear curves of one of the sauces at different temperatures is shown in Fig. 3.1. The sauces exhibited shear-thinning (also called pseudoplastic) behaviour. This may be attributed to disentanglement of polymer chains and its subsequent re-alignment in the direction of flow (Hosseini-Parvar et al., 2010). The shear thinning behavior for all the sauces became more apparent with increasing temperature. Shear thinning behavior was also reported in white sauce studied within 20 – 80 °C (Bortnowska et al., 2016) and chili sauce studied at 25 °C (Gamonpilas et al., 2011). The definitive yield stress observed in all the sample at all the studied temperatures represent the minimum shear stress that must be overcome to initiate product flow. At stresses below the yield stress, semi-solid foods experience elastic deformation, manifesting solid properties; beyond the yield stress, viscous properties become dominant and product flow is initiated. Yield stress is important for optimal design of food processing systems, such as those required during thermal processing (Steffe, 1996).

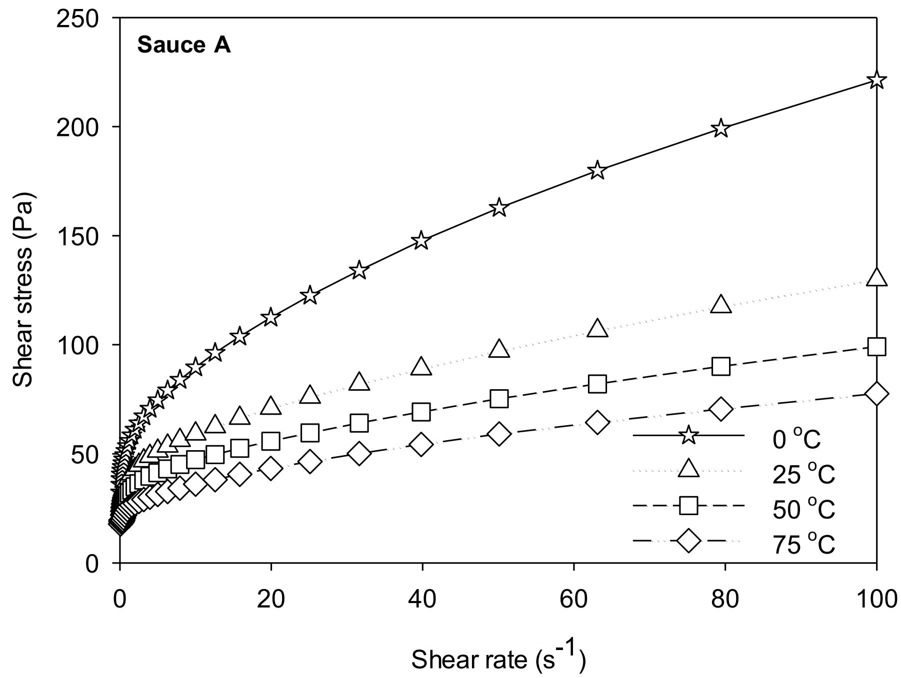
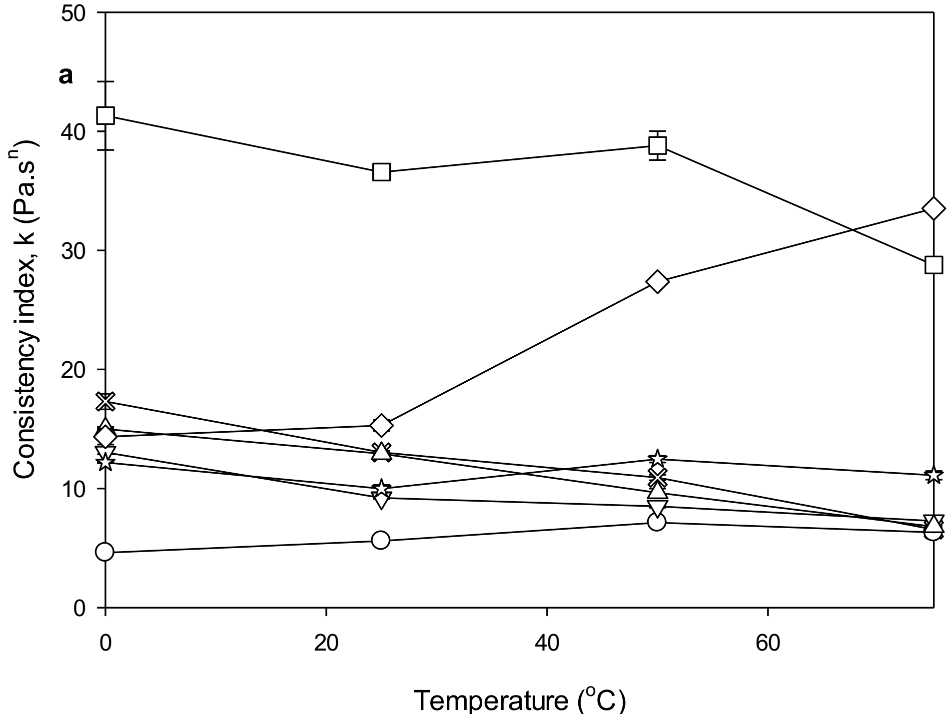


Fig. 3.1: Flow profiles of the Sauce A at different temperatures

The data obtained from steady shear rheological measurements were fitted to the Hershel-Bulkley model. The Hershel-Bulkley model showed high goodness of fit ($0.994 \leq R^2 \leq 0.999$; $0.087 \leq RMSE \leq 3.331$). The flow behaviour of strawberry dessert sauce (Sikora et al., 2007) and mustard sauce (T. Wang et al., 2016) were also well described by the Hershel-Bulkley model. Viscosities of the different sauces were in the range of 0.2125-366.5 Pa.s. Viscosity decreased with increasing shear rate and temperature.

All the sauces were marked with a high consistency as represented by the magnitudes of k. Yield stress values ranged from 1.001-33.985 Pa. High values of yield stress in sauces may indicate a higher composition of thickening substances. In a more practical sense, sauces with low yield stress values are highly deliquescent and may not adhere to the dish; hence may not be accepted by the customer (Juszczak et al., 2013). Yield stress values were reported to increase with increasing starch concentration in mustard sauce (T. Wang et al., 2016), white sauce (Bortnowska et al., 2016), and sweet and sour sauce (Gibiński et al., 2006). The consistency index quantifies the resistance to flow. High value for consistency index is indicative of a stable structure. Values for Hershel-Bulkley consistency index ranged from 4.614-41.313 Pa.s^n (Fig. 3.2a). Similar values were reported for chili sauce (Gamonpilas et al., 2011) and white sauce (Román et al., 2018). The n values at each temperature level were always less than unity (Fig. 3.2b), confirming pseudoplastic behaviour earlier claimed (Mierczyńska et al., 2015). Temperature had a statistically significant effect ($p < 0.05$) on σ_0, k, and n. In most sauces, their respective values appear to decrease with increasing temperature in all the sauces. Decreasing n values signify a higher degree of pseudoplasticity. This trend was also reported in tomato ketchup, studied at 25 – 55 °C (Koocheki et al., 2009) and rose hip marmalade, studied at 5 – 45 °C (Sagdic et al., 2015).



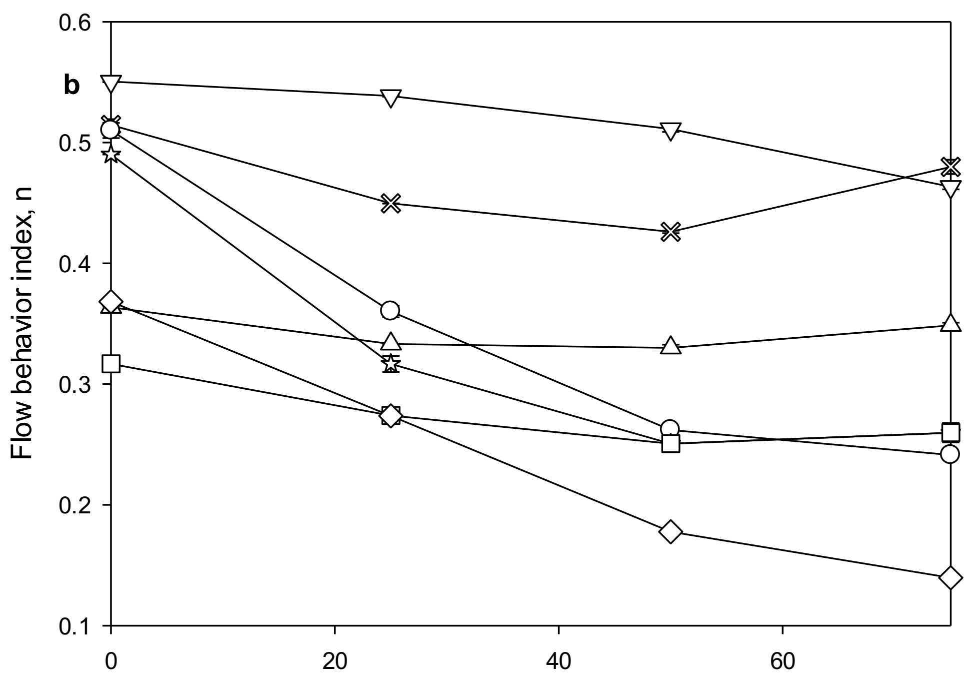


Fig. 3.2: Consistency index (a), and flow behavior index (b) of the different sauces (Cross: A, circle: B, inverted triangle: C, triangle: D, star: E, square: F, diamond: G)

3.3.1.1 Effect of Temperature on Oral Shear Viscosity

Steady state rheological measurement also provided another important parameter, η_{50} (apparent viscosity at a shear rate of 50 s^{-1}), often regarded as typical shear rate of the mouth cavity (Ong et al., 2018). Temperature significantly affected ($p < 0.05$) the η_{50} values for all the sauces, which showed a decreasing tendency (Fig. 3.3). The reduction in viscosity may be attributed to increased thermal energy which causes the destruction of the cohesive forces holding the sauce together. This confirmed the shear thinning behaviour earlier stated and is corroborated by the work of Toker, Karaman, et al. (2013). Moreover, the temperature dependency of η_{50}, values ranging from 0.342 – 3.247 Pa.s, was adequately modelled with the Arrhenius equation (Eqn. 3.5), since $p < 0.05$ and $R^2 > 0.85$ (Table 3.2) (Salinas et al., 2019).

$$\eta_{50} = A \exp\left(\frac{E_a}{R \cdot T_K} \right) \tag{3.5}$$

Where A is the pre-exponential factor, E_a is the activation energy (kJ/mol), R is the universal gas constant (kJ/K.mol), and T_K is the absolute temperature (K).

The Arrhenius equation parameters were obtained through least square regression. Table 3.2 also shows that the estimates of the pre-exponential factor and activation energy for the sauces ranged from 0.012 – 0.188 and 4.535 – 10.523 kJ/mol, respectively. Activation energy quantifies a material's sensitivity to temperature changes (Ngadi & Yu, 2004). The viscosity of sauces with higher E_a values are more susceptible to temperature increase. The consistency index and flow behavior constant were fitted to the Arrhenius model. Their respective magnitudes for the pre-exponential factor and activation energy is shown in Table 3.2.

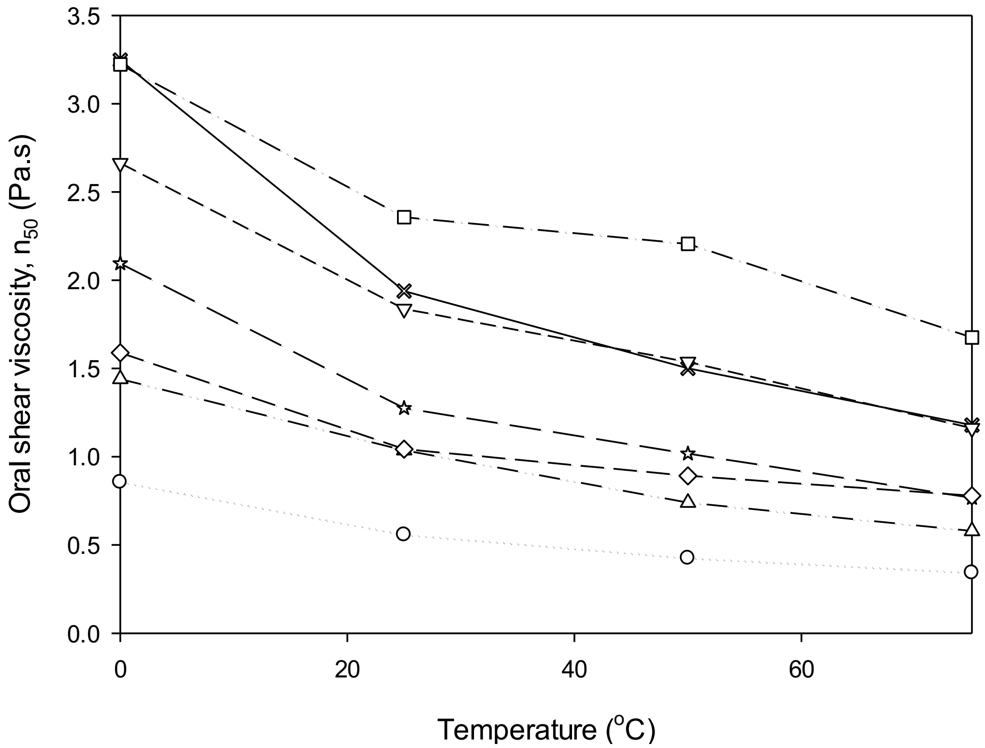


Fig. 3.3: Oral shear viscosity as influenced by temperature

Table 3.2: Effect of temperature on flow behavior parameters

Sauce	k			n			η_{50}		
	A	E_a	R^2	A	E_a	R^2	A	E_a	R^2
A	0.263	9.627	0.928	0.321	0.959	0.230	0.030	10.523	0.982
B	26.735	-3.895	0.732	0.013	8.209	0.969	0.012	9.637	0.994
C	0.943	5.859	0.945	0.259	1.758	0.874	0.063	8.457	0.989
D	0.416	8.299	0.942	0.283	0.501	0.210	0.020	9.732	0.998
E	821.304	-8.713	0.401	0.021	6.980	0.857	0.021	10.333	0.985
F	10.544	3.148	0.662	0.114	2.245	0.796	0.188	6.417	0.953
G	962.073	-9.775	0.896	0.004	10.550	0.988	0.058	7.378	0.952

A (Bull's eye sauce), B (Daina sauce), C (HP sauce), D (Kraft sauce), E (Lagrille sauce), F (Le Steak sauce), G (St Hubert sauce)

3.3.2 Viscoelastic Properties

3.3.2.1 Stress Sweep

Determining the relationship between molecular structure and viscoelastic behaviour often requires oscillatory rheological measurements to be conducted within a boundary where the properties of viscoelasticity (G′ and G″) are unaffected by stress/strain. Such boundary, called the LVE region, provides information about the dynamic yield stress of the material. This was achieved by conducting an oscillatory stress sweep test at constant temperature and frequency. The results are presented in Fig. 3.4. A closer attention was given to the G′ curve because of its more vulnerability to structural deformation.

The point beyond which the viscoelastic functions deviate from a constant plateau signified departure from the LVE region. In some cases, a 10% deviation from the constant plateau has been considered to still be within the LVE region (Agirre-Olabide et al., 2015; Mezger, 2014). The corresponding stress value is called the dynamic yield stress of the material. The dynamic yield stress is defined as the critical stress at which irreversible plastic deformation occurs. The critical stress for the sauces were taken as the onset values of the G′ curve, and ranged from 7.53-46.23 Pa. Temperature had a statistically significant effect ($p < 0.05$) on the critical stress. Gamonpilas et al. (2011) reported values ranging from 0.2-1.50 Pa for chili sauce. The apparent difference in magnitude may be attributed to difference in material composition. The LVE regions of Sauce F and Sauce B at 50 °C are compared in Fig. 3.4. A wider LVE region (greater value for critical stress), is an indication that the sauce will better withstand external stresses (Gamonpilas et al., 2011). Results obtained from oscillatory stress sweep experiments reveal that Sauce B had the shortest LVE region, hence the lowest value for critical stress. This means Sauce B had the least ability to resist external stresses. Conversely, Sauce F had the widest LVE region, signifying a higher value of stress will be required to deform its structure.

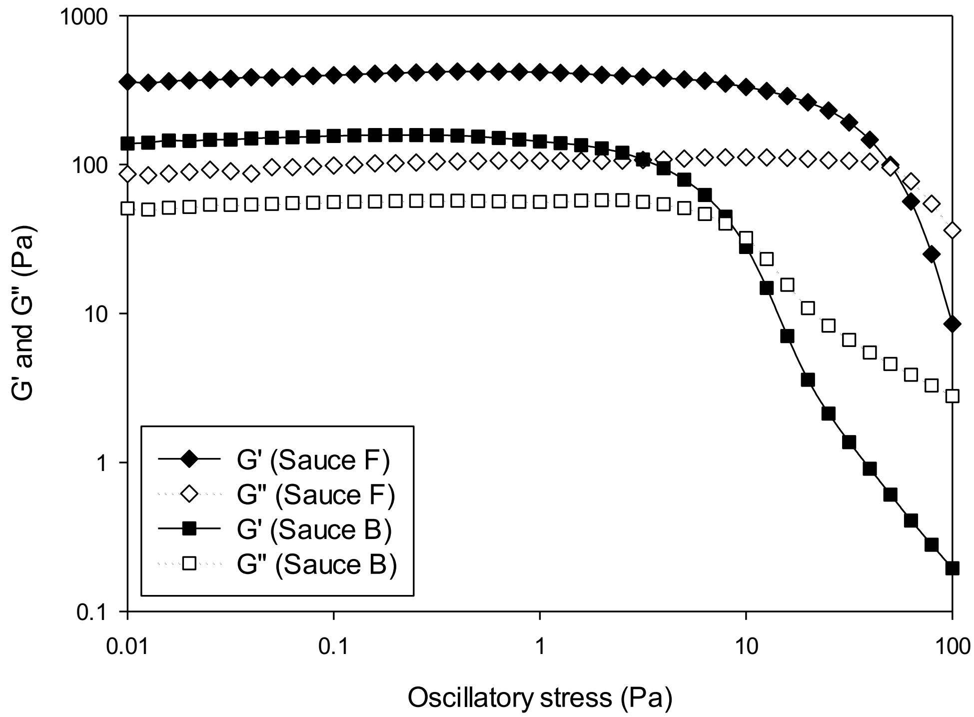


Fig. 3.4: Stress sweep profiles for Sauce B and Sauce F at 50 °C

3.3.2.2 Frequency Sweep

Frequency sweep is used to characterize dispersions. Four common classes of dispersions are dilute solution, concentrated solution, weak gel, and strong/true gel (Ross-Murphy, 2012; Steffe, 1996). The representative mechanical spectra of the sauces at 0 – 75 °C is shown in Fig. 3.5. Foods being complex, exhibit both liquid and solid properties, hence they are described as being viscoelastic. Viscoelastic properties are used to characterize the three-dimensional network structure of materials (Chaisawang & Suphantharika, 2005). The elastic property denoted by G′ is a measure of the deformation energy stored by the sample. Conversely, the viscous property, G″, is measure of the energy dissipated per oscillation. Frequency sweep experiments were conducted within the LVE of the sauces. The results show that G′ and G″ increased with frequency, with the values G′ always greater than G″ (no modulus crossover was observed) within the temperature range investigated, indicating the sauces possess the structure of a weak gel (Palavecino et al., 2020). This could have been due to the oscillation period of reassociation of chains being greater than that of disentanglement, leading to dominant solid/elastic behaviour over viscous properties (Ahmed et al., 2007). Similar behaviour has been reported for similar food products, such as mayonnaise (Ma & Barbosa-Cánovas, 1995), white sauce (Román et al., 2018; T Sanz et al., 2016), and mustard sauce (Wang et al., 2016).

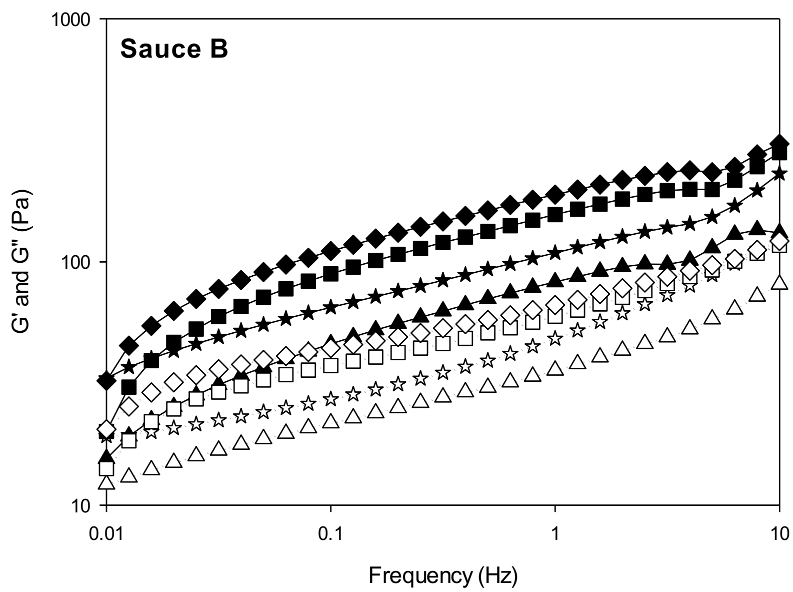


Fig. 3.5: Mechanical spectra of the different sauces. (G′: closed symbols; G″: open symbols). (Star: 0 °C, triangle: 25 °C, square: 50 °C, diamond: 75 °C)

Since the values of G′ and G″ increased with frequency, it was possible to model them as a power law function of angular frequency (Eqns. 3.2 and 3.3). Estimates for k′, n′, k″, and n″ for the different sauces obtained through non-linear regression are shown in Fig. 3.6 and Fig. 3.7. R^2 ranged from 0.958 – 0.999, indicating that the power law model adequately fit the experimental data. The values of k′ and k″ were estimated to be between 23.99 – 2176.25 Pa.s$^{n'}$ and 7.77 – 926.90 Pa.s$^{n''}$, respectively. At all temperatures studied, the estimates of k′ were always greater than k″, further confirming that the sauces exhibited dominant solid-like behaviour over viscous properties. The parameters, n' and n'', are the slopes of ln (G') and ln (G'') against ln (ω). From a structure standpoint, both parameters have a value of zero for true/strong gels (Ross-Murphy, 2012). The estimates obtained, 0.11 – 0.27 and 0.08 – 0.35 for n' and n'', respectively, were found to be positive, confirming the weak gel-like structure (Sagdic et al., 2015).

Nikolidaki et al. (2019) investigated the dynamic rheological properties (15 – 35 °C) of currant paste and reported values of 0.6 – 2310.9 $Pa.s^{n'}$ and 0.3 – 1236.5 $Pa.s^{n''}$ for k' and k'', respectively. The values of n' and n'' were in the range of 0.24 – 0.32 and 0.26 – 0.39, respectively. These values agree with the current study.

Though temperature was seen to have a statistically significant effect ($p < 0.05$) on k', k'', n', and n'', it appears there was no consistent trend. A non-systemic temperature effect on k', k'', n', and n'' was also reported for vegetable puree-based baby food studied at 20 – 80 °C (Ahmed & Ramaswamy, 2006).

The loss/damping factor, tan δ, which is a measure of the ratio of G'' to G', also quantifies whether solid properties or viscous behaviour is dominant. For ideally elastic behaviour, tan $\delta = 0$, since there is no viscous portion, G' completely dominates; whereas tan $\delta = \infty$ for an ideal liquid. A perfect balance between elastic and viscous behaviour has a tan δ value of unity (Mezger, 2014). Tan δ showed an increasing tendency within the frequency range studied, indicating the variation in the interactive forces maintaining the gel network (Liu & Tang, 2011). For all the sauces and within the temperature and frequency range studied, the results (data not shown) for tan δ is $0.1 <$ tan $\delta < 1$, indicating a viscoelastic behaviour and the existence of a weak gel. The tan δ values at a frequency of 1 Hz was used to compare the viscoelastic properties as affected by temperature (Fig. 3.8). Temperature had a statistically significant effect ($p < 0.05$) on tan δ, though no definitive trend was observed. Overall, the tan δ values are less than 0.5, further confirming dominant solid behaviour over viscous properties. The obtained values agree with those reported in the literature for white sauce studied at 20 – 80 °C (Bortnowska et al., 2016).

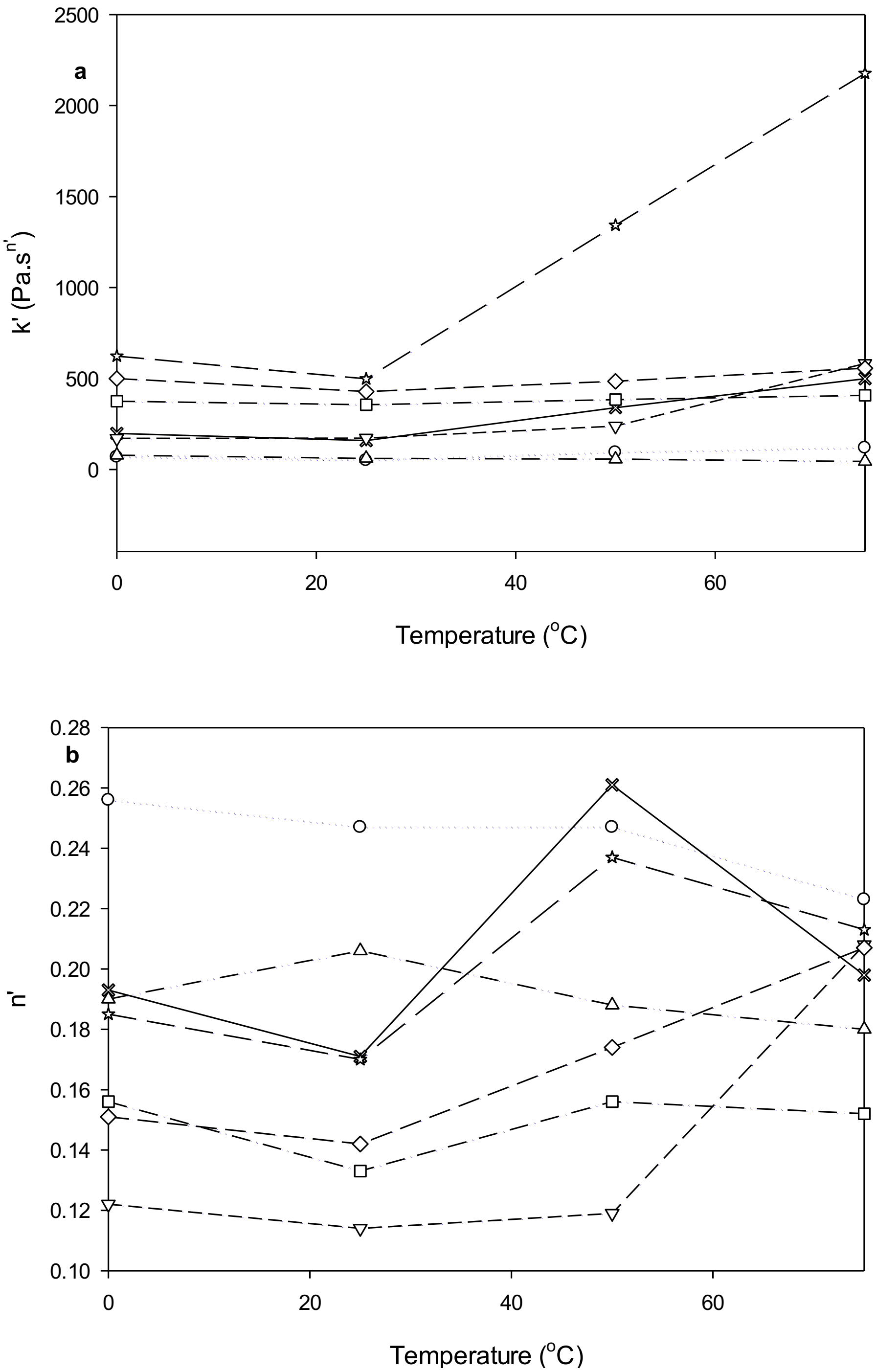


Fig. 3.6: Consistency index (a), and flow behavior index (b) of storage modulus for the different sauces (Cross: A, circle: B, inverted triangle: C, triangle: D, star: E, square: F, diamond: G)

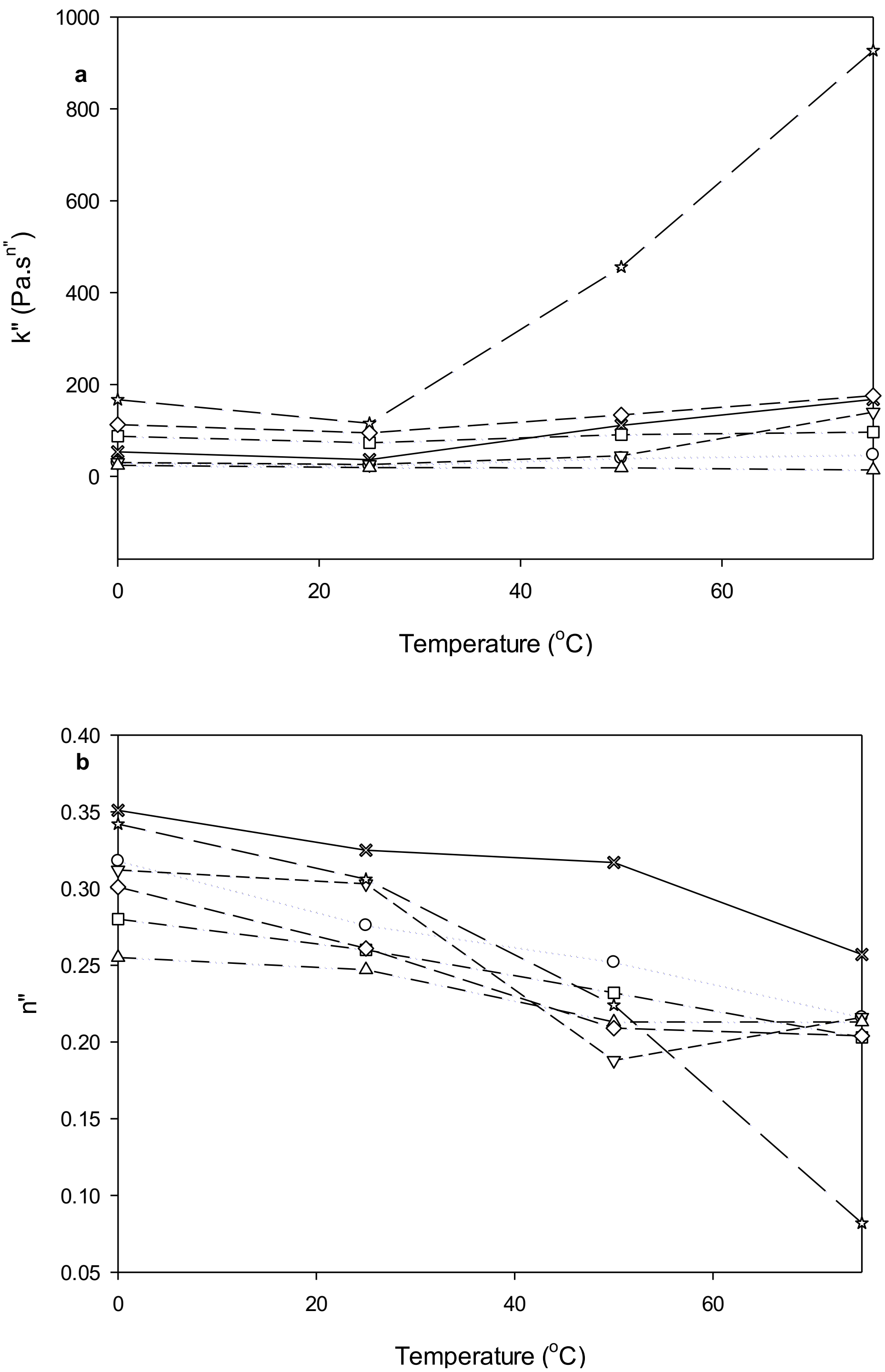


Fig. 3.7: Consistency index (a), and flow behavior index (b) of loss modulus for the different sauces (Cross: A, circle: B, inverted triangle: C, triangle: D, star: E, square: F, diamond: G)

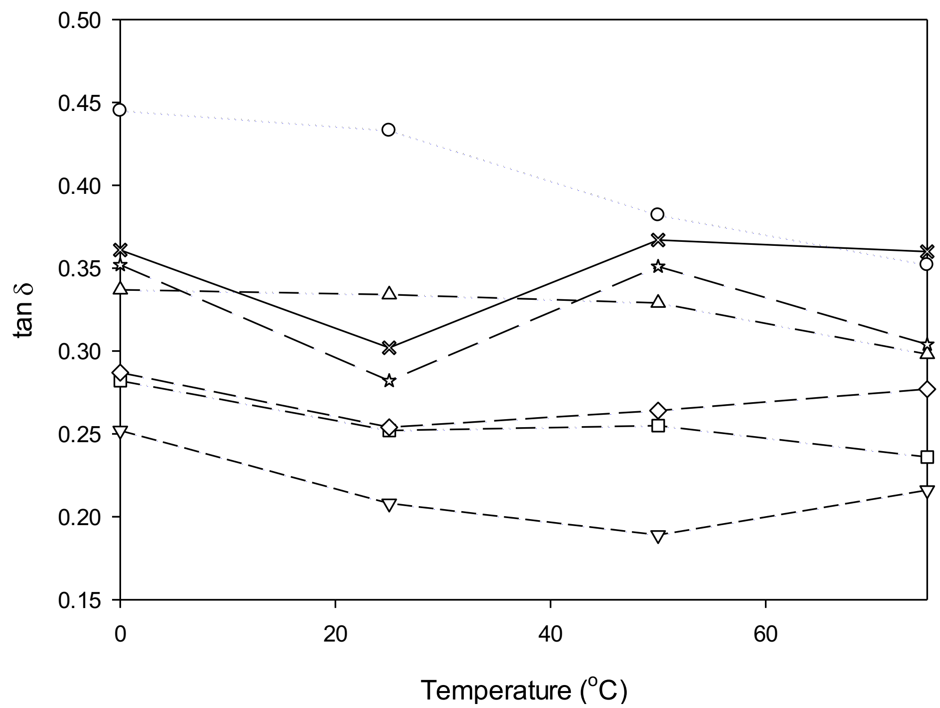


Fig. 3.8: Effect of temperature on loss factor (Cross: A, circle: B, inverted triangle: C, triangle: D, star: E, square: F, diamond: G)

3.3.3 Evaluation of the Cox-Merz Correlation

The applicability of classical Cox-Merz rule was evaluated for all the sauces at the stated temperatures, and it was found not to hold. This is because the curve of complex viscosity against angular frequency did not overlay but was evidently parallel (Fig. 3.9) to apparent viscosity against shear rate at all temperatures (Augusto et al., 2012). The non-conformity of the sauces to classical Cox-Merz rule could have been due to the destruction of the network structure resulting from excessive strain during steady shear measurements (Zhang et al., 2018). Thus, the rheological properties of meat sauces differ from that of polymer melts and colloidal systems and more related to that of structured fluids (Ahmed & Ramaswamy, 2006).

To correctly correlate steady state and oscillatory rheological data, it becomes necessary to modify the classical Cox-Merz rule. The curves on Fig. 3.9 being parallel suggests that an approximate linear relationship exists between complex and apparent viscosities (Rao & Cooley, 1992). Four linear modification approaches are possible. One could either multiply η_a, γ, η^*, or ω (in classical Cox-Merz rule, Eqn. 3.4) by some shift factor, as described in the Eqns. 3.6 – 3.9.

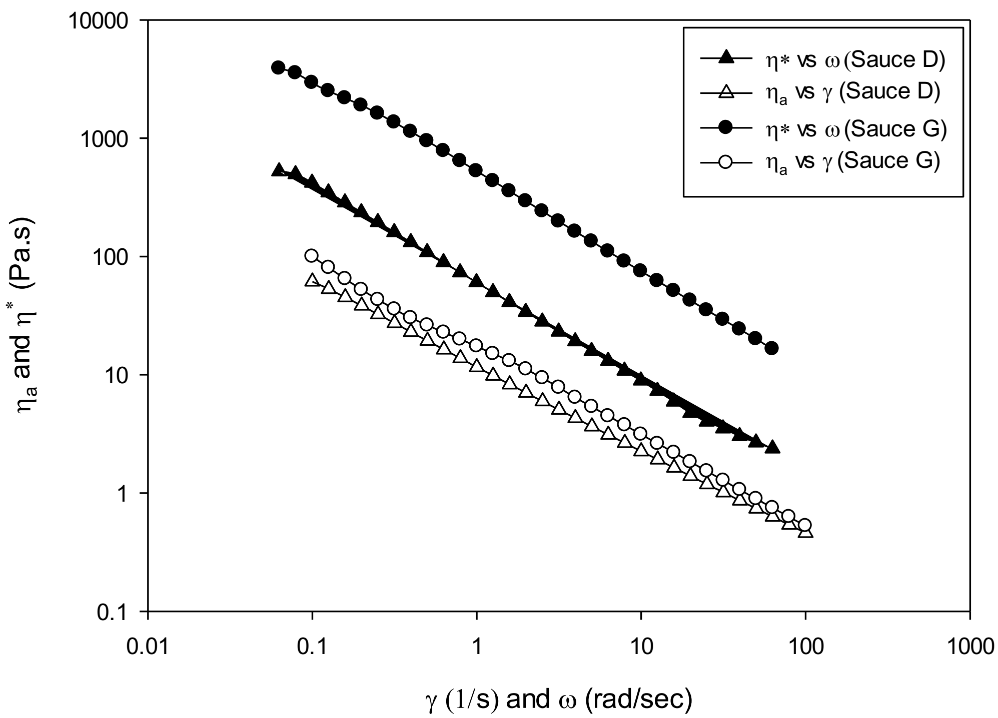


Fig. 3.9: Steady state and oscillatory rheological properties of Sauce G and D at 50 °C

$$\eta_a\left(\tau\cdot\dot{\gamma}\right)=\eta^*\left(\omega\right)\Big|_{\dot{\gamma}=\omega} \tag{3.6}$$

$$\sigma\cdot\eta_a(\dot{\gamma})=\eta^*(\omega)\Big|_{\dot{\gamma}=\omega} \tag{3.7}$$

$$\eta_a\left(\dot{\gamma}\right)=\eta^*\left(\alpha\cdot\omega\right)\Big|_{\dot{\gamma}=\omega} \tag{3.8}$$

$$\eta_a\left(\dot{\gamma}\right)=\mu\cdot\eta^*\left(\omega\right)\Big|_{\dot{\gamma}=\omega} \tag{3.9}$$

Though in the current study, angular frequency was multiplied by a shift factor, α (Eqn. 3.8), when any of the described approach is used, both curves will be superimposed on each other. The estimates of α are obtained through linear regression.

It is also possible to achieve a correlation between apparent and complex viscosities using a non-linear modification. A power modified Cox-Merz rule is shown in Eqn. 3.10. The estimates of α_2 and C are obtained through non-linear regression.

$$C\left[\eta_a\left(\dot{\gamma}\right)\right]^{\alpha_2} = \eta^*\left(\omega\right)\Big|_{\dot{\gamma}=\omega} \tag{3.10}$$

Where C is a multiplicative constant and α_2 is a power index. The estimates of α, C and α_2 presented in Table 3.3.

The obtained estimates of α, C, and α_2 are close to those described for mashed potatoes (Alvarez et al., 2011) and tamarind juice concentrates (Ahmed et al., 2007). The applicability of classical or modified Cox-Merz rule in sauces is not widely reported in the literature. A power modified Cox-Merz rule has been found to apply to white sauce (Bortnowska et al., 2016) and chili sauce (Gamonpilas et al., 2011), though the authors reported smaller values for the multiplicative constant, C. The multiplicative constant is a measure of the difference between complex and apparent viscosities (Augusto et al., 2012). The relatively large values of C obtained in some cases could imply large variability between complex and apparent viscosity values, which can be seen in Fig. 3.9. Temperature had a statistically significant effect ($p < 0.05$) on α, C, and α_2. No trend was observed on the values of C and α_2 with relation to temperature. A similar result was reported for potato puree (Alvarez et al., 2004), siriguela pulp (Augusto et al., 2012), and tamarind juice (Ahmed et al., 2007).

Table 3.3: Estimates of parameters of the modified Cox-Merz rule

Sauce	Temp (°C)	Linear modification		Non-linear modification		
		α	R^2	α_2	C	R^2
A	0	0.349±0.017a	0.979	0.718±0.000b	10.997±0.463b	0.999
	25	0.290±0.002b	0.985	0.734±0.005b	10.728±0.251b	0.999
	50	0.086±0.007c	0.987	1.052±0.005a	9.299±0.842b	0.988
	75	0.053±0.004d	0.988	0.853±0.054c	33.040±4.152a	0.992
B	0	0.224±0.017a	0.996	0.915±0.024b	6.099±0.951b	0.998
	25	0.216±0.006a	0.993	1.039±0.044c	4.141±0.667c	0.994
	50	0.090±0.003b	0.995	1.075±0.001ac	8.954±0.257d	0.996
	75	0.063±0.001c	0.996	1.015±0.016acd	15.278±0.409a	0.996
C	0	0.358±0.005a	0.878	0.402±0.021b	39.205±4.037b	0.999
	25	0.261±0.000b	0.892	0.404±0.002b	43.029±0.531b	0.999
	50	0.158±0.000c	0.896	0.414±0.012b	61.457±2.419a	0.994
	75	0.044±0.001d	0.977	0.795±0.008a	48.086±0.122bc	0.986
D	0	0.410±0.003a	0.986	0.751±0.034a	6.611±0.887b	0.999
	25	0.367±0.006a	0.984	0.785±0.000a	5.724±0.000b	0.998
	50	0.285±0.020b	0.968	0.652±0.043b	11.192±2.422a	0.996
	75	0.288±0.029bc	0.964	0.624±0.038bc	10.775±0.092ac	0.997
E	0	0.074±0.004a	0.981	0.726±0.013b	44.642±4.860b	0.999
	25	0.063±0.002b	0.990	0.779±0.010b	37.548±2.727b	0.999
	50	0.016±0.000c	0.989	1.101±0.035c	41.837±6.329b	0.999
	75	0.009±0.000d	0.988	1.167±0.029ac	66.028±5.323a	0.991
F	0	0.215±0.008a	0.982	0.688±0.006a	20.574±0.147b	0.999
	25	0.176±0.002b	0.977	0.627±0.026a	29.880±3.601c	0.999
	50	0.147±0.011c	0.987	0.720±0.033ab	23.836±4.837bc	0.999
	75	0.105±0.010d	0.979	0.664±0.025a	37.809±0.772ace	0.998
G	0	0.083±0.008b	0.991	0.771±0.023a	30.862±0.415b	0.999
	25	0.065±0.004c	0.989	0.729±0.028a	41.150±1.789c	0.999
	50	0.045±0.000d	0.985	0.709±0.027a	61.829±5.347a	0.998
	75	0.101±0.005a	0.981	0.673±0.015ab	37.340±0.303bce	0.998

Results are mean of three replicates ± standard deviation; within the column for each sauce, values followed by different letters are statistically different ($p < 0.05$); $R^2 \geq 0.784$ in each regression.

3.3.4 Principal Component Analysis

Data obtained from steady shear and oscillatory rheological measurements were further subjected to PCA to determine if any similarities exist between the sauces. The adjusted correlation (accounting for temperature) between estimates of the analyzed variable are presented in Table 3.4. Two principal components (PC) explained 63.73% variation in the observed data. The first principal component (PC1) described 41.57% of the total data variability, with n, η_{50}, k′, k″, and n″ being the dominant variables (loading values > 0.4). The second principal component (PC2) accounted for 22.16% of the total data variability, with n′, and tan δ being dominant. PC3 has an eigen values less than one, hence is non-significant in explaining data variability (Granato et al., 2018; Toker et al., 2013). Fig. 3.10 shows loading plot of the samples. Rheological variables, such as k′, k″, η_{50}, and k form a cluster to the right, while n′, n, and σ_0 cluster at the left, explaining the negative correlation between the variable in Table 3.4. From the score plot in Fig. 3.11, there appears to be two clusters (P and K) of sauces with similar rheological properties.

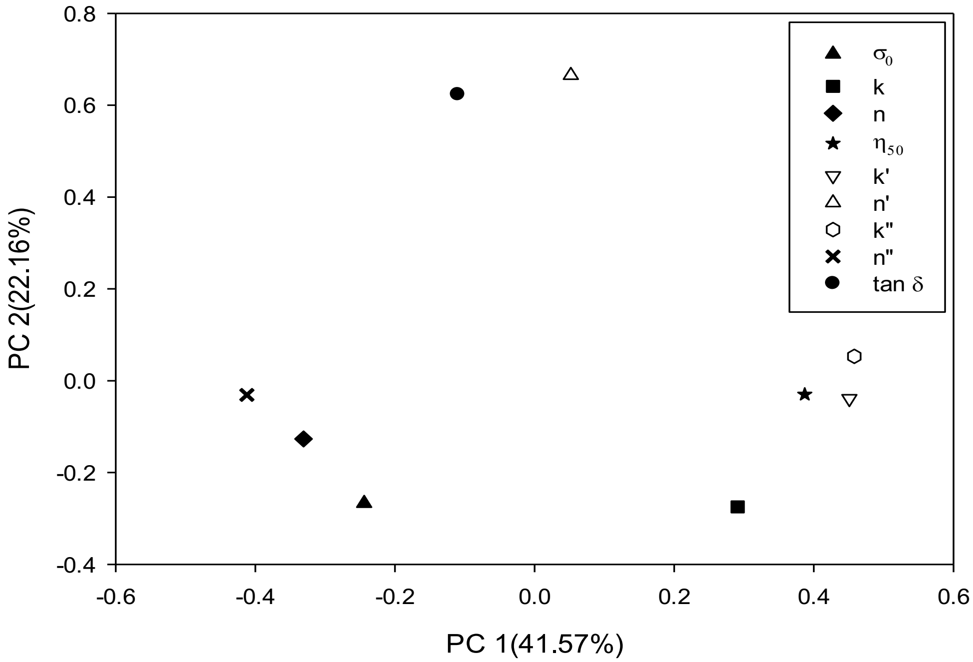


Fig. 3.10: Principal components showing the loading plots for sauce samples

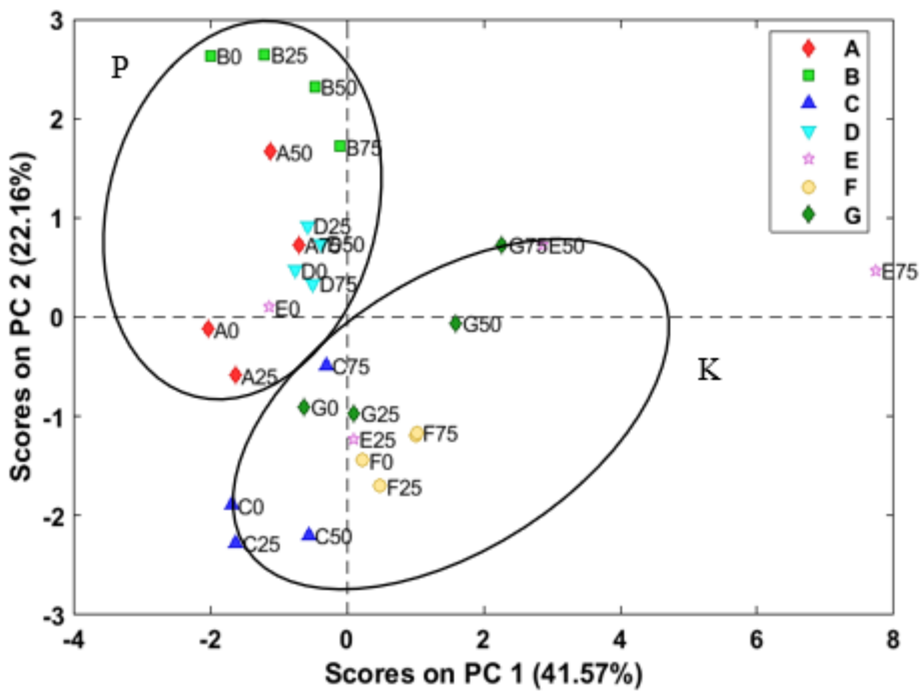


Fig. 3.11: Distribution of sauce samples on score plot

Table 3.4: Partial correlation coefficients between parameters of steady shear and oscillatory rheological measurements

Variable	σ_0	k	n	η_{50}	k′	n′	k″	n″	tan δ
σ_0	1.000								
k	-0.131	1.000							
n	0.673*	-0.632*	1.000						
η_{50}	0.084	0.178	-0.039	1.000					
k′	0.113	0.478*	-0.182**	0.596*	1.000				
n′	-0.166	-0.237*	-0.071	0.000	0.054	1.000			
k″	0.036	0.403*	-0.202**	0.652*	0.959*	0.138	1.000		
n″	0.413*	-0.278*	0.394*	-0.447*	-0.466*	0.175	-0.515*	1.000	
tan δ	-0.145	-0.359*	-0.023	-0.01	-0.099	0.877*	0.060**	0.233*	1.000

*$p < 0.05$; **$p < 0.1$

3.4 Conclusion

The current study investigated the temperature dependency of steady state and oscillatory rheology of some commercial meat sauces. All the studied sauces demonstrated a shear thinning/pseudoplastic behaviour with a definitive yield stress. The shear thinning behaviour became more evident with increasing temperature and was well described by the Hershel-Bulkley model. Oral shear viscosity followed an Arrhenius-type model. Oscillatory rheological analysis revealed that storage modulus was always greater than loss modulus (no crossover), within the frequency range studied, indicating the existence of a weak gel and dominant elastic properties over viscous behaviour. Oscillatory rheological data were well described by a power law model. Moreover, both linear and non-linear/power modified Cox-Merz rule were applied to correlate steady shear and oscillatory rheological properties. The effect of sugar and carbohydrate concentration was not clearly seen, possibly due to their interaction with other ingredients used in the formulation. Overall, the data obtained are potentially useful for product development and process design and optimizations.

CONNECTING TEXT TO CHAPTER FOUR

In the preceding chapter, selected commercial meat sauces were investigated to understand the effect of temperature (0, 25, 50, and 75 °C) on their steady state and oscillatory rheological properties. In addition, the applicability of the Cox-Merz rule in correlating both rheological measurements were evaluated. Chapter three of this thesis has been accepted for oral presentation at the CIGR conference 2020[2] as:

Valentine C. Okonkwo, Ogan I. Mba, Ebenezer M. Kwofie, Michael O. Ngadi. "Steady state and oscillatory rheology of meat sauces: applicability of the modified Cox-Merz rule".

It has also been prepared for publication in a peer-reviewed journal as follows:

Valentine C. Okonkwo, Ogan I. Mba, Ebenezer M. Kwofie, Michael O. Ngadi. "Rheological properties of meat sauces as affected by temperature".

There has been significant increase in the consumption of gluten-free foods. This is heightened by increasing cases of immune-mediated diseases, such as celiac disease. Currently, the only treatment for celiac disease is to maintain gluten-free diets, which may have increased the consumption of gluten-free starch-based sauces. Chapter four assesses the flow characteristics and viscoelastic properties of gluten-free white sauces formulated with native rice and potato starches.

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[2] This paper will be presented next year because the conference has been postponed to May 2021 due to the outbreak of COVID-19 pandemic.

CHAPTER FOUR

4. IMPACT OF TEMPERATURE ON RHEOLOGICAL PROPERTIES OF GLUTEN-FREE WHITE SAUCES

Abstract

Gluten-free diets are currently the only available treatment for celiac disease. This study was conducted to assess the effect of temperature on rheological properties of gluten-free white sauces formulated with native rice and potato starches. Rice and potato starch sauces both exhibited thixotropic and pseudoplastic flow behavior. Temperature significantly affected the flow behavior, which was well described by the Ostwald de Waele model ($R^2 \geq 0.92$). The consistency index for both sauces followed an Arrhenius-type relationship ($R^2 \geq 0.957$). Oscillatory rheological data revealed that storage modulus was mostly greater than loss modulus, within the frequency range evaluated, indicating that native white sauces had the behavior of a weak gel; though an exception was observed for potato starch sauce at high temperatures.

4.1 Introduction

Increasing cases of celiac disease among different populations has been an issue of global concern. Celiac disease is an immune-mediated condition characterized by chronic bowel inflammation from ingestion of gluten. In Canada, it is estimated that about 1% of the population are affected by celiac disease, though 87% of cases remain undiagnosed (Jamnik et al., 2017). Globally, over 42,000 infant deaths are related to celiac disease annually (Byass et al., 2011). At present, the only intervention for celiac disease is to maintain a life-long gluten-free diet (La Vieille et al., 2016); which may have contributed to increased consumption of gluten-free starch-based sauces, like white sauce. White sauces are multiphase emulsions that could either be consumed by themselves or used as a base in preparing other food products, such as pasta or casseroles. Basic ingredients used in the formulation of white sauce are milk, salt, oil, spices, and starch or flour (Arocas et al., 2009b). Milk proteins serve as vehicles for delivering essential macronutrients available in white sauce (Arranz & Corredig, 2017). While starch is used to enhance viscosity, adhesion, texture, and gel formation properties. In the formulation of white sauce, the desired functional properties of starch are developed during gelatinization (Sanz et al., 2016). In its polymeric form, it is essentially composed of straight-chain amylose (≈ 30%), connected by α-1,4-glycosidic bond, and branched-chain amylopectin (≈ 70%), which is connected by α-1,6-glycosidic bond (Zhong et al., 2020). Starch is stored in well-ordered granules within the plant cell; in an aqueous solution, however, increased temperature causes granular swelling and disruption of the molecular orderliness within the granules, loss of birefringence, leaching of amylose into the solution, and eventual development of viscosity (Punia, 2020).

Industrial production of white sauces requires complex flow processes, thereby creating a need to study their rheological properties. Common measurements used to assess the rheological properties of white sauces are flow and viscoelastic behavior (Sanz et al., 2016). Flow behavior of sauces is described by the relationship between shear rate and shear stress. Flow behavior measurement of sauces provides information about important material functions, such as viscosity. Sauces, as is the case with many foods, exhibit a response which resembles that of a solid under certain conditions, while under other circumstances, they behave like a liquid. With this complex behavior, called viscoelasticity, viscosity alone is insufficient in describing their flow behavior. Additional material functions, such as storage and loss moduli, which provides relevant information regarding the amount of structure present in the sauce, are needed to reflect such complex behavior. Knowledge of flow behavior and viscoelastic property is crucial in optimizing pumping efficiency, handling, quality control, storage stability, and general process design (Ngadi

& Yu, 2004). Rheological properties of sauces are not only affected by the formulation components (Genovese et al., 2007), they are also influenced by other process conditions, such as temperature. Bortnowska et al. (2016) showed that increased starch concentration led to enhanced viscosity and viscoelastic properties of white sauce; while increased temperature caused a reduction in viscosity. Many studies have been reported that evaluated the rheological properties of white sauce. For instance, Román et al. (2018) reported that increased particle size of pregelatinized wheat flour reduced the shear thinning flow behavior and increased the viscoelastic functions of white sauce in contrast to rice flour-based sauces. Arocas et al. (2009a) observed that increased shearing speed led to decreased values of viscoelastic functions, possibly due to reduced granular swelling and increase in breakdown viscosity. Limited studies, such as reported by Bortnowska et al. (2016), have evaluated the rheological properties of gluten-free white sauces. Specifically, studies that have detailed the effect of temperature on flow behavior and viscoelastic properties of white sauce formulated with rice and potato starches have not been reported. Hence, the objective of the current study is to evaluate the effect of temperature on the flow behavior and viscoelastic property of rice and potato starch-based white sauces.

4.2 Materials and Methods

4.2.1 Materials

Commercially available native rice starch (S7260) and native potato starch (S514) was obtained from Sigma Aldrich Chemical Co LLC (Milwaukee, WI, USA) and Fisher Scientific Co (Fair Lawn, NJ, USA), respectively. The starches were of chemical grade and were used as received. Distilled water was used in all experiments.

4.2.2 White Sauce Preparation

White sauce was prepared using the method described by Arocas et al. (2009b). 9.3 g powdered skimmed milk (Selection, Metro Brands, Québec, Canada), 2.55 g sunflower oil (Selection, Metro

Brands, Québec, Canada), 0.23 g salt (Sifto Table salt, Compass Minerals Canada Corp., Ontario, Canada), 6 g starch, and 82 mL of water were placed in a cooking device (Thermomix TM31, Vorwerk Electrowerke GmbH & Co. KG, Wuppertal, Germany) and heated to 90 °C at a shearing speed of 1100 rpm in 5 min. The prepared sauces were transferred to glass containers, covered with aluminum foil, and allowed to cool to room temperature.

4.2.3 Rheological Measurements

Rheological properties were measured using a controlled stress rheometer (AR2000, TA Instruments, New Castle, Delaware, USA). The instrument was equipped with a 40 mm parallel plate geometry using a gap of 1000 μm. Laboratory grade compressed air (30 psi) was maintained throughout the experiment. Rheological properties were measured at four temperature levels (0, 25, 50, and 75 °C), regulated using a Peltier plate with an accuracy of ±0.1 °C. For each procedure, samples without mechanical history, i.e. fresh samples, were utilized. Before measurements were taken, five minutes was allowed for sample equilibration or structure recovery. Excess samples were trimmed using a spatula, after the head of the rheometer was lowered. Silicon oil (Fisher Scientific, Fair Lawn, New Jersey, USA) was placed around the edges of the samples to prevent drying during testing. Data analysis was performed using TRIOS software v5.1.1 (TA Instruments, New Castle, Delaware, USA).

4.2.3.1 Flow Behavior

Flow properties were measured by recording the shear stress obtained when shear rate was linearly increased from 1 – 100 s^{-1} in 2 min (upward curve), then 100 – 1 s^{-1} (downward curve) at the same time. The data obtained from the upward curve was adjusted to the power law model (Eqn. 4.1), previously used to model the flow behavior of white sauce (T Sanz et al., 2016).

$$\sigma = k\dot{\gamma}^{n} \tag{4.1}$$

Where σ is shear rate (Pa), k is consistency index (Pa.s^n), $\dot{\gamma}$ is shear rate (s^{-1}), and n is flow behaviour index (dimensionless). Additionally, the percentage relative hysteresis (PRH) was calculated (Eqn. 4.2) as a means of comparing the structural integrity of the sauces.

$$PRH = \frac{A_{uc} - A_{dc}}{A_{uc}} \times 100 \quad (4.2)$$

Where A_{uc} and A_{dc} are areas of the upward and downward curves, respectively.

4.2.3.2 Dynamic Properties

4.2.3.2.1 Frequency Sweep

Small amplitude oscillatory shear measurement was first conducted to determine the linear viscoelastic (LVE) region of each sauce. This was achieved by logarithmically ramping stress from 0.1 – 100 Pa at a frequency of 1 Hz. The samples were next subjected to dynamic frequency sweep experiments between 0.1 – 10 Hz, using a controlled variable within the LVE region. Values of viscoelastic parameters, such as storage modulus (G′), loss modulus (G″), and loss tangent (tan δ = G″/G′) were recorded as a function of frequency.

4.2.3.2.2 Temperature Sweep

Dynamic temperature sweep was conducted from 20 – 80 °C at a rate of 1.5 °C/min to simulate the effect of heating on the sauce structure. A strain amplitude of 2% was chosen to guarantee LVE response to temperature. Values of viscoelastic parameters, such as storage modulus (G′), loss modulus (G″), and loss tangent (tan δ = G″/G′) were recorded as a function of temperature.

4.2.2 Statistical Analysis

All experiments were conducted in three replicates. The data obtained were subjected to one-way analysis of variance (ANOVA) using the generalized linear model procedure (PROC GLM) in SAS software v9.4 (SAS Institute Inc., Cary, NC, USA). Treatment means were separated using

Bonferroni's adjustment for multiple comparison, while statistical significance was determined at 5% probability level.

4.3 Results and Discussion

4.3.1 Flow Behavior

The flow behavior profile of rice and potato starch white sauce is shown in Fig. 4.1. At all temperatures studied, the upward curve of both sauces exhibited a non-ideal or shear thinning flow behavior, characterized by decreasing viscosity in response to shear. A reverse phenomenon is observed with the downward curves; viscosity was seen to increase when shear stress was ramped down, signifying thixotropy in the sauces. Thixotropy is a time-dependent flow behavior which explains why food products, like ketchup, have the behavior of solids while at rest, but flows when the container is squeezed. The shear thinning behavior became more apparent with increasing temperature. Thixotropy in the sauces is depicted by the area of hysteresis between both curves; the downward curve lags behind the upward curve when shear rate is ramped down. At all temperatures evaluated, the magnitude of viscosity in potato starch sauce were greater than their rice starch counterparts (Fig. 4.1), signifying that rice starch sauce had a weaker structure and offered less resistance to shear.

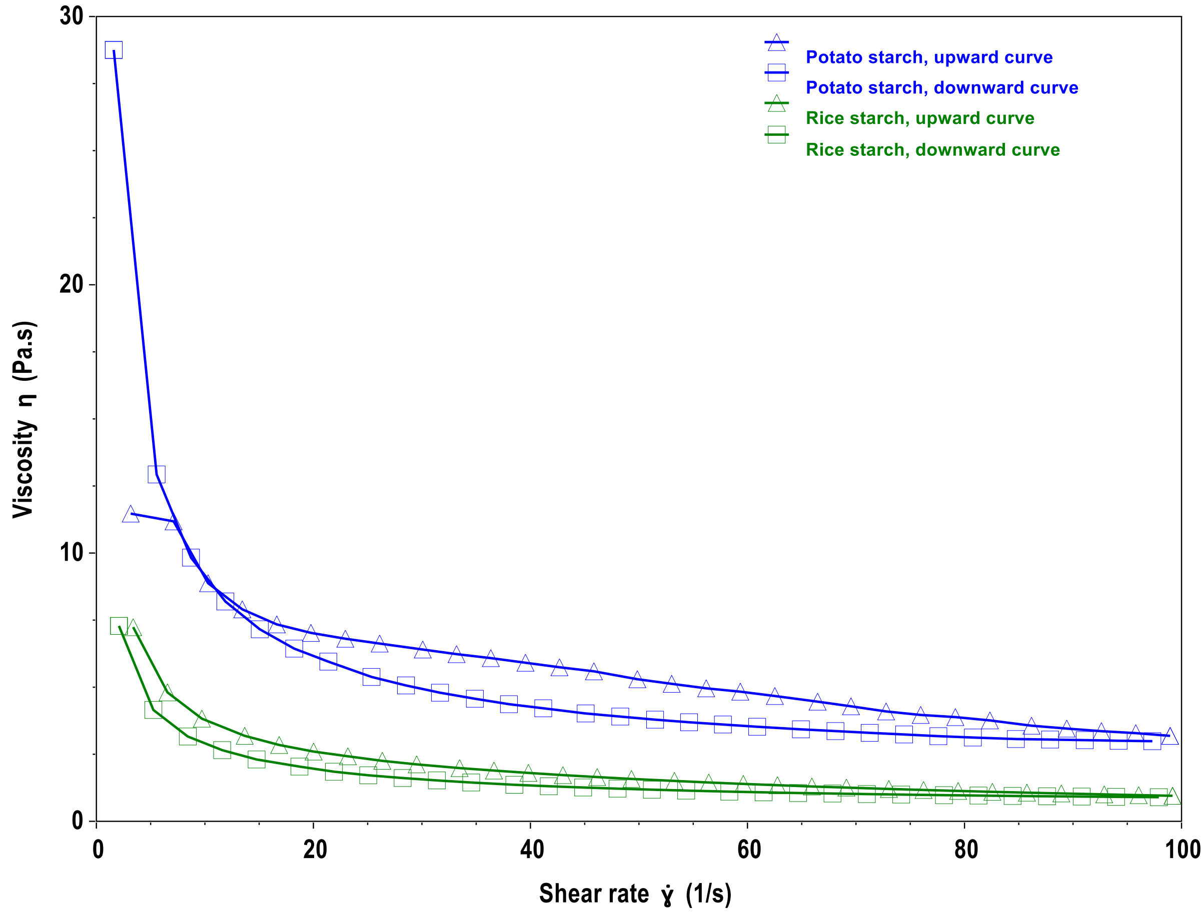

Fig. 4.1: Rheograms of rice and potato starch-based sauces at 25 °C

At rest, starch polymer chains are entangled, forming a stabilized molecular structure. Upon application of shear, the polymer chains begin to disentangle and re-align themselves in the direction of shear. This leads to a reduction in the internal resistance of the sauces and consequently causes the pseudoplastic behavior, also called shear-thinning, observed (Horstmann et al., 2018). Shear thinning flow behavior has also been reported for other white sauces (Bortnowska et al., 2016; T Sanz et al., 2016). At all temperatures, a linear relationship was observed, on double logarithmic plot, between viscosity and shear rate (data not shown), indicating the power law model is appropriate in describing the flow behavior of both potato and rice white sauces (Chen et al., 2019). Hence, data from the upward curve was fitted to the Ostwald de Waele model; estimates of k, n, and PRH are shown in Table 4.1; with values of coefficient of determination (R^2) all greater than 0.9, indicating a strong power law dependency of viscosity on shear rate. The results indicate that temperature had a statistically significant effect ($p < 0.05$) on the model parameters for both potato and rice starch white sauces. The consistency index, k, is a measure of the viscosity of a material. Between 0 – 75 °C, a reduction of 87 and 97% was observed in the magnitudes of k for rice starch sauce and potato starch sauce, respectively. At all temperatures evaluated, the magnitudes of k were always greater in potato starch sauce in comparison to rice starch sauce, confirming the data reported in the Fig. 4.1. Elevated magnitudes of k in potato starch white sauce can also be explained by its high amylose content. During the gelatinization process, potato starch granules increases to several times its original size, ruptures, and amylose leaches into the solution, thereby forming a more stable three-dimensional structure compared to it rice counterpart (Singh et al., 2003). Similarly, increased temperature treatment significantly reduced ($p < 0.05$) the hysteresis loop. Reduced consistency index and hysteresis values, as an influence of temperature, signifies a disintegration in the structural stability of the sauces (Wang et al., 2016). Conversely, increasing temperature treatment significantly increased the flow behavior index, n, in both potato starch and rice starch sauces. Increasing flow behavior index symbolizes the formation of more mutual molecular entanglements in the sauces (Ma & Boye, 2013). The flow behavior index also gives relevant information regarding the extent of non-Newtonian characteristics of a material. At all temperatures studied, the values of n were all less than unity, further confirming pseudoplasticity in both sauces; though a greater shear thinning flow behavior was observed in rice starch white sauces, given their lesser n values.

Table 4.1: Estimates of Ostwald de Waele model parameters and PRH for rice starch and potato starch-based sauces

Starch	Temp (°C)	k	n	R^2	PRH
Rice	0	48.19±2.67a	0.30±0.02a	0.93	14445.45±227.75a
	25	16.32±0.55b	0.39±0.01b	0.99	6995.40±5.93b
	50	7.45±0.80c	0.41±0.01cb	0.99	3397.29±241.22c
	75	6.09±0.37dc	0.46±0.04dc	0.99	2769.04±67.47d
Potato	0	213.91±12.22a	0.35±0.00a	0.92	74242.05±469.75a
	25	32.44±2.42b	0.51±0.02b	0.96	22237.25±317.65b
	50	8.10±0.16c	0.61±0.00c	0.99	7961.10±211.59c
	75	4.56±0.14dc	0.63±0.01dc	0.99	4835.18±19.43d

Results are mean of three replicates ± standard deviation; within each column for each sauce, values followed by different letters are statistically different ($p < 0.05$)

The values of consistency index were modelled with the Arrhenius equation (Eqn. 4.3)

$$k = A\exp\left(\frac{E_a}{R \cdot T_K}\right) \tag{4.3}$$

Where A is the pre-exponential factor, E_a is the activation energy (kJ/mol), R is the universal gas constant (kJ/K.mol), and T_K is the absolute temperature (K).

The estimates of the Arrhenius equation parameters were obtained through least squared regression (Table 4.2). Consistency index was adequately followed an Arrhenius-type equation, since $p < 0.05$ and $R^2 > 0.85$ (Salinas et al., 2019). Activation energy quantifies a material's sensitivity to temperature changes. The estimated values for activation energy can be interpreted to mean the higher the value of activation energy, the greater the impact of temperature on consistency index. From the values of E_a in Table 4.2, rice starch white sauce was more susceptible to temperature changes compared to its potato starch counterpart. This inference is in line with Fig. 4.1.

Table 4.2: Estimates of Arrhenius equation parameters for consistency index

Starch type	A	E_a	R^2	p-value
Rice	0.000	41.412	0.977	0.012
Potato	0.002	22.462	0.957	0.021

4.3.2 Dynamic Properties

4.3.2.1 Amplitude Sweep

Dynamic amplitude sweep was conducted to determine the limit of the LVE region. In the LVE region, the properties of viscoelasticity are unaffected by stress/strain. Fig. 4.2 shows the LVE region of rice starch sauce, and it is representative of both sauces. The point beyond which the viscoelastic functions deviate from a constant plateau is signifies

4.3.2.2 Frequency Sweep

Small amplitude oscillatory measurements results revealed a boundary, called LVE region, where the properties of viscoelasticity were unaffected by the applied stress (Fig. 4.2). The LVE reveals critical information regarding the structural stability of the sauces in response to shear. Fig. 4.2 is representative of both sauces; however, increased temperature treatment appeared to reduce the extent of linear viscoelasticity. The point beyond which the viscoelastic functions deviate from a constant plateau signifies departure from the LVE region. The results obtained show that a value of 2 Pa was well within the LVE region of both sauces at all temperatures evaluated; hence this value was used as a controlled variable for subsequent frequency and temperature sweep experiments.

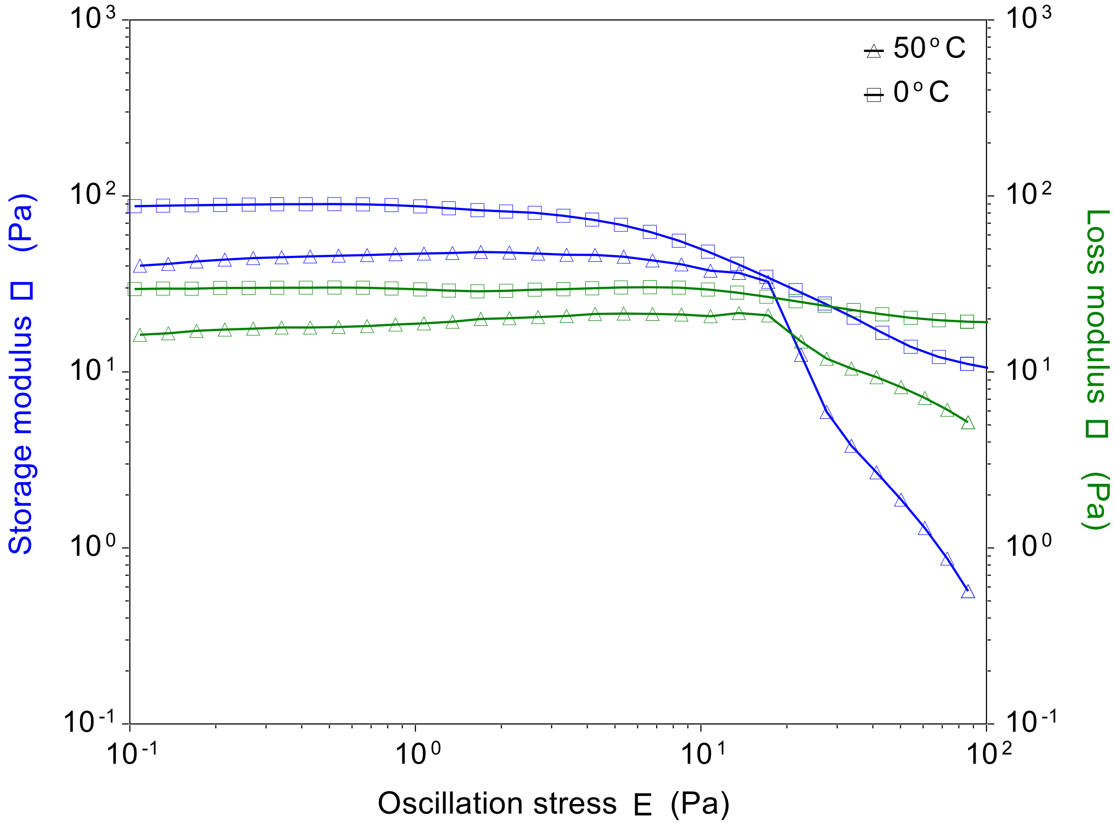

Fig. 4.2: Stress sweep profile for rice starch sauce

Frequency sweep was conducted at the various temperatures to understand the structural changes that occurred on the sauces. The mechanical spectra for both potato and rice starch-based sauces (Fig. 4.3) showed the existence of a weak gel. This means that the viscoelastic moduli are strongly dependent on frequency. With increased frequency, more deformation energy can be stored, thereby causing an increase in G′ values. Conversely, with decreasing frequency, more deformation energy is lost by friction between the molecules due to increased relative motion between polymer chain, hence making a material more flexible and mobile (Ditudompo et al., 2013). Overall, the results show that G′ and G″ increased with frequency, with the values of G′ always greater than G″ throughout the frequency range studied, indicating the existence of superior elastic properties over liquid/viscous behavior, widely reported for other white sauces (Arocas et al., 2011; Bortnowska et al., 2016). Two exceptions were seen in potato starch sauce at 50 and 75 °C, where a crossover was observed between both moduli and G″ became greater than G′. Temperature increase appeared to increase the impact of frequency and reduce the distance between both moduli in both potato and rice starch-based sauces, thereby indicating a less stable structure and the proximity of a crossover point, beyond which liquid properties become dominant (Román et al., 2018). Table 4.3 shows the values of G′ and G″ at 1 Hz. Increasing temperature was observed to significantly reduce ($p < 0.05$) the magnitudes of the viscoelastic moduli of both sauces, further confirming their weak molecular structure (Sherahi et al., 2018). The loss tangent (tan δ), which is a ratio of energy dissipated to energy stored in a cyclic deformation, is also an indication of structural stability. For ideal solids, tan δ = 0, since there is no liquid/viscous portion, G′ completely dominates; whereas tan δ = ∞ for an ideal liquid. A perfect balance between elastic and viscous behaviour has a tan δ value of unity (Mezger, 2014). Temperature treatment significantly increased ($p < 0.05$) the values obtained for tan δ. Values greater than unity, observed for potato starch sauce at high temperature (Table 4.3) could be explained by the existence of dominant liquid properties (G″ > G′) observed. This is further elucidated in Fig. 4.4, where tan δ values greater than unity is reported for potato starch sauce at 50 and 70 °C. In contrast, rice starch sauce had tan δ values less then unity (G′ > G″; data not shown) at all temperatures and within the frequency range evaluated, depicting dominant solid-like properties over viscous behavior.

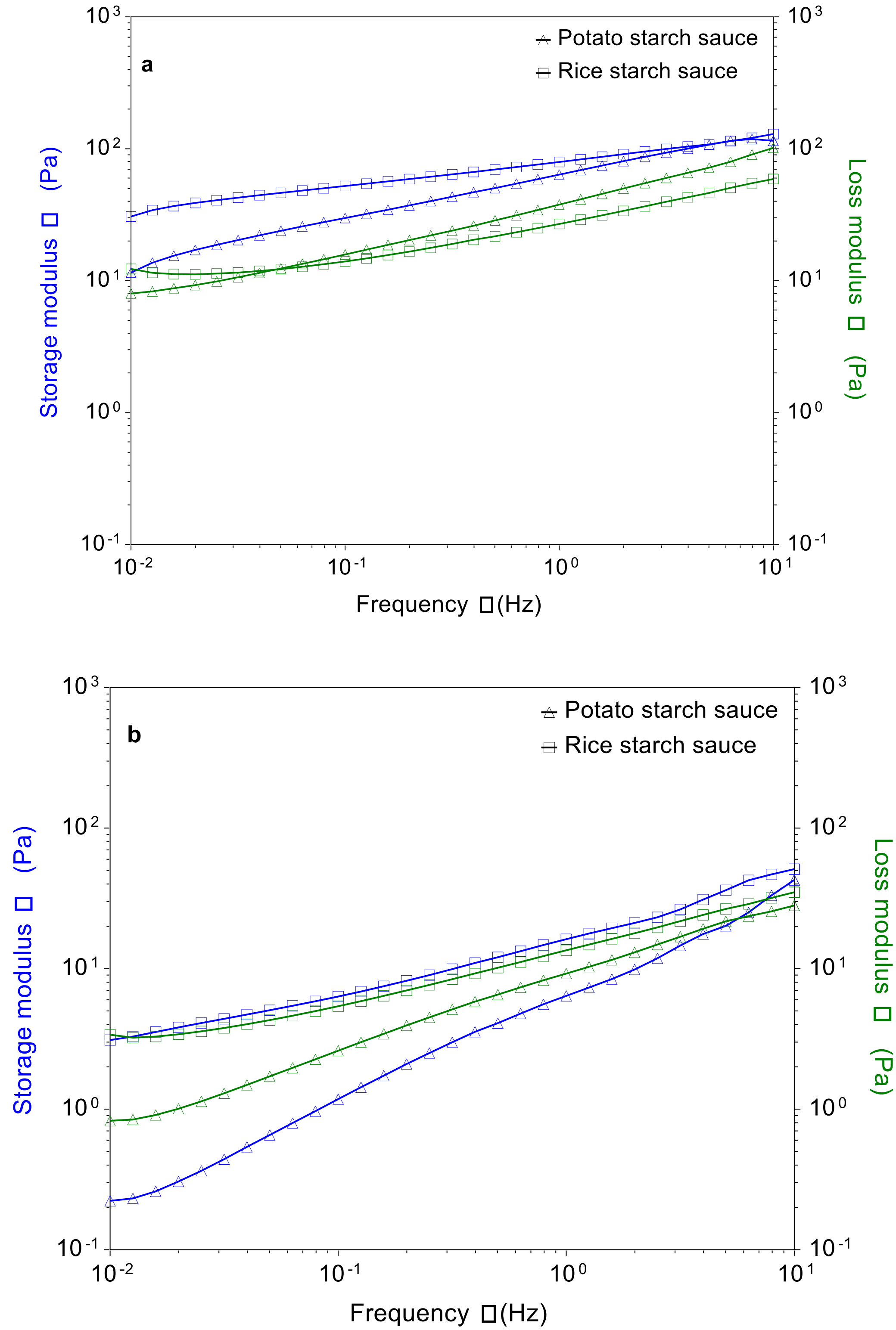

Fig. 4.3: Frequency sweep profile for potato and rice starch-based sauces (a) 0 °C (b) 50 °C

Table 4.3: Values of viscoelastic parameters for rice and potato starch sauces at 1 Hz

Temp (°C)	Rice starch sauce			Potato starch sauce		
	G′ (Pa)	G″ (Pa)	tan δ	G′ (Pa)	G″ (Pa)	tan δ
0	82.39±2.96a	27.36±0.44a	0.33±0.01b	65.29±1.57a	38.15±0.04a	0.59±0.01b
25	72.015±4.71b	24.51±0.78b	0.34±0.01b	27.83±3.36b	24.17±3.23b	0.86±0.01c
50	19.96±3.75c	15.05±1.54c	0.77±0.07c	7.35±0.95c	9.82±0.60c	1.35±0.09d
75	10.84±0.06dc	10.15±0.13d	0.94±0.01a	2.56±0.50dc	2.59±0.34d	1.03±0.07ac

Results are mean of three replicates ± standard deviation; within each column, values followed by different letters are statistically different ($p < 0.05$)

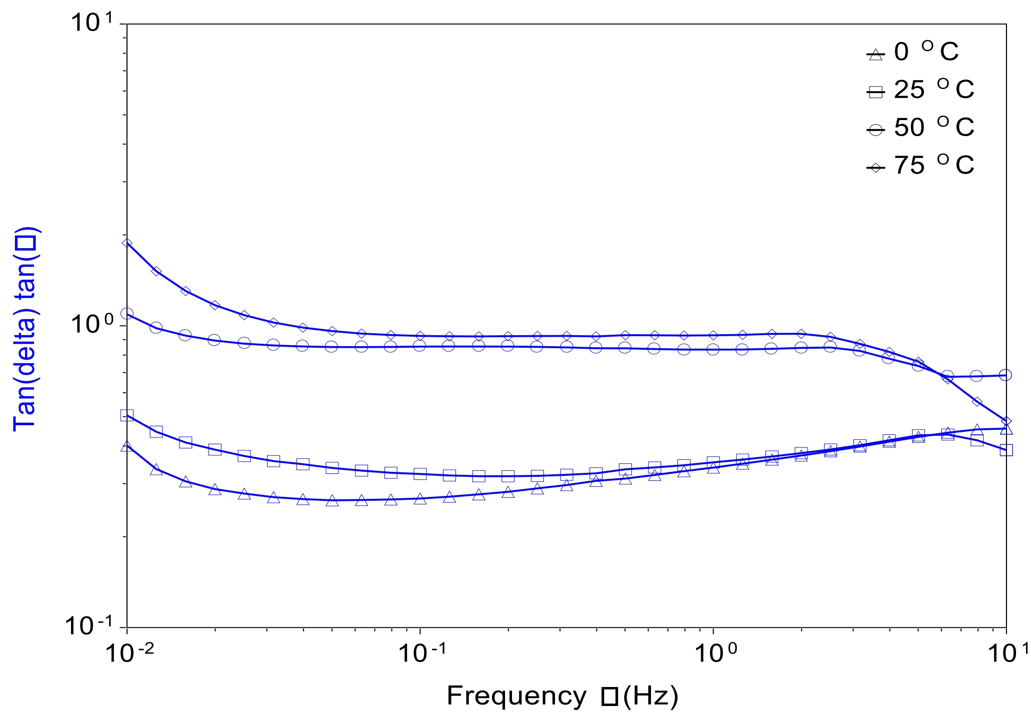

Fig. 4.4: Variation of loss tangent for potato starch sauce as an influence of temperature and frequency

4.3.2.3 Temperature Sweep

Temperature sweep was conducted to simulate the effect of reheating on the sauce structure. The evolution of G′ and G″ as influenced by temperature is illustrated in Fig. 4.5. Though there was a slight decline and subsequent inflexion in the magnitude of viscoelastic moduli, there was no phase transition observed for rice starch sauce within the temperature range evaluated; dominant solid properties were always maintained (G′ > G″). For potato starch sauce, the decline in viscoelastic moduli appeared to be more pronounced, as seen by the steep slope in Fig. 4.5. At 56 °C, potato starch sauce seemed to transition to dominant liquid properties and subsequently back to dominant solid, confirming results reported in frequency sweep experiments. This behavior is commonly seen in native starch sauces (Sanz et al., 2016).

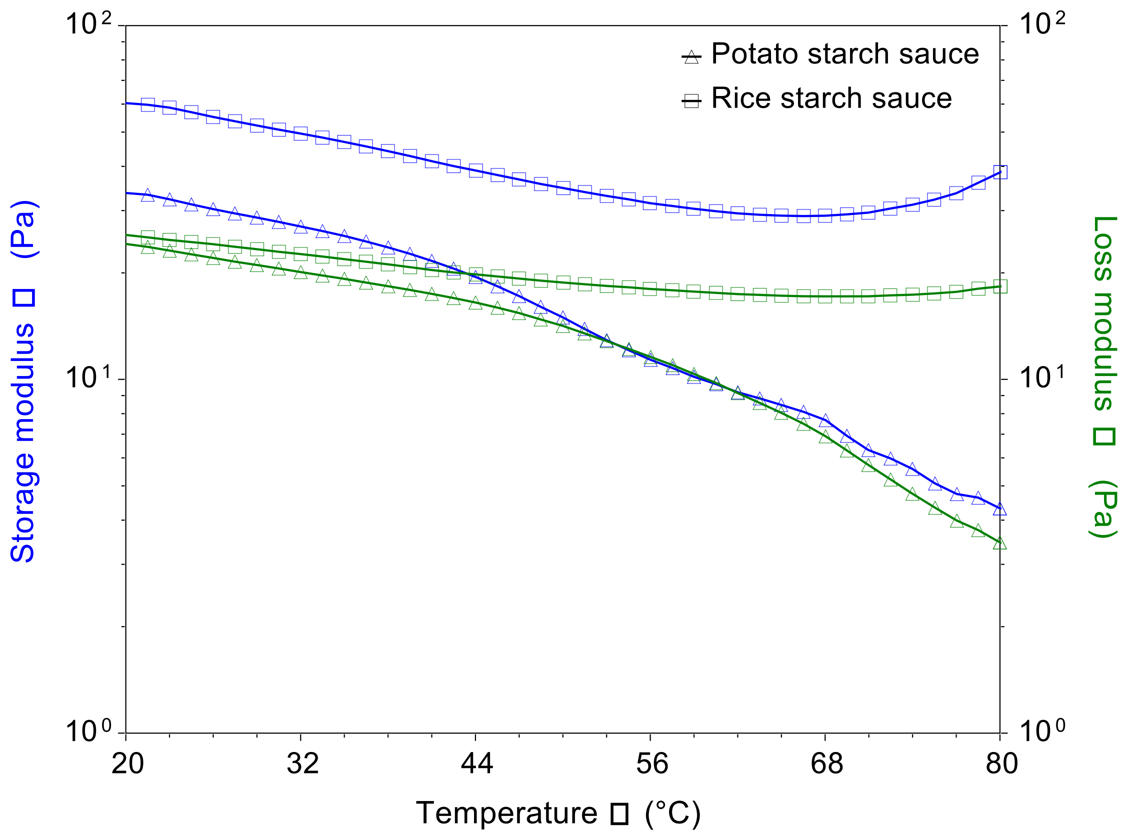

Fig. 4.5: Variation of G′ and G″ as affected by temperature

4.4 Conclusion

Gluten-free diets are presently the only available treatment for celiac disease. The current study evaluated the effect of temperature on flow behavior and viscoelastic properties of native starch white sauces. Both rice and potato starch-based sauces exhibited thixotropic and shear thinning flow behavior. The shear thinning flow behavior became more apparent with increasing temperature and was well modelled by the Ostwald de Waele model. Consistency index of both sauces followed an Arrhenius-type model. Oscillatory rheological data revealed that storage modulus was mostly greater than loss modulus, within the frequency range evaluated, indicating that native white sauces had the behavior of a weak gel; though an exception was observed for potato starch at high temperatures. Temperature treatment was observed to reduce the magnitude of the viscoelastic moduli. These results are potentially useful for developing gluten-free starch-based sauces.

CONNECTING TEXT TO CHAPTER FIVE

In the preceding chapter, white sauces formulated with native rice and potato starches were investigated to understand the effect of temperature (0, 25, 50, and 75 °C) on flow behavior and oscillatory rheological properties. Starch generally plays a huge role in determining customer acceptance. This is because it imparts desirable attributes, such as improved rheological and textural properties. However, the applicability of starch in its native form is limited due to certain properties, such as retrogradation and poor thermal and shear properties. The utilization of chemically modified starches in food formulations comes with its disadvantages. Chapter five explores modification of starch using ultrasonic treatment, which is a physical means of modification, and its eventual effect on the rheological and textural properties of Béchamel sauce. It has been accepted for publication in *Ultrasonics sonochemistry* as:

Valentine C. Okonkwo, Ebenezer M. Kwofie, Ogan I. Mba, Michael O. Ngadi. "Impact of thermo-sonication on quality indices of starch-based sauces".

The format of the manuscript has been altered to be consistent with this thesis. All the literatures cited in this chapter are listed in the references section of this thesis.

CHAPTER FIVE

4. ASSESSING THE IMPACT OF HIGH-INTENSITY ULTRASONICATION ON QUALITY INDICES OF STARCH-BASED SAUCES

Abstract

In this study, ultrasonication, a physical, relatively cheap, and environmentally benign technology, was investigated to characterize its effect on functional properties of rice starch and rice starch-based sauces. High-intensity ultrasound treatment improved the granular swelling power, fat and water absorption capacities, and thermal properties of rice starch, signifying its suitability in formulation of starch-based sauces. Rheological characterization of the formulated sauces revealed a shear thinning flow behavior, well described by the Ostwald de Waele model, while viscoelastic properties showed the existence of a weak gel. Results indicated that ultrasonication significantly enhanced the pseudoplastic behavior of starch-based sauces. Additionally, textural analysis showed that textural attributes (stickiness, stringiness, and work of adhesion) were also improved with ultrasonication. Moreover, enhanced freeze/thaw stability was also achieved with ultrasound treated starch-based sauces. Overall, the results from this study shows that ultrasound treated starches can be used in the formulation of sauces and potentially other food products, which meets the requirements for clean label and minimally processed foods.

5.1 Introduction

Nowadays, starch is increasingly finding numerous applications in the food processing, cosmetic, and pharmaceutical industries. This is because it is ubiquitous, affordable, biodegradable, biocompatible, non-toxic, and possesses peculiar physicochemical properties (Chen et al., 2020). Starch is contained in the amyloplast as discrete granules with varying morphology depending on plant type. In its polymeric form, it is essentially composed of straight-chain amylose (≈ 30%), connected by α-1,4-glycosidic bond, and branched-chain amylopectin (≈ 70%), which is connected by α-1,6-glycosidic bond (Zhong et al., 2020).

Native starch is extracted from naturally existing roots and cereals, such as cassava, wheat, and rice. However, the industrial application of native starch in food formulations is limited mainly due to syneresis, retrogradation, poor thermal and shear stability (Zhu, 2019). To overcome these impediments, several starch modification technologies have been developed. These methods are designed to improve the functional properties of starch desired during processing and include chemical, enzymatic, genetic, and physical manipulations. Detailed reviews on these modification techniques have been discussed by several authors (Fan & Picchioni, 2020; Zia-ud-Din et al., 2017). Chemical modification techniques, such as acetylation and cross-linking, subsumes new functional groups without affecting the morphological properties of the starch granules (Sneh Punia, 2020). Though desired functional properties are achieved, chemical modification utilizes chemical reagents that are non-eco-friendly. Genetic and enzymatic modification are usually associated with high cost (Hu et al., 2015) and the need to prove their safety, especially when it is intended to be used as food ingredient (Park et al., 2018). Moreover, chemical modification techniques conflict with the increasing consumer demand for clean label and minimally processed foods. Clean label foods are foods that are organic, natural, and free from artificial additives. With this definition, food products formulated with starches modified through chemical, enzymatic, and genetic means do not meet the description of clean label foods, and are usually identified by an E number on the label of the product (Alting & Van De Velde, 2012). Against this background, the food industry generally favors the use of physically modified techniques, such as high-pressure processing, and ultrasonication. Over the past decade, ultrasonication has gained increased usage owing to its shorter processing time, lower operation, and maintenance cost, increased product yield, and its ability to inactivate pathogens (Zhu, 2015).

Ultrasonication is designed as a non-thermal environmentally friendly modification technique that disrupts the arrangement of the polymers within the starch granule (BeMiller & Huber, 2015). Ultrasound refers to sound wave possessing a frequency beyond the threshold of human hearing (16 – 20 kHz). High-intensity ultrasound is usually characterized by a frequency of 20 – 500 kHz and intensity >1 W/cm^2 (Guimarães et al., 2019). The severity of ultrasonication effect depends on origin and moisture content of starch sample, intensity, frequency, temperature, and duration of application (Punia, 2020). Amini et al. (2015) reported that temperature and time of exposure to ultrasonication strongly influenced functional and rheological properties of corn starch, while concentration and amplitude of ultrasonication had little effect. Indeed, ultrasound waves create cavities or bubbles in the medium through which it is passed (Ampofo & Ngadi, 2020). When these cavities implode, they lead to the formation of fissures or holes on the granular surface; thereby weakening its structural integrity and eliciting gelatinization and enhanced functional properties (Zhu & Li, 2019).

Many studies have scrutinized the effect of ultrasound treatment on the functional and physicochemical properties of starch paste (Asrofi et al., 2018; Sujka & Jamroz, 2013; Zuo et al., 2009). Ultrasonication was reported to reduce retrogradation and improve intrinsic viscosity and textural properties of potato starch paste (Nie et al., 2019); though Fourier transform infrared spectroscopy did not demonstrate any noticeable molecular degradation. Fan Zhu and Li (2019) showed that ultrasonication increased water solubility and *in vitro* starch digestibility of quinoa flour, while decreasing gelatinization temperature, *in vitro* antioxidant activity, and total phenolic content. Low-intensity ultrasonication has been shown to enhance the aroma profile of soy sauce (Gao et al., 2020). To the best of our knowledge, there have been few studies that examined the effect of ultrasonication on starch-based derivatives, like glucomannan salep (Karaman et al., 2012). Studies that have evaluated the effect of other physical methods of starch modification, such as thermal inhibition (Sanz et al., 2016) and extrusion (Román et al., 2018) on quality properties of starch-based sauces, did not consider the area of textural analysis, despite its notable influence on food intake and satiety (Stribiţcaia et al., 2020). Specifically, there is paucity of reports on ultrasonic treatment effect on quality parameters of starch-based foods, like Béchamel sauce (white sauce) despite increased consumption of sauces in Canada and elsewhere around the world (Global Trade Tracker, 2019). Béchamel sauce, in addition to velouté, espagnole, hollandaise, and tomato sauce is one of the five *mother sauces* in the French sauce system (Rognså et al., 2014). Moreover, food quality parameters, such as rheology and texture, have been proven to significantly influence customer acceptance (Varela et al., 2014). Hence, the focus of the current study is to extensively investigate the effect of high-intensity ultrasound on the functional properties of rice starch, as well as the rheological and textural characteristics, and the freeze/thaw stability of its derivative.

5. 2 Materials and Method

5.2.1 Materials

Commercially available native rice starch (S7260) was obtained from Sigma Aldrich Chemical Co LLC (Milwaukee, WI, USA). The starch was of chemical grade and was used as received. Distilled water was used in all experiments.

5.2.2 Ultrasound Treatment

The method previously described by Amini et al. (2015) was adopted with slight modification. Briefly, native rice starch (40 g) in water (100 mL) was treated for 20 min at different temperature levels (15, 30, 45, 60, and 75 °C, coded as S1, S2, S3, S4, and S5, respectively) by a high intensity ultrasonic processor (Sonics Vibracell VCX500, Sonics & Materials Inc., Newton CT, USA) equipped with a 3 mm tapered probe. The processor was operated at a frequency of 20 kHz, power of 500 W, and amplitude of 40%. The probe was immersed into the sample at an approximate depth of 2 cm. The equipment was operated under an 80% pulse mode to ensure inhibition of heat build-up and enhance particle aggregation under the probe. During sonication, appropriate temperature levels were maintained using an unstirred water bath (JB Nova, Grant Instrument Ltd, Royston, United Kingdom). The sonicated samples were transferred into Ziploc bags and lyophilized for 70 hours (Thermo Savant Modulyo Benchtop Freeze Dryer, Thermo Electron Corporation, Beverly, MA, USA). Holes were made on the top of the Ziploc bags to enhance moisture loss during drying. The control/non-sonicated sample (S0) was prepared by dispersing the appropriate weight of native starch in water. The dry samples were ground to powder and placed in a desiccator before further use. Temperature was chosen as operating variable because it is one of the most influential factors affecting the severity of ultrasound treatment (Amini et al., 2015).

5.2.3 Starch Characterization

5.2.3.1 Granular Swelling Power

Granular swelling power was determined using a method described by Hang Liu et al. (2016). 50 mg of the native and modified starches were transferred into dry 15 mL centrifuge tubes, weighed (M_1), and mixed with 5 mL of water. The tubes were heated in a water bath at different temperature levels (55, 65, 75, 85, and 95 °C). The samples were homogenized at intervals of 5 min using a vortex mixer at 1000 rpm (Corning LSE, Corning Inc., New York, USA). After heating, the samples were cooled to room temperature and centrifuged at 657 ×g (Sorvall Legend XTR, Thermo Electron LED GmbH) for 20 min. The supernatant was decanted and the tube with its residue was weighed (M_2). The granular swelling power was computed using Eqn. 5.1.

$$Granular\ swelling\ power = \frac{M_2 - M_1}{weight\ of\ starch} \tag{5.1}$$

5.2.3.2 Fat and Water Absorption Capacities

Fat absorption capacity (FAC) and water absorption capacity (WAC) were determined separately. Starch (0.5 g) was transferred into dry centrifuge tubes with predetermined weight (W_1). For determination of WAC, 5 mL of water was added using a bottle top dispenser (Thermo Fisher Scientific, Ontario, Canada), while for fat absorption capacity, 5 mL of sunflower oil was added to the centrifuge tubes using a syringe. The resultant sample was homogenized for 1 min at 1000 rpm using a vortex mixer. The mixture was allowed to rest for 5 min, homogenized again and centrifuged at 1500 rpm for 15 min at an operating temperature of 23 °C. The supernatant was carefully decanted and the tube with its residue was weighed (W_2). FAC or WAC was determined using Eqn. 5.2.

$$FAC\ (or\ WAC) = \frac{W_2 - W_1}{weight\ of\ starch} \times 100\% \tag{5.2}$$

5.2.3.3 Thermal Analysis

Starch gelatinization behavior was evaluated using a differential scanning calorimeter (DSC250, TA Instruments, New Castle, Delaware, USA). The instrument was calibrated using an indium standard before sample measurements. Starch samples (14±2 mg) of 1:1.3 (starch-water ratio) were transferred into aluminum pans and hermetically sealed. The samples were then heated from 25 – 80 °C at a heating rate of 2 °C/min. An empty aluminum pan was used as reference and a flow rate of 50 mL/min for dry nitrogen was maintained throughout the experiment. Onset (T_0), peak (T_p), conclusion (T_c) temperatures and the enthalpy of gelatinization (ΔH) were evaluated.

5.2.4 White Sauce Preparation

White sauce was prepared using the method described by A Arocas et al. (2009b). 9.3 g powdered skimmed milk (Selection, Metro Brands, Québec, Canada), 2.55 g sunflower oil (Selection, Metro Brands, Québec, Canada), 0.23 g salt (Sifto Table salt, Compass Minerals Canada Corp., Ontario, Canada), 6 g starch, and 82 mL of water were placed in a cooking device (Thermomix TM31, Vorwerk Electrowerke GmbH & Co. KG, Wuppertal, Germany) and heated to 90 °C at a shearing speed of 1100 rpm in 5 min. The prepared sauces were transferred to glass containers, covered with aluminum foil, and allowed to cool to room temperature.

5.2.5 Rheological Measurements

Rheological properties were measured using a controlled stress rheometer (AR2000, TA Instruments, New Castle, Delaware, USA). The instrument was equipped with a 40 mm parallel plate geometry using a gap of 1000 μm. Laboratory grade compressed air (30 psi) was maintained throughout the experiment. Rheological properties were measured at 23 °C, regulated using a Peltier plate with an accuracy of ±0.1 °C. Measurements for freshly prepared sauces were conducted four hours after preparation, while the other portion was frozen at –18 °C for three days to study the effect of a freeze/thaw cycle. At the end of the third day, the samples were allowed to thaw in a water bath (at room temperature) before rheological measurements were taken. For each procedure, samples without mechanical history, i.e. fresh samples, were utilized. Before measurements were taken, five minutes was allowed for sample equilibration or structure recovery. Excess samples were trimmed using a spatula, after the head of the rheometer was lowered. Silicon oil (Fisher Scientific, Fair Lawn, New Jersey, USA) was placed around the edges of the samples to prevent drying during testing. Data analysis was performed using TRIOS software v5.1.1 (TA Instruments, New Castle, Delaware, USA).

5.2.5.1 Flow Behavior

Flow properties were measured by recording the shear stress obtained when shear rate was linearly increased from 1 – 200 s^{-1} in 2 min (upward curve), then 200 – 1 s^{-1} (downward curve) at the same time. The data obtained from the upward curve was adjusted to the power law model (Eqn. 5.3), previously used to model the flow behavior of white sauce (T Sanz et al., 2016).

$$\sigma = k\dot{\gamma}^{n} \tag{5.3}$$

Where σ is shear rate (Pa), k is consistency index (Pa.s^{n}), $\dot{\gamma}$ is shear rate (s^{-1}), and n is flow behaviour index (dimensionless). Additionally, the percentage relative hysteresis (PRH) was calculated (Eqn. 5.4) as a means of comparing the structural integrity of the sauces.

$$PRH = \frac{A_{uc} - A_{dc}}{A_{uc}} \times 100 \tag{5.4}$$

Where A_{uc} and A_{dc} are areas of the upward and downward curves, respectively.

5.2.5.2 Viscoelastic Properties

Oscillatory strain sweep was first conducted to determine the linear viscoelastic (LVE) region of each sauce. This was achieved by ramping strain from 0.5 – 100% at a frequency of 1 Hz. The samples were next subjected to dynamic frequency sweep experiments between 0.1 – 10 Hz, using a controlled variable of 2% strain within the LVE region. Values of viscoelastic parameters, such as storage modulus (G′), loss modulus (G″), and loss tangent (tan δ = G″/G′) were recorded as a function of frequency.

5.2.6 Textural Analysis

Sauce texture analysis was performed using a texture analyzer (TA.HD*plus*, Stable Micro Systems, Surrey, United Kingdom) fitted with a 25 mm Perspex cylindrical probe (P/25P). The compression was carried out in a Perspex extrusion rig using a 50 kg load cell. The pre-test speed, test speed, and post-test speed were 4.0, 2.0, and 10.0 mm.s^{-1}, respectively. Once a trigger force of 5 g has been detected on the surface of the sauce, the probe proceeds to compress it by travelling 5 mm. The maximum force required to separate the probe from the sample was termed stickiness. During the retraction of the probe, the sample was noticed to form a string. The distance (which quantifies the measure by which the sample stretches) the sample remain connected to the probe upon withdrawal was termed stringiness. The total amount of force (area under the force-deformation curve) required to withdraw the probe was termed work of adhesion. Textural analysis of the fresh sauces was conducted four hours after preparation. The same test was repeated after the samples were frozen for three days and allowed to thaw in a water bath at room temperature.

5.2.7 Freeze/Thaw Stability of White Sauce

The freeze/thaw stability of white sauce was determined as described by Román et al. (2018). 15 g (W_s) of thawed white sauce after three days of frozen storage was weighed into 50 mL falcon tubes and centrifuged at 3800 ×g for 15 min. The supernatant was decanted and weighed (W_c). Syneresis was evaluated using eqn. 4.5. For freshly prepared sauces, syneresis was evaluated on the same day it was formulated.

$$Syneresis\ (\%) = \frac{W_c}{W_s} \times 100 \tag{4.5}$$

5.2.8 Statistical Analysis

All experiments were conducted in three replicates. The data obtained were subjected to analysis of variance (ANOVA) using the generalized linear model procedure (PROC GLM) in SAS software v9.4 (SAS Institute Inc., Cary, NC, USA). Treatment means were separated using Tukey's adjustment for multiple comparison, while statistical significance was determined at 5% probability level.

5.3. Results and Discussion

5.3.1 Granular Swelling Power

The swelling power of both native and ultrasonicated starch are presented in Fig. 5.1. Here, ultrasonication is seen to have a significant effect ($p < 0.05$) on swelling power of rice starch. Native starch initially had a higher swelling power compared to S1 and S2 samples, but at higher ultrasonication temperature (≥ 45 °C), they swelling power significantly increased. Similar results were reported for sonicated corn starch (Amini et al., 2015). Studies have shown that high-intensity ultrasonication causes severe physical damage on the granular surface, by creating fissures or cracks, thereby increasing the ability of the granules to retain more water (Falsafi et al., 2019). The increase in swelling power as consequence of ultrasonication may be explained by disruption of the crystalline molecular structure of starch and bonding of water molecules to free covalently bonded hydroxyl groups of amylose and amylopectin (Babu et al., 2019) and morphological changes as a result of increased cavitation leading to permeation of water into the granules (Majzoobi et al., 2015). Additionally, temperature remarkably increased the swelling power of both native and modified starches. This is also in agreement with studies reported for potato, wheat, corn, and rice starches (Sujka & Jamroz, 2013).

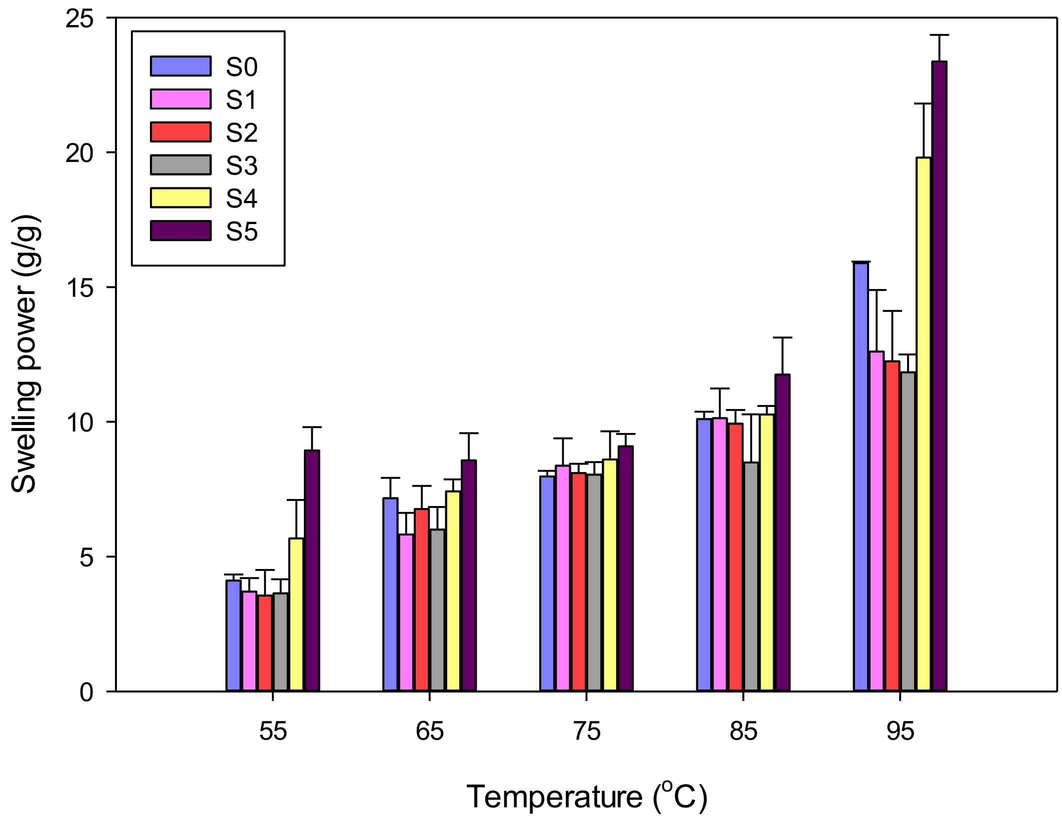

Fig. 5.1: Swelling power of rice starch as affected by ultrasonication

5.3.2 Fat and Water Absorption Capacities

Fat and water absorption capacities of native and modified corn starches are shown in Table 5.1. Water absorption capacity quantifies the ability of starch to hold water owing to the hydrophilic sites of its polymer chain. It is also important because it is an indication of the starch viscosity. Starch modification through ultrasonic treatment is known to create pores or visible fissures on the surface of the granules (Sujka, 2017). High-intensity ultrasonication had a statistically significant effect ($p < 0.05$) on water absorption capacity. This effect became more apparent with increasing sonication temperature; the least effect observed in native starch. The significant increase in water absorption capacity can be associated with movement of water through the pores and subsequent increase in granular surface area. Similar effect was reported in lentil starch (Majeed et al., 2017), corn, wheat, and rice starches (Sujka & Jamroz, 2013). Ultrasonication may also induce a reduction in the amylopectin fraction of starch, which has less affinity for water (Ahmad et al., 2020).

Table 5.1: Fat and water absorption capacity of ultrasonicated starch

Sample code	S0	S1	S2	S3	S4	S5
FAC	2.43±0.74a	3.24±0.31a	3.64±0.72a	4.62±0.43b	6.73±0.38c	8.36±0.02d
WAC	2.01±0.13a	2.05±0.08a	2.14±0.02a	2.39±0.02a	6.74±1.53b	7.51±0.65c

Results are mean of three replicates ± standard deviation; across each row, values followed by different letters are statistically different ($p < 0.05$)

Likewise, ultrasonication significantly affected ($p < 0.05$) the fat absorption capacity of native and modified starches. Fat absorption is an entrapment of oil within the starch granules, following porosity and cavitation created by sonication. These morphological changes may have increased the immensity of granular surface area available for fat absorption. Additionally, loose helical and hydrophobic inner structure of amylose, forming a crystalline structure may have influenced the increased fat absorption capacity (Chen et al., 2019). The results obtained agree with the study reported for modified oat starch (Falsafi et al., 2019) and modified wheat starch (Jamalabadi et al., 2019). On the contrary, fat absorption capacity of ultrasound-treated starch nanoparticles decreased significantly after size reduction (Ahmad et al., 2020). The authors attributed the decreasing fat content to reduced particle size and change in the molecular structure affecting the hydrophobicity of the starch nanoparticles.

5.3.3 Thermal Properties

The results of thermal properties of rice starch as affected by ultrasonication is reported in Table 5.2. Native starch dispersion witnessed a thermal transition from 59.04 – 70.46 °C, very similar to studies reported in the literature (Falsafi et al., 2019). Ultrasonication temperature was seen to significantly ($p < 0.05$) reduce enthalpy, onset, and conclusion gelatinization temperatures. Within the gelatinization range (60 – 70 °C), results obtained for starch dispersion treated with the most severe ultrasonication conditions (S4 and S5), did not show any thermal transition or endothermic peak (Fig. 5.2), indicating complete gelatinization was achieved (Román et al., 2018). Monroy et al. (2018) suggested that the reduction in enthalpy and gelatinization temperature may be attributed to disruption of the crystalline region of the granules. Moreover, the destruction of the double helical structure following ultrasonication may also have contributed to reduced gelatinization temperatures (Li et al., 2018). Though the data obtained shows a downward trend in ΔH values with increasing ultrasound treatment in accordance with the literature, it is however noted that values reported here for ΔH is smaller in magnitude, in comparison to values ranging between 6.3 – 9 J/g reported for ultrasound-treated corn starch (Amini et al., 2015) and oat starch (Falsafi et al., 2019). There is strong evidence in literature to support the assertion that increased heating rate (Malumba et al., 2018) and moisture content (Chang et al., 2014) leads to elevated enthalpy values. Though many studies reported a heating rate of 10 °C/min, Saeed et al. (2016) opined that a lower heating rate, like 2 °C/min used in the current study, can help reduce thermal gradient effect and distinguish transition peaks.

Table 5.2: Thermal properties of rice starch as influenced by ultrasonication

Sample code	T_0 (°C)	T_p (°C)	T_c (°C)	ΔH (J/g)
S0	59.04±0.81a	65.63±0.17a	70.46±0.01a	3.85±0.05a
S1	57.99±0.02a	64.41±0.31b	69.38±0.15a	1.91±0.01b
S2	57.56±1.55a	64.49±0.40bc	64.36±0.26b	1.61±0.01c
S3	53.70±1.60b	65.94±0.09a	71.54±0.84ac	1.04±0.05d
S4	nd	nd	nd	nd
S5	nd	nd	nd	nd

Results are mean of three replicates ± standard deviation; within each column, values followed by different letters are statistically different ($p < 0.05$); nd: not determined

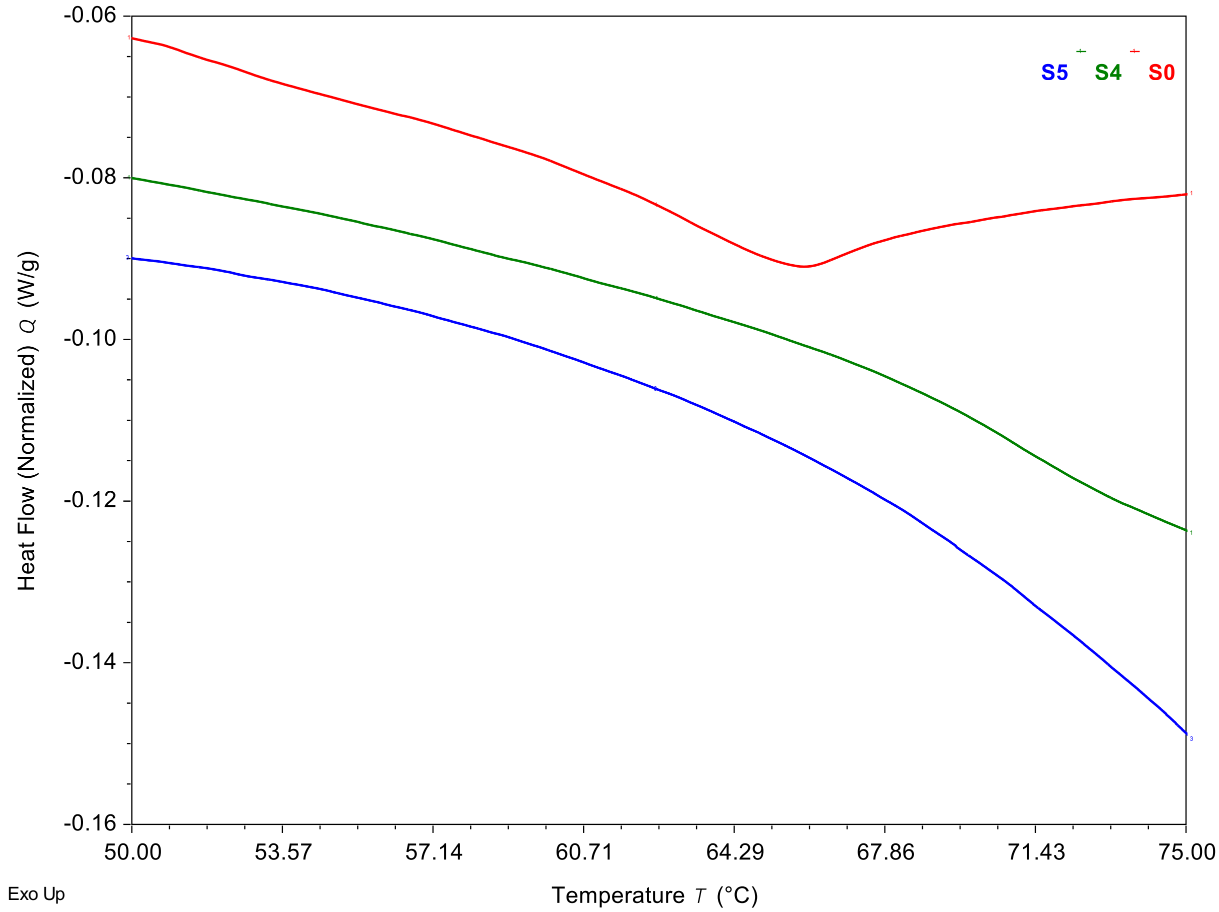

Fig. 5.2: Thermogram of native and ultrasonicated starch

5.3.4 Flow Properties

The upward curve demonstrated a non-ideal or pseudoplastic behavior in all the sauces, characterized by decreasing viscosity in response to rising shear rate or shear stress (Fig. 5.3). A reverse phenomenon is observed with the downward curves; viscosity was seen to increase when shear stress was ramped down, signifying thixotropy in the sauces. It is important to note that thixotropy is a time-dependent pseudoplastic behavior of fluids, because it explains why food products, like ketchup, have the behavior of a solid when at rest, but behaves like a liquid (flows) when the container is squeezed. In time-independent pseudoplastic behavior, the fluid recovers along the same path when the shear is removed. In time-dependent fluids, however, when shear rate is ramped down, the downward curve lags behind the upward curve, leaving an area between both curves called the hysteresis loop.

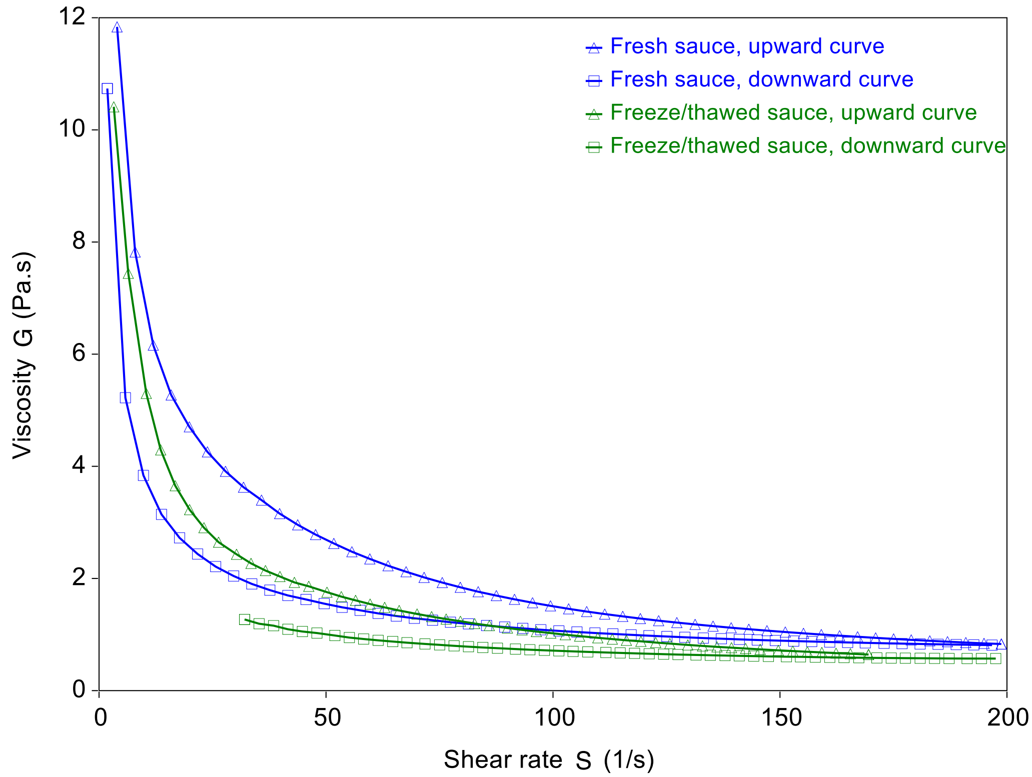

Fig. 5.3: Flow profile of ultrasonicated starch sauce (S5)

At rest, starch polymer chains are entangled, forming a stabilized molecular structure. Upon application of shear, the polymer chains begin to disentangle and re-align themselves in the direction of shear. This leads to a reduction in the internal resistance of the sauces and consequently causes the pseudoplastic behavior, also called shear thinning, observed (Horstmann et al., 2018). Shear thinning behavior has also been reported for other starch-based sauces (Román et al., 2018; Sanz, 2016). The data from the upward curve was adjusted to the Ostwald de Waele model; the k, n, and PRH values are shown in Table 5.3. The results show that ultrasonication had a significant effect ($p < 0.05$) on the model parameters, for both freshly prepared and freeze/thawed sauces. Consistency coefficient is a measure of the thickening capacity or viscosity of a material. Increased ultrasonication temperature significantly reduced the consistency coefficient (viscosity) of the modified starch sauces. Studies on loss of viscosity as an effect of ultrasonication is well documented in the literature (BeMiller & Huber, 2015; Cheng et al., 2010; Nie et al., 2019). Reduction in viscosity is an indication of structural disintegration. This can be explained by the collapse of cavitation bubbles formed during ultrasonication, leading to the emergence of high shear forces that are able to dissociate the covalent bonds between amylose and amylopectin, culminating in structural disintegration and loss of viscosity (Majzoobi, Seifzadeh, et al., 2015). A freeze/thaw cycle further reduced the viscosity of modified starch sauces (Fig. 5.3) and increased the viscosity of native starch sauce. The values of flow behavior index were always less than unity, confirming the pseudoplastic behavior earlier claimed (Mierczyńska et al., 2015). Similarly, ultrasonication significantly affected ($p < 0.05$) the percent relative hysteresis. The values show reduced degree of hysteresis, indicating a more stable structure (Wang et al., 2016). Overall, results from flow behavior tests are well in agreement with studies reported for starch (Izidoro et al., 2011) and starch-based sauces (Bortnowska et al., 2016; Román et al., 2018; Sanz, 2016).

Table 5.3: Estimates of the Ostwald de Waele model parameters and percentage relative hysteresis for the sauces

Sample code	Freshly prepared				Freeze/thawed			
	k	n	R^2	PRH	k	n	R^2	PRH
S0	31.94±0.10a	0.13±0.00a	0.94	28187.90±963.57a	45.37±1.31a	0.15±0.01a	0.97	16787.15±118.55a
S1	40.30±1.12b	0.25±0.01b	0.92	23667.95±437.55b	32.03±3.23b	0.25±0.00b	0.95	19034.05±596.45b
S2	35.34±0.81c	0.24±0.01bc	0.92	27765.65±874.45a	26.24±0.00c	0.19±0.00c	0.95	14427.58±364.08c
S3	28.01±0.88d	0.21±0.01cd	0.87	25026.45±6.15bc	21.20±0.57d	0.21±0.01d	0.90	15428.15±216.05cd
S4	20.92±0.39e	0.22±0.02de	0.91	25026.30±217.50bd	17.82±.38de	0.27±0.00e	0.94	17682.93±372.03ac
S5	17.67±1.05f	0.22±0.01bdf	0.92	27127.68±646.89a	10.22±0.27bf	0.24±0.00bf	0.97	16030.45±620.65af

Results are mean of three replicates ± standard deviation; within each column, values followed by different letters are statistically different ($p < 0.05$).

5.3.5 Viscoelastic behavior

Strain sweep experiments, used to access the extent of linear viscoelasticity, showed a boundary where the properties of viscoelasticity (G′ and G″) were unaffected by the applied strain (Fig. 5.4). Such boundary is called the LVE region, and it provides valuable information regarding the structural integrity of the sauces in response to shear; however, more attention is paid to the G′ curve since it is more vulnerable to structural deformation (Gamonpilas et al., 2011). Within the strain range evaluated, the values of G′ were always greater than G″, signifying dominant solid-like properties. The results obtained show that a value of 2% strain was well within the LVE region of the sauce, hence this value was used as a controlled variable for subsequent frequency sweep experiments.

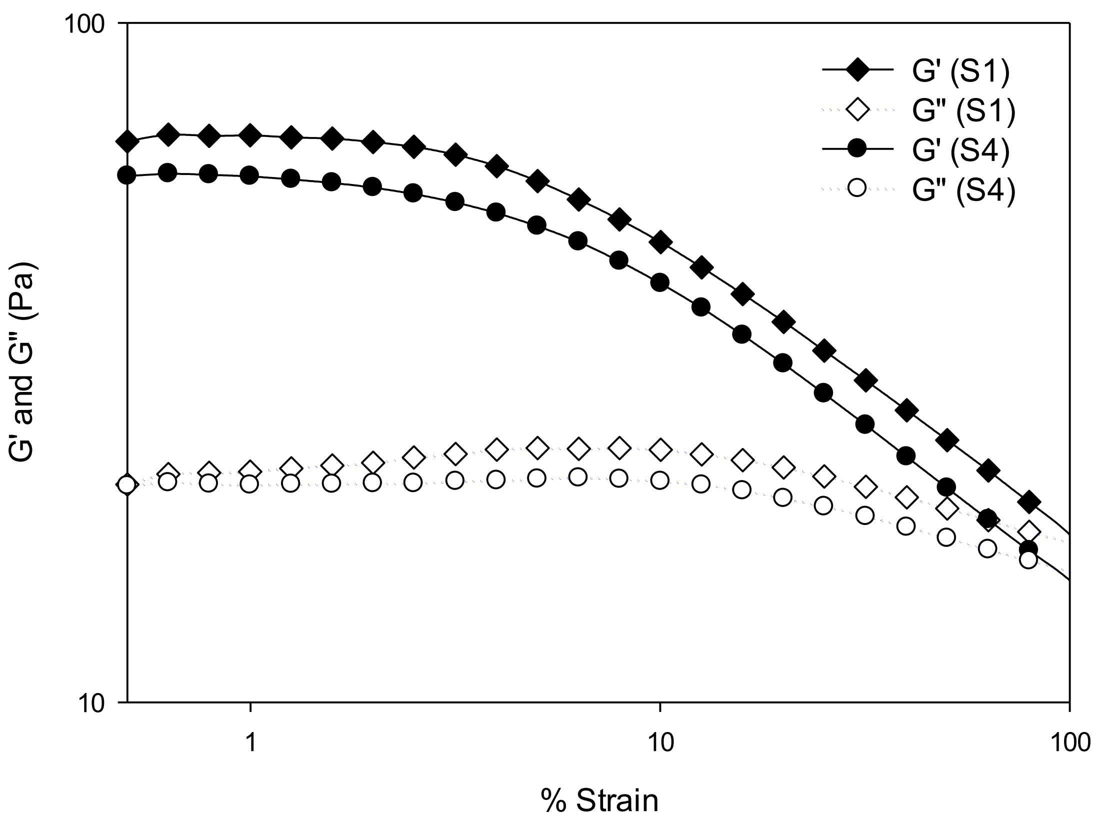

Fig. 5.4: Stress sweep profile of modified starch sauces

The oscillatory spectra (Fig. 5.5) for both native starch and ultrasonicated starch sauces were very similar to those reported for white sauce formulated with chemically modified starch (Arocas et al., 2011) and physically modified starch (Román et al., 2018). Overall, the results show that G′ and G″ increased with frequency, with the values of G′ always greater than G″ (no crossover) throughout the frequency range studied, indicating superior elastic properties over liquid/viscous behavior, and the existence of a weak gel (Palavecino et al., 2020). Ultrasonication was seen to increase the distance between both moduli compared to native starch sauce. The small difference between viscoelastic moduli in native starch sauce indicates it is very close to a crossover point, beyond which it possesses dominant viscous characteristics, and a less stable structure (Román et al., 2018). In both native starch and ultrasonic treated starch sauces, a freeze/thaw cycle led to an increase in viscoelastic moduli (Table 5.4). Syneresis and rearrangement of starch ghost within the continuous matrix may have caused the increased viscoelastic moduli (Vernon‐Carter et al., 2016); thereby leading to a more closely packed or denser structure. The loss tangent (tan δ), which is a ratio of loss modulus to storage modulus, is also an indication of structural integrity. For ideal solids, tan δ = 0, since there is no liquid/viscous portion, G′ completely dominates; whereas tan δ = ∞ for an ideal liquid. A perfect balance between elastic and viscous behaviour has a tan δ value of unity (Mezger, 2014). Over the frequency range evaluated, tan δ values increased, depicting variability in interactive forces holding the gel structure (Liu & Tang, 2011). The values obtained for tan δ is $0.1 < \tan\delta < 1$, indicating a viscoelastic behaviour and the existence of a weak gel. Unlike viscoelastic moduli, a freeze/thaw cycle decreased tan δ values (Table 4). In terms of the magnitude of the viscoelastic property, we did not notice any clear trend with increasing ultrasonication temperature.

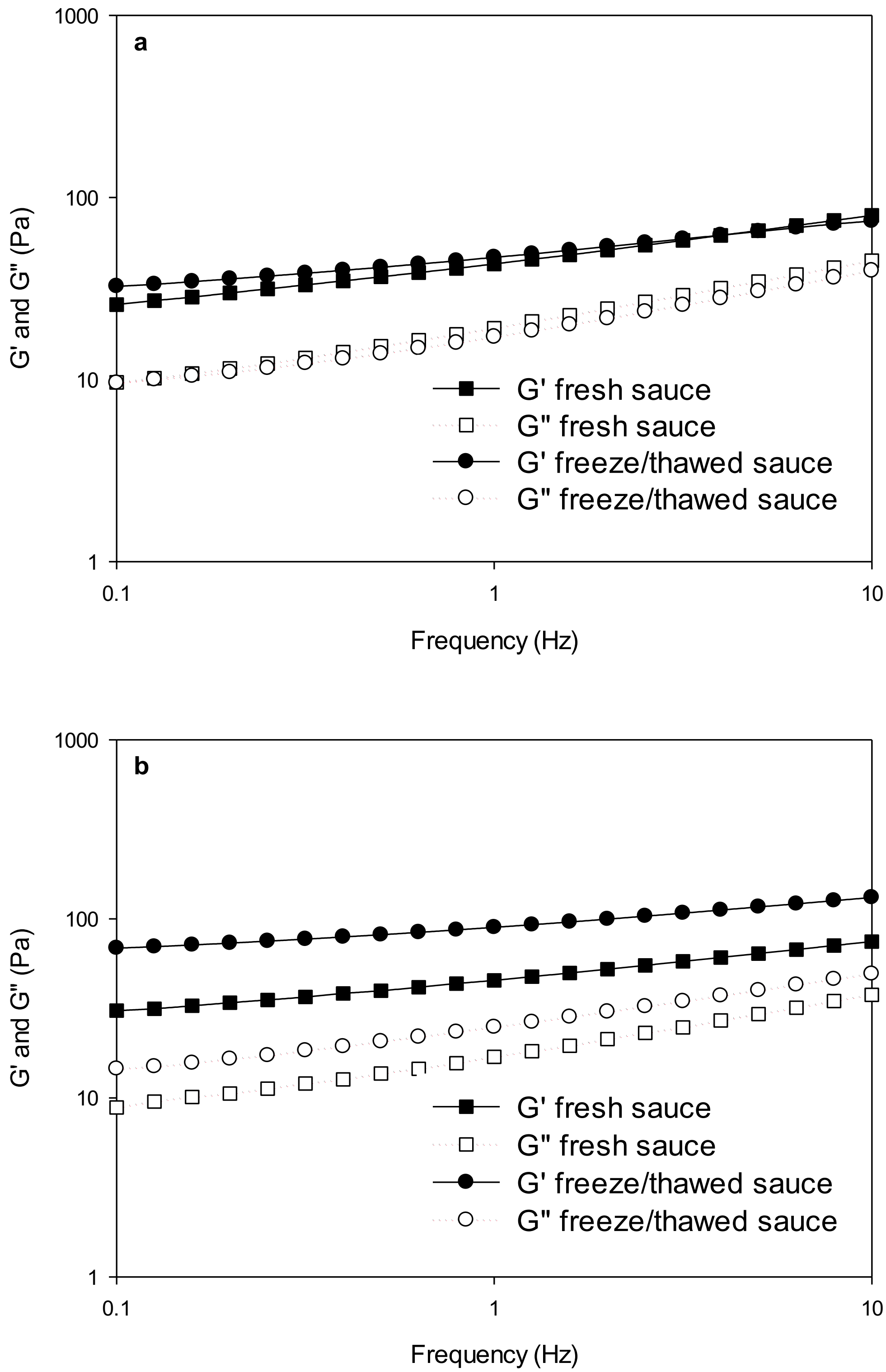

Fig. 5.5: Oscillatory spectra of (a) native starch sauce and (b) ultrasonicated starch sauce (S5)

Table 5.4: Variation of viscoelastic properties of white sauces at 1 Hz

Sample code	G′ (Pa)		G″ (Pa)		tan δ	
	Fresh	Freeze/thawed	Fresh	Freeze/thawed	Fresh	Freeze/thawed
S0	43.12±3.99a	46.87±1.64a	19.14±1.25a	17.14±0.75a	0.44±0.01a	0.37±0.00a
S1	31.35±3.09b	91.22±2.67b	14.46±0.88b	23.63±0.66b	0.46±0.02a	0.26±0.00b
S2	39.35±2.67abe	141.65±9.15cb	17.36±1.04abd	32.26±0.93cg	0.44±0.00a	0.23±0.01c
S3	28.47±1.78bcf	105.3±0.00db	13.11±0.50cbe	25.03±0.16db	0.46±0.01a	0.24±0.00cd
S4	32.49±0.26abe	120.75±2.45eb	14.73±0.08fbd	29.49±0.04eh	0.45±0.01a	0.24±0.00de
S5	45.29±7.56ade	89.61±5.15fb	16.94±2.68abd	24.85±0.71fb	0.37±0.00b	0.28±0.01f

Results are mean of three replicates ± standard deviation; within each column, values followed by different letters are statistically different ($p < 0.05$)

5.3.6 Textural Analysis

Texture is a critical quality attribute of foods that influences consumer acceptance. In white sauce, starch provides a stabilizing effect (gelation) when amylose leaches out from the starch granule due to increased temperature. Results from textural analysis are shown in Table 5.5. Textural properties evaluated (stickiness, stringiness, and work of adhesion) were seen to decrease significantly ($p < 0.05$) with increasing ultrasound treatment. The reduced textural properties observed may be explained by weakened structural integrity of the starch granules owing to mechanical vibration and cavitation effect (Karaman et al., 2017). Stickiness and work of adhesion values of mild ultrasound treated white sauces (S1 and S2) were generally higher compared to their native counterpart. After a freeze/thaw cycle, the values of textural properties were significantly reduced ($p < 0.05$) in both native and modified starch sauces, in response to increased severity of ultrasonication temperature, indicating that softer gels could be obtained with increased ultrasonication intensity; though a non-significant ($p < 0.05$) effect was noticed in stringiness of freeze/thawed sauces. The reduced textural properties (due to increased ultrasound treatment) reported here is useful in the formulation of white sauce, and indeed other food applications, because adherence of foods to the teeth and palate is unappealing (Nie et al., 2019). Overall, the data obtained from textural analysis further confirms the results reported in flow behavior measurement and are well in agreement with related studies (Hu et al., 2014).

Table 5.5: Effect of ultrasonication on textural properties and syneresis of starch-based sauces

Sample code	Stickiness (g)		Stringiness (mm)		Work of adhesion (g.mm)		% Syneresis after freeze/thaw cycle
	Fresh	Freeze/thawed	Fresh	Freeze/thawed	Fresh	Freeze/thawed	
S0	346.42±15.20a	325.49±13.92a	5.16±0.00a	5.08±0.01	1040.75±36.52a	541.90±132.92b	11.84±0.08a
S1	426.54±34.17b	416.96±8.97a	5.15±0.00a	5.09±0.00	1198.08±128.42a	872.25±12.19a	9.04±0.26b
S2	419.52±14.83bc	345.08±70.24a	5.13±0.00b	5.09±0.01	1173.38±63.59a	750.84±50.09cae	7.41±0.71c
S3	315.30±19.23a	313.59±31.67a	5.14±0.00abc	5.08±0.01	882.63±66.82ade	505.91±4.19b	6.09±0.44d
S4	247.63±4.40d	309.50±18.31a	5.14±0.01abcd	5.08±0.01	715.59±14.91be	457.37±6.72b	3.00±0.74e
S5	229.08±3.34df	282.35±57.79ab	5.13±0.01abe	5.07±0.01	690.10±3.01ce	426.15±5.73d	1.30±0.04f

Results are mean of three replicates ± standard deviation; within each column, values followed by different letters are statistically different ($p < 0.05$).

5.3.7 Syneresis

Frozen starchy foods experience textural changes that may be explained by amylose and amylopectin retrogradation and undergo syneresis after a freeze/thaw cycle (Katekhong & Charoenrein, 2012). The phenomenon of syneresis happens when water leaches out from the food matrix after thawing and portends negative quality. In both native and ultrasound treated freshly prepared sauces, syneresis was not observed, which signifies an initial stable structure. This was reported in other studies conducted on white sauce and has been related to high water absorption capacity (Arocas et al., 2009b; Román et al., 2018). Conversely, syneresis was observed after a freeze/thaw cycle. Additionally, the percentage syneresis significantly reduced with increasing ultrasound treatment (Table 5.5), indicating ultrasonication can be used to enhance the freeze/thaw stability of starch-based sauces. Luo et al. (2008) explained reduced syneresis in ultrasound treated starch to be due to cleavage of starch chains in the amorphous region which caused considerable re-ordering of chain segments. Hence, after a freeze/thaw cycle, more water leached out from native starch sauce in comparison to ultrasound treated starch sauces. Román et al. (2018) reported greater freeze/thaw stability in coarse-grained wheat and rice starch sauces compared to their fine-grained counterparts, indicating that coarse grain starches provided a larger surface area needed to absorb more water.

5.4. Conclusion

The study described in this paper adopted ultrasonication, a physical, inexpensive, and 'green' starch modification technology, and investigated its suitability in the formulation of starch-based sauces. Ultrasonication improved the functional properties of native starch, indicating its suitability in the formulation of sauces. Rheological measurements showed a shear thinning flow behavior, which was well described by the Ostwald de Waele model, while the viscoelastic behavior showed dominant solid properties over viscous behavior. Ultrasound treatment improved rheological properties and textural characteristics (stickiness, stringiness, and work of adhesion) of starch-based sauces compared to the native counterparts. Moreover, enhanced freeze/thaw stability was also achieved in ultrasonicated starch sauces. Overall, the results from this study shows that ultrasound treated starches can be used in the formulation of sauces and potentially other food products. This is in line with current consumer interest in clean label and minimally processed foods.

CHAPTER SIX

6. GENERAL SUMMARY, CONCLUSION AND FUTURE RESEARCH DIRECTION

6.1 Summary and Conclusion

The global market for sauces is dynamic, largely characterized by differences in consumption pattern across different countries. As consumer preference for incorporating sauces and other condiments into ready-to-eat and home cooked meals continue to evolve, a large window for economic opportunities remain open for strategic investors. A wide range of opportunities exist for the formulation of different sauces with varying texture, flavor, flow behavior, nutritional, and functional properties. The overarching goal of this work was to investigate the rheological and textural properties of sauces. It was stated that food quality parameters, like rheological properties of sauces, are not only dependent on formulation ingredients, but also on processing conditions, such as temperature. The first objective of this thesis was focused on how the steady state and oscillatory rheology of selected commercial meat sauces are influenced by temperature. The application of hydrocolloids, such as starches, in sauce formulations serves to enhance their rheology, texture, and consumer acceptability. They function as thickening, gelling, emulsifying and stabilizing agents. However, the applicability of starch in its native form is limited due to retrogradation, syneresis, poor thermal and shear properties; thereby creating a necessity for modification. Chemical and enzymatic modification techniques are often characterized by utilization of toxic chemical and the need to prove their safety from a public health standpoint. This in addition to the ever-growing customer demand for minimally processed or clean label foods has led the food industry to formulating foods with physically modified starch. Hence, the second objective of this thesis focused on adopting a physical starch modification technology – ultrasonication. The modified starch was characterized and used in the formulation of white sauce.

In addition, the rheological and textural properties of the white sauce were evaluated before and after a freeze/thaw cycle.

The following conclusions were drawn from this research:

1) The flow property of sauces is characterized by a non-ideal or pseudoplastic behavior, typified by decreasing viscosity in response to rising shear rate or shear stress. Their flow behavior can well be described by Hershel-Bulkley and Ostwald de Waele models.
2) In meat sauces, temperature dependency on oral shear viscosity followed an Arrhenius-type model.
3) Overall, the viscoelastic properties of sauces showed dominant elastic behavior over viscous properties and behaved like a weak gel.
4) Both linear and power modified Cox-Merz rule can be satisfactorily applied to correlate steady state and oscillatory rheological properties of sauces.
5) Quality parameters, such as rheological and textural properties, of starch-based sauces can be enhanced using ultrasonication.

6.2 Recommendation for Future Studies

1) Beyond rheological behavior (flow behavior and viscoelastic properties) of sauces, future research should also focus on tribology of sauces, since traditional rheometry cannot provide information on certain friction-related attributes, such as astringency and grittiness. Tribology can also provide information helpful in differentiating sauces with different texture but related rheological behavior.
2) It appears the area of texture profiling of sauces is still dependent on instrumental analyses and subjective (sensory) evaluation. The evolution of artificial intelligence systems has been widely deployed in quantifying physical and chemical attributes of foods. It is herein

recommended that these non-destructive and non-invasive technologies, such as hyperspectral imaging, be explored for possible application in textural evaluation of sauces.

3) The current study utilized starch modified through ultrasonication in the formulation of white sauce. Other physical modification technologies, such as cold plasma and pulsed electric field, are yet to be studied for possible application in formulation of sauces.

CHAPTER SEVEN

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